

***VISCOSITY INDEX IMPROVER AND POUR POINT
DEPRESSANT PROPERTIES OF ADDITIVES FOR
LUBRICATING OIL***

A Thesis submitted to the University of North Bengal

**For the Award of
Doctor of Philosophy
in
Chemistry**

**BY
MAINUL HOQUE, M. Sc**

**GUIDE
Prof. Pranab Ghosh**

**Department of Chemistry
University of North Bengal
December, 2016**

◆◆◆◆◆ ***DEDICATED TO MY***

BELOVED PARENTS

DECLARATION

I declare that the thesis entitled *VISCOSITY INDEX IMPROVER AND POUR POINT DEPRESSANT PROPERTIES OF ADDITIVES FOR LUBRICATING OIL* has been prepared by me under the guidance of Prof. Pranab Ghosh, Department of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

Mainul Hoque

Mainul Hoque

Department of Chemistry

University of North Bengal

Raja Rammohunpur, Darjeeling - 734013

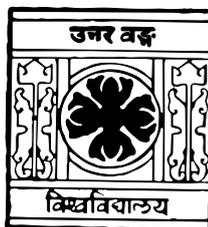
West Bengal, India

Date:

05/12/16

UNIVERSITY OF NORTH BENGAL

Prof. P. Ghosh,
DEPARTMENT OF CHEMISTRY
University of North Bengal,
Darjeeling – 734 013, India.



Ph: +91 3532776 381 (off)
+91 9474441468 (M)
Fax: +91 353 2699 001
Email: pizy12@yahoo.com

Ref. No.....

Dated: 05/12/2016

CERTIFICATE

I certify that **Mr. Mainul Hoque** has prepared the thesis entitled ***VISCOSITY INDEX IMPROVER AND POUR POINT DEPRESSANT PROPERTIES OF ADDITIVES FOR LUBRICATING OIL*** for the award of Ph.D Degree of the University of North Bengal, under my guidance. He has carried out the research work at the Department of Chemistry, University of North Bengal. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

Professor
Department of Chemistry
University of North Bengal
Darjeeling - 734013, India

Prof. Pranab Ghosh (Research Supervisor)
Department of Chemistry
University of North Bengal
Raja Rammohunpur, Darjeeling - 734013
West Bengal, India

Date: 05/12/2016

ACKNOWLEDGEMENT

At first, I would like to express my heartfelt gratitude and sincerest thanks to my supervisor, Prof. Pranab Ghosh, Department of Chemistry, University of North Bengal, Darjeeling, who has supported me throughout my thesis work with his invaluable guidance. I will always remain grateful to him.

I am very much thankful to my beloved son, wife, parents and other family members for their constant support and encouragement. I am grateful to the omnipresent God, for answering my prayers, for giving me the strength to be positive in every situation.

I want to acknowledge the Head, Department of Chemistry, Prof. M. N. Roy and other faculty members of this Department for their imperative support.

I want to express my respect and thanks to the entire non teaching staff and all the research scholars of this department for their selfless cooperation. I wish to thank my fellow lab mates for the exciting discussions, with whom I enjoyed many more unforgettable moments during this journey.

I am also grateful to the principal and colleagues of my college, Kokrajhar Govt. College, BTAD, Assam.

I specially thank to Indian Oil Corporation Limited and Bharat Petroleum Corporation Limited for providing base oils.

Finally, I would like to thank UGC, New Delhi, India, for granting my leave under Faculty Development programme (FDP) due to which it became possible to carry out my research work.

Mainul Hoque

05/12/16

Mainul Hoque

Department of Chemistry

University of North Bengal

Abstract

Lubricant comprises lubricating oil and a package of additives. Lubricants are generally liquids or semi-liquids which are used to lubricate the automotive engine for their longevity and better performances. The key functions of a lubricant are to keep moving parts apart, reduce friction, protect against wear, transfer heat, prevent rust and corrosion, as antioxidant, as detergent/dispersant etc.

In the present work synthesis, characterization and performance evaluation of methacrylate, acrylate, maleic anhydride and Mannich base type multifunctional lube oil additives along with biodegradable multifunctional lube oil additives based on vegetable oils (sunflower and castor oil) have been investigated. The additives were prepared by thermal method by using azobisisobutyronitrile (AIBN) / benzoyl peroxide (BZP) initiator. Characterization of the additives were carried out by spectral techniques (FT-IR, ^1H NMR and ^{13}C NMR), followed by molecular weight determination (GPC / viscometric method). Thermal stability and in some cases shear stability of the prepared polymers were also investigated. The performance of the additives were investigated in different lube oils as viscosity index improver (VII), pour point depressant (PPD) and in some cases as anti wear (AW), detergents/ dispersants and antioxidants additive according to standard ASTM methods. In case of biodegradable additives, biodegradability test was carried out by disc diffusion method against fungal pathogens and by soil burial degradation test. Since most of the additives are multifunctional in nature, the interest of research on this field gives a new direction in the lubrication technology.

After a general introduction of the present investigation, the complete research work has been divided into three parts: **Part I**, **Part II** and **Part III**. **Part I**, “**Methacrylate based polymeric additives as multifunctional lube oil additives**” is divided into three chapters (chapter I, chapter II and chapter III). Chapter I discussed the background study of part I. Chapter II discussed about the homopolymer of decylmethacrylate and its copolymer with styrene. Ten polymers (two homopolymers and eight copolymers) were prepared at different percentage composition of styrene by using two types of initiators BZP and AIBN. All the prepared polymers are characterised by FT-IR and NMR. The molecular weight was determined by Gel Permeation Chromatography (GPC) instrument. The molecular weight of homopolymer prepared by using BZP initiator is higher than homopolymer prepared by using

AIBN initiator but molecular weight of copolymers prepared by BZP are lower than copolymers prepared by AIBN initiator. The performance of the prepared polymers in different base oils were evaluated as viscosity index improver (VII), also known as viscosity modifier (VM) and pour point depressant (PPD). Shear stability of the polymers in lube was investigated. Thermal stability of the prepared polymers was determined by thermo gravimetric analysis and it was found that the thermal stability of copolymers decrease with increasing the styrene content.

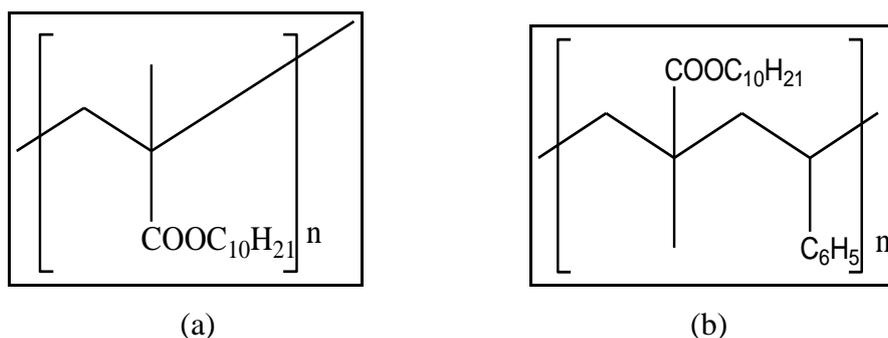


Figure I Structure of (a) homopolymer of decylmethacrylate and (b) copolymer with styrene

Chapter III discussed the application of homo polymers of dodecyl methacrylate (DDMA) and its copolymers with vinyl acetate (VA) as multifunctional additives for lubricant formulation. Homo polymer of DDMA and five copolymers of DDMA with VA at different molar ratios were synthesized by free radical polymerization method. The characterization of the polymers was carried out through FTIR, NMR and GPC analysis. The thermal stability of the polymers was determined by thermo gravimetric analysis (TGA). The performance of all the polymers as viscosity index improver and pour point depressant additive in two different base oils were evaluated. The action mechanism of pour point depressant was studied by photo micrographic analysis. Rheological study of the base oils blended with these additives was also carried out. It was found that thermal stability, VI and molecular weights of copolymers are higher than the homopolymer which showed better PPD property.

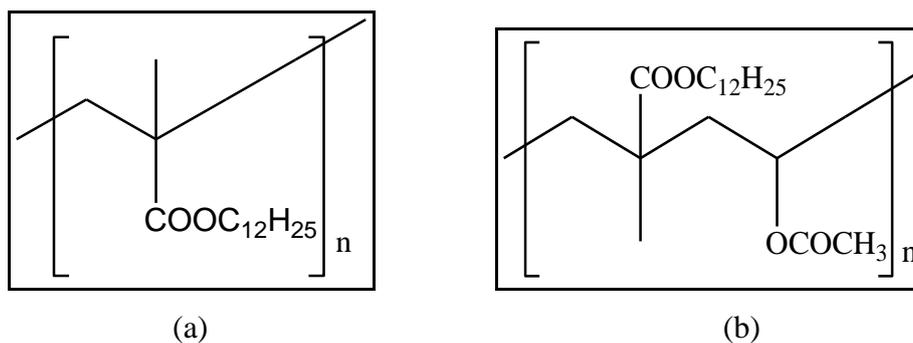


Figure II Structure of (a) homopolymer of dodecylmethacrylate and (b) copolymer with vinyl acetate

Part II, “Maleic anhydride based additives - synthesis, characterization and performance evaluation as multifunctional additive for lube oil” is divided into five chapters (chapter I, chapter II, chapter III, chapter IV and chapter V). The first chapter deals with the background of respective work. Chapter II is “synthesis and performance evaluation of maleic anhydride – 1 decene copolymer for lubricating oil.” Copolymer of maleic anhydride with 1-decene was synthesised and the prepared copolymer was esterified with different alcohols (isooctanol, n- decanol and n- dodecanol). The performance of the polymers in three types of base oils was evaluated as viscosity index improver and pour point depressant by standard ASTM methods. The molecular weight of the polymers was determined by Gel Permeation Chromatography. TGA value of the prepared polymers was also evaluated. It was found that the efficiency of the polymers as a VII increases with increasing the concentration of polymers in base oil and with decreasing polydispersity index (which determines the distribution of molecular mass in a given polymer sample) of the polymer. Whereas, the efficiency as a pour point depressant increases with decreasing concentration of the prepared polymer in base oil and with the increasing polydispersity index of the polymers.

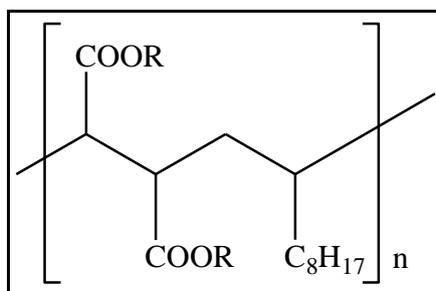


Figure III General structure of the prepared copolymers

Chapter III is “synthesis and performance evaluation of vinyl acetate maleic anhydride based polymeric additives for lubricating oil.” Copolymer of vinyl acetate with maleic anhydride was synthesised and the prepared copolymer was esterified with different long chain alcohols (n- octanol, n- decanol and n- dodecanol). The performance of the polymeric additives in three types of base oils was evaluated as viscosity index improver and pour point depressant by standard ASTM methods. Intrinsic viscosity and viscometric molecular weight of the polymers were determined by Huggins and Mark-Houwink equation respectively. TGA value was also determined. It was found that the efficiency of the polymers as VII increases with increasing the alkyl chain length of the used alcohols, but the efficiency as pour point depressant increases with decreasing alkyl chain length of the alcohols used in esterification.

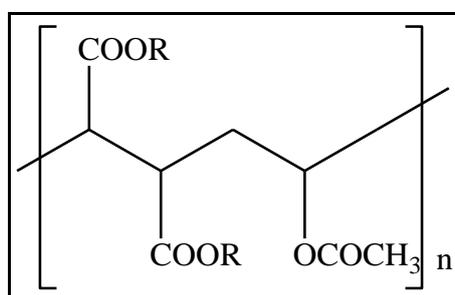


Figure IV General structure of the prepared copolymers

Chapter IV is “multifunctional lube oil additives based on maleic anhydride and 1- decene” Copolymer of maleic anhydride with 1-decene was synthesised by using AIBN as an initiator in toluene solvent and the prepared copolymer was reacted with different long chain amines (octylamine, decylamine and dodecylamine) to get three different polymers. The performance of the polymers in different base oils was evaluated as viscosity index improver, pour point depressant and dispersant by standard ASTM methods. The molecular weight of the polymers was determined by Gel Permeation Chromatography method. The TGA value was determined by standard ASTM method. Photo micrographic image was used to study the pour point of lube oil without and with additives. It was found that the efficiency of the polymers as a VM and dispersant increases with increasing the molecular weight of the polymers as well as with increasing the alkyl chain length. Whereas, the efficiency as a pour point depressant increases with decreasing molecular weight of the prepared polymers and with the decreasing the alkyl chain length.

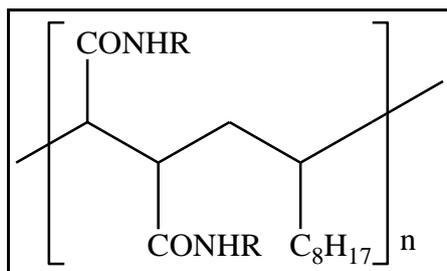


Figure V General structure of the prepared copolymers

Chapter V is “Mannich bases and phosphosulphurized Mannich bases: synthesis characterization and performance evaluation as potential lube oil additives.” In this study, three Mannich bases were prepared by using p-cresol, formaldehyde and different polyethylene polyamines (ethylenediamine, diethylenetriamine and triethylenetetramine). The prepared Mannich bases were treated with P_2S_5 to get three phosphosulphurized Mannich bases. Structures of the prepared compounds have been confirmed by IR, NMR spectroscopy and molecular weight determination. The performance of the prepared Mannich bases as well as Phosphosulphurized Mannich bases was investigated as antioxidants, detergents/dispersants, viscosity index improver and pour point depressant for lube oil. But it was found that the prepared additives have no any action on viscosity index and pour point of lube oil. Therefore, our study was directed for the study of antioxidant and detergent/dispersant property of lube oil.

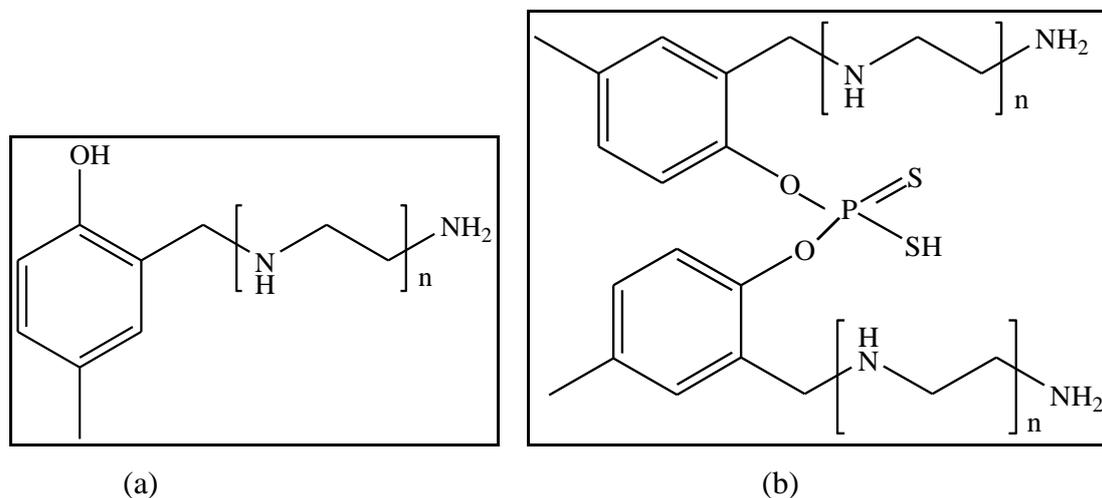


Figure VI General structure of (a) Mannich bases and (b) Phosphosulphurized Mannich bases

Part III, “Biodegradable multifunctional lube oil additives” is divided into four chapters (chapter I, chapter II, chapter III and chapter IV). Chapter I is brief review on the background of the biodegradable multifunctional lube oil additives. Chapter II describes biodegradable lube oil additives obtained from alkyl acrylates, sunflower oil and styrene. Three terpolymers consisting of n-octyl acrylate, sunflower oil and styrene in the ratio of 1:1:1(w/w), 2:1:1(w/w) and 3:1:1(w/w) and two terpolymers consisting of different alkyl acrylates (n-decyl acrylate and n-dodecyl acrylate), sunflower oil and styrene in the ratio of 2:1:1(w/w) were synthesized in toluene by free radical polymerization in the presence of AIBN initiator. The polymers were characterized by FT-IR and NMR spectroscopy. Molecular weight of the prepared polymers was determined by Gel Permeation Chromatography method. The performance of the prepared polymers in different base oils was evaluated as viscosity index improver, pour point depressant and antiwear additive. Powder XRD and photo micrographic image were used for the study the mechanism action of pour point depressant. The TGA value of the prepared polymers was determined by standard ASTM method. The rheological study of lube oil without and with polymer was also carried out. The biodegradability test of the prepared polymers was carried out by disc diffusion method. It was found that the terpolymer prepared by taking monomers in 2:1:1 ratio (w/w) was found to be the most efficient compared to the others. The antiwear and VI performance of the prepared terpolymers increase with increasing the alkyl chain length whereas PPD performance decreases. Chapter III investigates the performance of polymers prepared from castor oil and n-dodecyl acrylate as biodegradable multifunctional additive in the formulation of eco-friendly lubricant. Homopolymer of castor oil (CO) and its copolymers with dodecyl acrylate (DDA) at different percentage ratios (w/w) were synthesized using AIBN as initiator. The polymers were characterized by spectral techniques (FT-IR and NMR spectroscopy). The molecular weight of all the prepared polymers was determined by Gel Permeation Chromatography (GPC) instrument. The thermal stability of the polymers was determined by TGA method. Performance evaluation of all the prepared polymers in mineral base oil as viscosity index improver, pour point depressant and antiwear was carried out according to standard ASTM methods. The mechanism of action of the additives as PPD was studied by photo micrographic image. Biodegradability of all the samples was tested through soil burial test (SBT). It was found that the copolymers of dodecyl acrylate and castor showed better performance as viscosity modifier, pour point depressant and antiwear additive than homopolymer of DDA as well as homopolymer of castor oil for lubricating oil.

Chapter IV investigates the performance of homopolymer of castor oil and four copolymers of it as biodegradable multifunctional mineral lube oil additive. Homopolymer of castor oil (CO) and its copolymers with 10% (w/w) of methyl methacrylate (MMA), 10% (w/w) of n-dodecyl acrylate (DDA), 10% (w/w) of 1-decene and 10% (w/w) of styrene were synthesized using AIBN as initiator. The polymers were characterized by spectral techniques (FT-IR and NMR spectroscopy). The molecular weight of all the prepared polymers was determined by GPC instrument. The thermal stability of the polymers was determined by thermo gravimetric analysis (TGA) method. Performance evaluation of all the polymers in two types of mineral oils as viscosity index improver, pour point depressant and antiwear was carried out according to standard ASTM methods. Biodegradability of all the samples was tested through soil burial test (SBT) method. It was found that the copolymers of castor oil with MMA and castor oil with DDA are more efficient as PPD and AW. The copolymer of castor oil with styrene was found more efficient as VII.

PREFACE

The present thesis embodied the results of research work carried out by the author under the supervision of Prof. Pranab Ghosh, at the department of chemistry, Universality of North Bengal, Dist. Darjeeling, West Bengal, during the period of 2012 to 2016. It comprises the synthesis and characterization of multifunctional lube oil additives. The performance of the prepared additives was evaluated in different mineral base stocks as viscosity index improver, pour point depressant, antiwear additives, antioxidant and detergent/dispersant additives.

Lubricant is a combination of lubricating oil or base oil and a package of additives. Additives increase the performance of the lubricating oil already present or add some new properties. The key function of a lubricant is to minimize the friction and wear between two moving metal surfaces, removal of heat and contaminant suspension. In modern technology, the application of multifunctional lube oil additives is of great interest.

In the present work, the author has prepared some multifunctional lube oil additives and additive performances were evaluated in different base stocks. In Part I, methacrylate based polymeric additives has been synthesized and their performances were evaluated in different base stocks. In Part II, some maleic anhydride based multifunctional lube oil additives were synthesized and additive performance was evaluated in different base oils. Synthesis, characterization and performance evaluation of vegetable oils (sunflower oil and castor oil) based polymeric additives have been reported in Part III of the thesis.

TABLE OF CONTENTS

Contents	Page No.
Declaration	i
Certificate	ii
Acknowledgement	iii
Abstract	iv - x
Preface	xi
Table of contents	xii - xvii
List of Tables	xviii-xx
List of Figures	xxi-xxvi
List of Appendices	xxvii
1. Appendix A: List of Paper Published/Accepted/communicated	xxviii
2. Appendix B: List of published research papers in the Proceedings of National / International Seminar / Conference / Workshop	xxix
3. Appendix C: Abbreviations	xxx-xxxi
<hr/>	
General introduction of the present investigation	1-8
<hr/>	
PART I	9
<hr/>	
Methacrylate based polymeric additives as multifunctional lube oil additives	
<hr/>	
Chapter I	10-14

Background of the present investigation

Chapter II 15

Homo and copolymers of decyl methacrylate as performance additives for lube oil

1.2.1 Introduction	16-17
1.2.2 Experimental section	17-18
1.2.3 Measurements	18-20
1.2.4 Results and discussion	20-23
1.2.5 Conclusions	23-24
1.2.6 References	24
1.2.7 Tables and figures	24-30

Chapter III 31

Dodecyl methacrylate based polymeric additives as viscosity modifier and pour point depressant for lube oil

1.3.1 Introduction	32-33
1.3.2 Experimental section	33-34
1.3.3 Measurements	34-35
1.3.4 Results and discussion	35-39
1.3.5 Conclusions	39
1.3.6 References	39
1.3.7 Tables and figures	39-47

PART II

48

Maleic anhydride based additives - synthesis, characterization and performance evaluation as multifunctional additive for lube oil

Chapter I	49-53
Background of the present investigation	
Chapter II	54
Synthesis and performance evaluation of maleic anhydride –1decene copolymer for lubricating oil	
2.2.1 Introduction	55-56
2.2.2 Experimental section	56-57
2.2.3 Measurements	57-58
2.2.4 Results and discussion	58-60
2.2.5 Conclusions	60
2.2.6 References	60
2.2.7 Tables and figures	60-68
Chapter III	69
Synthesis and performance evaluation of vinyl acetate - maleic anhydride based polymeric additives for lubricating oil	
2.3.1 Introduction	70
2.3.2 Experimental Section	71-72
2.3.3 Measurements	72-73
2.3.4 Results and discussion	73-75
2.3.5 Conclusions	75
2.3.6 References	75
2.3.7 Tables and figures	75-79

Chapter IV	80
Multifunctional lube oil additives based on maleic anhydride and 1-decene	
2.4.1 Introduction	81-82
2.4.2 Experimental section	82-83
2.4.3 Measurements	83-84
2.4.4 Results and discussion	84-87
2.4.5 Conclusions	87
2.4.6 References	87
2.4.7 Tables and figures	87-93
Chapter V	94
Mannich bases and phosphosulphurized Mannich bases: synthesis, characterization and performance evaluation as potential lube oil additives	
2.5.1 Introduction	95-96
2.5.2 Experimental section	96-98
2.5.3 Measurements	98
2.5.4 Performance evaluation of the prepared compounds as lube oil additives	98-99
2.5.5 Results and discussion	99-100
2.5.6 Performance analysis of Mannich bases	100-101
2.5.7 Performance analysis of phosphosulphurized Mannich bases	101
2.5.8 Conclusions	101
2.5.9 References	102
2.5.10 Tables and figures	102-108

PART III 109

Biodegradable multifunctional lube oil additives

Chapter I	110-113
Background of the present investigation	
Chapter II	114
Sunflower oil based terpolymer as sustainable lubricant additive	
3.2.1 Introduction	115-116
3.2.2 Experimental section	116-117
3.2.3 Measurements	117-119
3.2.4 Results and discussion	119-123
3.2.5 Conclusions	123
3.2.6 References	123
3.2.7 Tables and figures	123-133
Chapter III	134
Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant	
3.3.1 Introduction	135-136
3.3.2 Experimental section	136-137
3.3.3 Measurements	137
3.3.4 Performance evaluation	137-138
3.3.5 Results and discussion	138-143
3.3.6 Conclusions	143
3.3.7 References	143
3.3.8 Tables and figures	143-156

Chapter IV	157
Castor oil based multifunctional greener additives for lubricating oil	
3.4.1 Introduction	158-159
3.4.2 Experimental section	159-160
3.4.3 Measurements	160
3.4.4 Performance evaluation	161
3.4.5 Results and discussion	161-164
3.4.6 Conclusions	164
3.4.7 References	164
3.4.8 Tables and figures	164-174
<hr/> Bibliography	175-205
<hr/> Index	206-210
<hr/>	

LIST OF TABLES

Table No.	Title of Table	Page No.
Table 1.2.1	Physical properties of the base oils	24
Table 1.2.2	Different percentage composition of the prepared polymers	25
Table 1.2.3	M_n , M_w and PDI values of the polymers, P-1 to P-10	25
Table 1.2.4	TGA values of polymers (P-1 to P-10)	26
Table 1.2.5	Viscosity Index (VI) of polymer doped base oil	26
Table 1.2.6	Pour point of polymer doped base oil	27
Table 1.3.1	Base oil properties	39
Table 1.3.2	Molar ratio and molecular weight of the prepared polymers	40
Table 2.2.1	Physical properties of the base oils	61
Table 2.2.2	The abbreviation of the prepared compounds (esters)	61
Table 2.2.3	Molecular weight of A, B and C (determined by GPC)	61
Table 2.2.4	TGA data for the polymers A, B and C	62
Table 2.2.5	Viscosity index of polymer of A, B and C at different concentrations in different base oil (BO1, BO2 and BO3)	62
Table 2.2.6	Pour point of polymer A, B and C at different concentrations in different base oil (BO1, BO2 and BO3).	63
Table 2.3.1	Physical properties of the base oils	76
Table 2.3.2	Intrinsic viscosity, Viscometric molecular weight and thermo gravimetric analysis (TGA) values of polymer A, B and C	76
Table 2.3.3	Viscosity index of polymer of A, B and C at different conc. (% in w/w) in different base oil (BO1, BO2 and BO3)	77

Table 2.3.4	Pour point of polymer A, B and C at different concentrations (% in w/w) in different base oil (BO1, BO2 and BO3)	77
Table 2.4.1	Physical properties of the base oils	87
Table 2.4.2	Monomers, polymer code and M_n , M_w and PDI values of copolymers	88
Table 2.4.3	Viscosity index values of polymers of A ₁ , A ₂ and A ₃ at different conc. (% in w/w) in different base oil (BO1, BO2 and BO3)	88
Table 2.4.4	Pour point values of polymers A ₁ , A ₂ and A ₃ at different conc. (% in w/w) in different base oil (BO1, BO2 and BO3)	89
Table 2.4.5	Dispersancy of the lube oils (BO1, BO2, BO3) and their blends containing polymers (A ₁ , A ₂ and A ₃) after different oxidation periods	90
Table 2.5.1	Physical properties of base oil	102
Table 2.5.2	Theoretical and determined mean molecular weights of compounds A ₁ , A ₂ , A ₃ , B ₁ , B ₂ and B ₃	102
Table 2.5.3	Dispersancy of the base oil and its blends containing additives (A ₁ , A ₂ and A ₃) after different oxidation periods	103
Table 2.5.4	Dispersancy of the base oil and its blends containing additives (B ₁ , B ₂ and B ₃) after different oxidation periods	103
Table 3.2.1	Composition of sunflower oil	123
Table 3.2.2	Physical properties of the base oils	124
Table 3.2.3	Polymers designation, monomers, monomers ratio, molecular weight values of the polymers A, B, C, D and E	124
Table 3.2.4	Results of biodegradability test	125
Table 3.2.5	Comparative molecular weight (determined by GPC method)	125
Table 3.2.6	Antiwear property in terms of wear scar diameter (WSD) values of different lubricant compositions	126

Table 3.3.1	Properties of castor oil	143
Table 3.3.2	Physical properties of the mineral base oil	144
Table 3.3.3	Percentage composition and molecular weight of the polymers	144
Table 3.3.4	Comparative molecular weight (determined by GPC method)	145
Table 3.4.1	Physical properties of the base oils	165
Table 3.4.2	Polymers designation, monomers, monomers ratio, molecular weight values of the polymers P-1, P-2, P-3, P-4 and P-5	165
Table 3.4.3	Viscosity Index (VI) of polymer doped base oil	166
Table 3.4.4	Pour point of polymer doped base oil	166
Table 3.4.5	Comparative molecular weight (determined by GPC)	167

LIST OF FIGURES

Figure No.	Title of figure	Page No
Figure 1	Effect of temperature on polymeric additive in lube oil	2
Figure 2	Structure of some commonly used viscosity index improvers	3
Figure 3	Schematic representation the mechanism action of polymeric additives on wax	3
Figure 4	Structure of some commonly used pour point depressants	4
Figure 5	Schematic representation of donor acceptor bond between AW additive and metal (Fe) surface.	4
Figure 6	Structure of some commonly used antiwear additives	5
Figure 7	Structure of some commonly used dispersant additives	6
Figure 8	Graphical representation of a dispersant molecule	6
Figure 9	Action mechanism of dispersant	7
Figure 1.2.1	IR spectra of homopolymer (P-1)	27
Figure 1.2.2	¹ H NMR spectra of homopolymer (P-1)	28
Figure 1.2.3	¹³ C NMR spectra of homopolymer (P-1)	28
Figure 1.2.4	IR spectra of copolymer (P-2)	29
Figure 1.2.5	¹ H NMR spectra of copolymer (P-2)	29
Figure 1.2.6	¹³ C NMR spectra of copolymer (P-2)	30
Figure 1.2.7	Variation of PSSI values of polymer doped base oil (BO2) at 2% and 5% concentrations	30
Figure 1.3.1	IR spectra of homopolymer, (P-1)	40

Figure 1.3.2	¹ H NMR spectra of homopolymer, (P-1)	41
Figure 1.3.3	¹³ C NMR spectra of homopolymer (P-1)	41
Figure 1.3.4	IR spectra of copolymers (P-2 to P-6)	42
Figure 1.3.5	¹ H NMR spectra of copolymer (P-2)	42
Figure 1.3.6	¹³ C NMR spectra of copolymer (P-2)	43
Figure 1.3.7	Thermal degradation of polymers P-1, P-2, P-3, P-4, P-5 and P-6	43
Figure 1.3.8	Variation of viscosity index of polymer doped base oil (in SN150) at different concentrations	44
Figure 1.3.9	Variation of viscosity index of polymer doped base oil (in SN500) at different concentrations	44
Figure 1.3.10	Variation of pour point of polymer doped base oil (in SN150) at different concentrations	45
Figure 1.3.11	Variation of pour point of polymer doped base oil (in SN500) at different concentrations	45
Figure 1.3.12	Variation of dynamic viscosity with shear rate at 40 °C	46
Figure 1.3.13	Variation of dynamic viscosity with shear rate at 100 °C	46
Figure 1.3.14	Photomicrograph images of Pure lube oil (SN150) and lube oil containing different additives	47
Figure 2.2.1	IR spectra of polymer C	64
Figure 2.2.2	¹ H NMR of polymer C	64
Figure 2.2.3	¹³ C NMR of polymer C	65
Figure 2.2.4	Comparison of VI values of three polymers in base oil, BO1	65
Figure 2.2.5	Comparison of VI values of three polymers in base oil, BO2	66

Figure 2.2.6	Comparison of VI values of three polymers in base oil, BO3	66
Figure 2.2.7	Comparison of pour point values of three polymers in base oil, BO1	67
Figure 2.2.8	Comparison of pour point values of three polymers in base oil, BO2	67
Figure 2.2.9	Comparison of pour point values of three polymers in base oil, BO3	68
Figure 2.3.1	IR spectra of copolymer of maleic anhydride and vinyl acetate	78
Figure 2.3.2	IR spectra of polymer A	78
Figure 2.3.3	¹ H NMR spectra of polymer A	79
Figure 2.3.4	¹³ C NMR spectra of polymer A	79
Figure 2.4.1	IR spectra of polymer A ₁	91
Figure 2.4.2	¹ H NMR spectra of polymer A ₁	91
Figure 2.4.3	¹³ C NMR spectra of polymer A ₁	92
Figure 2.4.4	Thermal degradation of polymers A ₁ , A ₂ and A ₃	92
Figure 2.4.5	Photomicrograph images of a) Pure lube oil b) lube oil + 3% (w/w) of A ₁ c) lube oil + 3% (w/w) of A ₂ d) lube oil + 3% (w/w) of A ₃	93
Figure 2.5.1	IR spectra of Mannich base A ₃	104
Figure 2.5.2	¹ H NMR spectra of Mannich base A ₃	104
Figure 2.5.3	¹³ C NMR spectra of Mannich base A ₃	105
Figure 2.5.4	IR spectra of phosphosulphurized Mannich base B ₁	105
Figure 2.5.5	IR spectra of phosphosulphurized Mannich base B ₂	106
Figure 2.5.6	IR spectra of phosphosulphurized Mannich base B ₃	106
Figure 2.5.7	Variation of V/V ₀ with oxidation time of lube oil without and with Mannich bases additives A ₁ , A ₂ and A ₃	107

Figure 2.5.8	Variation of $\Delta T.A.N$ with oxidation time of lube oil without and with Mannich bases additives A_1 , A_2 and A_3	107
Figure 2.5.9	Variation of V/V_0 with oxidation time of lube oil without and with Phosphosulphurized Mannich bases additives B_1 , B_2 and B_3 .	108
Figure 2.5.10	Variation of $\Delta T.A.N$ with oxidation time of lube oil without and with phosphosulphurized Mannich bases additives B_1 , B_2 and B_3	108
Figure 3.1	General structure of vegetable oil (triglyceride)	111
Figure 3.2.1	IR spectra of terpolymer E	126
Figure 3.2.2	1H NMR spectra of terpolymer E	127
Figure 3.2.3	^{13}C NMR spectra of terpolymer E	127
Figure 3.2.4	IR spectra of the terpolymer E after biodegradable	128
Figure 3.2.5	Thermal degradation of the polymers A, B, C, D and E	128
Figure 3.2.6	Variation of viscosity index of polymer doped base oil (BO1) at different concentrations	129
Figure 3.2.7	Variation of viscosity index of polymer doped base oil (BO2) at different concentrations	129
Figure 3.2.8	Variation of pour point of polymer doped base oil (BO1) at different concentrations	130
Figure 3.2.9	Variation of pour point of polymer doped base oil (BO2) at different concentrations	130
Figure 3.2.10	XRD (powder) patterns of lube oil without and with additives	131
Figure 3.2.11	Photomicrograph images of lube oil without and with different additives	132
Figure 3.2.12	Variation of dynamic viscosity with shear rate at $40^\circ C$	133

Figure 3.2.13	Variation of dynamic viscosity with shear rate at 100 ° C	133
Figure 3.3.1	Triricinolein, the major component of castor oil	145
Figure 3.3.2	IR spectra of homopolymer of DDA (P-1)	146
Figure 3.3.3	IR spectra of homopolymer of castor oil	146
Figure 3.3.4	IR spectra of copolymer of DDA with 15% (w/w) of CO (P-4)	147
Figure 3.3.5	¹ H NMR spectra of homopolymer of DDA(P-1)	147
Figure 3.3.6	¹ H NMR spectra of homopolymer of castor oil	148
Figure 3.3.7	¹ H NMR spectra of copolymer of DDA with 15% of CO (P-4)	148
Figure 3.3.8	¹³ C NMR spectra of homopolymer of DDA	149
Figure 3.3.9	¹³ C NMR spectra of homopolymer of castor oil	149
Figure 3.3.10	¹³ C NMR spectra of copolymer of DDA with 15%(w/w) of CO	150
Figure 3.3.11	TGA of the additive furnished lubricant	150
Figure 2.3.12	Variation of viscosity index of base oil blended with additives at different concentrations	151
Figure 3.3.13	Pour points of the lubricant at different additive concentration levels	151
Figure 3.3.14	Pour point of lubricant at 4% (w/w) additive concentration before and after addition of 10% (w/w) n- decane solvent	152
Figure 3.3.15	Photomicrograph images of a) Pure lube oil b) Lube oil + 4% (w/w) of P-1c) Lube oil + 4% (w/w) of P-2 d) Lube oil + 4% (w/w) of P-3 e) Lube oil + 4% (w/w) of P-4 f) Lube oil + 4% (w/w) of P-5 g) Lube oil + 4% (w/w) of P-6 h) Lube oil + 4% (w/w) of P-7	153
Figure 3.3.16	Wear scar diameter (WSD) of the lube oil blended with additives at different percentages (w/w)	154
Figure 3.3.17	Coefficient of friction (COF) of the lube oil blended with additives	154

at different percentages (w/w)

Figure 3.3.18	Biodegradability test (SBT) of the lubricant compositions	155
Figure 3.3.19	IR spectra of homopolymer of CO (P-7) after biodegradable	155
Figure 3.3.20	IR spectra of P-2, P-4 and P-6 after biodegradable	156
Figure 3.4.1	IR spectra of polymer P-1, P-2, P-3, P-4 and P-5	167
Figure 3.4.2	^1H NMR spectra of P-2 (castor 90% + MMA 10%)	168
Figure 3.4.3	^1H NMR spectra of P-3 (castor 90% + DDA 10%)	168
Figure 3.4.4	^1H NMR spectra of P-4 (castor 90% + 1- decene 10%)	169
Figure 3.4.5	^1H NMR spectra of P-5 (castor 90% + styrene 10 %)	169
Figure 3.4.6	^{13}C NMR spectra of P-2 (castor 90% + MMA 10%)	170
Figure 3.4.7	^{13}C NMR spectra of P-3 (castor 90% + DDA 10%)	170
Figure 3.4.8	^{13}C NMR spectra of P-4 (castor 90% + 1- decene 10%)	171
Figure 3.4.9	^{13}C NMR spectra of P-5 (castor 90% + styrene 10 %)	171
Figure 3.4.10	Thermal degradation of the prepared polymers P-1, P-2, P-3, P-4 and P-5	172
Figure 3.4.11	Wear scar diameter (WSD) of the base oil (BO1) blended with additives at different percentages (w/w) compositions	172
Figure 3.4.12	Wear scar diameter (WSD) of the base oil (BO2) blended with additives at different percentages (w/w) compositions	173
Figure 3.4.13	Results of biodegradability test (SBT) of the prepared additives	173
Figure 3.4.14	IR spectra of polymer P-1, P-2, P-3, P-4 and P-5 after biodegradable	174

LIST OF APPENDICES

Appendix A:	Page no.
List of paper published/ accepted/communicated	xxviii
Appendix B:	
List of oral and poster presentations	xxix
Appendix C:	
Abbreviations	xxx - xxxi

List of paper published/accepted/communicated

1. Mannich bases and Phosphosulphurized Mannich bases: Synthesis, characterization and performance evaluation as potential lube oil additives. P. Ghosh and **M. Hoque**, **Journal of Scientific & Industrial Research**, 2015, 74, 150-154.
2. Homo- and copolymers of decyl methacrylate as performance additives for lube oil. P. Ghosh, **M. Hoque** and D. Nandi, **Petroleum Science and Technology**, 2015, 33, 920-927.
3. Synthesis and performance evaluation of maleic anhydride based polymeric additives for lubricating oil. **M. Hoque** and P. Ghosh, **Research Journal of Chemistry and Environment**, 2015, 19(5), 24 – 31.
4. Synthesis and performance evaluation of vinyl acetate-maleic anhydride based polymeric additives for lubricating oil. P. Ghosh and **M. Hoque**, **Petroleum Science and Technology**, 2015, 33, 1182 -1189.
5. Sunflower oil based terpolymer as sustainable lubricant additive. P. Ghosh, **M. Hoque** and G. Karmakar, accepted for publication in the journal of **Polymer Bulletin**, MS ID: POBU-D-16-00465.
6. Synthesis and characterization of maleic anhydride based multifunctional lube oil additives. P. Ghosh and **M. Hoque**, accepted for publication in the journal of **Petroleum Science and Technology**, MS ID: LPET-2016-0777.
7. Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant. P. Ghosh, **M. Hoque** and G. Karmakar, communicated to **ACS Sustainable Chemistry and Engineering**, MS ID: sc-2016-00374s.
8. Dodecyl methacrylate and vinyl acetate copolymers as viscosity modifier and pour point depressant for lubricating oil. P. Ghosh, **M. Hoque**, G. Karmakar and M. K. Das, communicated to **International Journal of Industrial Chemistry**, MS ID: IJIC-D-16-00058.
9. Castor oil based multifunctional greener additives for lubricating oil. P. Ghosh, **M. Hoque**, G. Karmakar and S. Yeasmin, communicated to **Lubrication Science** MS ID: LS-16-0101-RA-LS.

List of oral and poster presentations

1. Synthesis, characterization and performance evaluation of maleic anhydride based polymeric additives for lubricating oil. **M. Hoque** and P. Ghosh; A oral presentation in the seminar of “West Bengal State Science and Technology Congress-2015” organized by University of North Bengal on 28th February & 1st March, 2015.
2. Viscosity modifier and pour point depressant additives for lube oil: Synthesis, characterization and performance evaluation. **M. Hoque**, D. Nandi, G. Karmakar, M. Upadhaya and P. Ghosh; A oral presentation in the national seminar of “Frontier in Chemistry- 2016” organized by Department of Chemistry, University of North Bengal on 7th & 8th march, 2016.
3. Detergent/dispersant and antioxidant additives for lube oil: Synthesis, characterization and performance evaluation. **M. Hoque** and P. Ghosh; A poster presentation in the national seminar of “Frontier in Chemistry- 2015”, organized by Department of Chemistry, University of North Bengal on 17th & 18th February, 2015.
4. Dodecyl methacrylate based polymeric additives as viscosity modifier and pour point depressant for lube oil. **M. Hoque**, G. Karmakar, S. Yeasmin and P. Ghosh; A poster presentation in the 19th CRSI National Symposium in Chemistry (CRSI NSC -19) organized by Department of Chemistry, University of North Bengal on 14th to 16th July, 2016.

Abbreviations

1. AIBN - Azobisisobutyronitrile
2. ASTM – American Society for Testing and Materials
3. AW - Antiwear
4. BO1 – Base oil 1
5. BO2 – Base oil 2
6. BO3 – Base oil 3
7. BPCL – Bharat Petroleum Corporation Limited
8. BZP – Benzoyl peroxide
9. COF – Coefficient of friction
10. CO – Castor oil
11. DMA- Decylmethacrylate
12. DDA- Dodecyl acrylate
13. DAM – Decyl amine
14. DDAM – Dodecyl amine
15. DDMA – Dodecyl methacrylate
16. FBWT – Four Ball Wear Test
17. GPC – Gel Permeation Chromatography
18. HPLC – High Performance Liquid Chromatography
19. IOCL – Indian Oil Corporation Limited
20. IR – Infra red
21. KV – Kinematic viscosity
22. M_n - Number average molecular weight
23. M_w - Weight average molecular weight
24. MHS- Mark-Houwink-Sakurada
25. NMR – Nuclear magnetic resonance
26. OAM – Octyl amine
27. OEM- Original equipment manufacturer
28. PIB - Polyisobutylene

29. PMA- Polymethacrylate
30. PPD- Pour point depressant
31. PSSI – Permanent shear stability index
32. SBT – Soil burial test
33. SSI – Shear stability index
34. SIP- Styrene isoprene polymer
35. TMS - Tetramethylsilane
36. TVL – Temporary viscosity loss
37. TGA – Thermo gravimetric analysis
38. VI – Viscosity index
39. VII – Viscosity index improver
40. VM – Viscosity modifier
41. WSD – Wear scar diameter
42. XRD – X-ray diffraction
43. ZDDP- Zinc dialkyl dithiophosphate
44. ZDP – Zinc dithiophosphate

General introduction of the present investigation

The development of engine and transmission technology is not possible without the development of chemistry of lubricant additives. The lubricant companies are working with the partnership of Oil Company and the automotive industries to enhance longevity and performances of engine and the drive line system through lubricant design.¹

Lubricating oil, also called base oil, is the basic building block of a lubricant. They are complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with molecular weights ranging from C₂₀-C₇₀ (boiling range 622-673K).² The main role of the base oil is to lubricate the engine and it is a carrier of additives. They are less volatile and with high value of viscosity index. The proportions of different hydrocarbon components determine the characteristics of the base oils. The performance of lubricant base oils is governed by their rheological properties such as low temperature fluidity, high viscosity and viscosity temperature relationship. For example, to provide an effective performance at low temperature as well as at high temperature, an engine lubricant should have good low temperature fluidity and small variation of viscosity with rise in temperature.³

Until the 1920s the engine oil contained no additives, containing only base oil. Due to increasing economic pressures and consumer demands, the internal combustion engines were becoming more innovatory. The base oil can't satisfy all the requirements of modern engines. To improve the performance of the base oil, different kinds of additives are blended. Additives are the polymeric or non polymeric synthetic compounds. The additives blended base oils are called lubricants. The lubricants are more compatible to the new technology.⁴ They not only improve the performance of the base stock that already present in it but also add some new properties.⁵ The main role of additives are to

- a) enhance the lifetime of machine
- b) enhance fuel economy
- c) induce better performance
- d) help in achieving green technology
- e) reduce pollution.

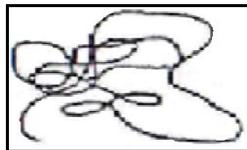
Thus research and development of additive chemistry for lube oil definitely improves the pursuit of original equipment manufacturer (OEM) in the technology sector. The combination

and quantities of different additives are determined by the lubricant type (engine oils, gear oils, hydraulic oils, compressor oils etc) and depending on operating conditions (temperature, loads, environment, parts of machine etc). The addition of amount of additives may reach up to 30% (w/w) to the lube oil.⁶

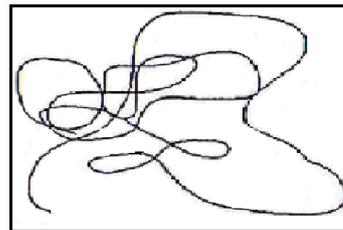
Types of lube oil additives: Different types of lube oil additives are

i) Viscosity index improver (VII) or Viscosity modifier (VM) ii) Pour point depressant (PPD) iii) Antiwear additive (AW) iv) Friction modifier (FM) v) Antioxidant (AO) vi) Detergent vii) Dispersant viii) Extreme pressure additive (EP) ix) Rust and corrosion inhibitor x) Anti-foam agent.

Viscosity Index Improver: The degree of susceptibility of viscosity of a fluid with rise in temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI). Viscosity index improvers (VII), also known as viscosity modifiers (VM) are additives that resist the change of viscosity of oil with change in temperature.⁷ They cause a minimum amount of increase in engine oil viscosity at low temperature, but considerable amount of increase at high temperature. A higher VI value signifies a lesser effect of temperature on viscosity. Viscosity index improvers keep the viscosity at acceptable level which provides stable oil film even at increased temperature. Acrylate based polymers are widely used as VII in lubricants. It is believed that in cold oil the polymer molecule adopt a coiled form but in hot oil the long chain polymer molecule swells up and interaction between the polymer molecule and the oil produces proportionally greater thickening effect which offsets the normal reduction of viscosity with rise in temperature.⁸



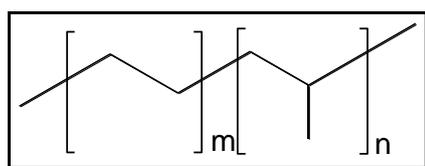
Polymer in lube oil at low temperature



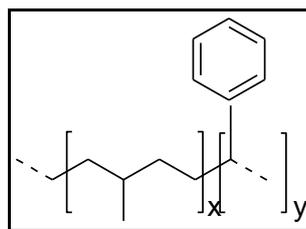
Polymer in lube oil at high temperature

Figure 1 Effect of temperature on polymeric additive in lube oil.

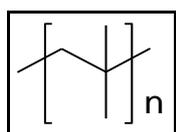
Higher molecular weight polymers are widely used as VII for multigrade lubricants. Olefin copolymers, hydrogenated styrene-diene copolymers, maleic anhydride based copolymers, polyisobutylene, polyalkylmethacrylates, vegetables oil based polymers etc. are widely used as VII for multigrade lubricants.



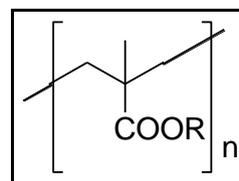
Ethylene-propylene copolymer



Hydrogenated styrene-isoprene copolymer



Polyisobutylene



Polyalkylmethacrylate

Figure 2 Structure of some commonly used viscosity index improver

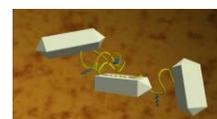
Pour point depressant: Pour point is the lowest temperature at which the flow of fluids is stopped. Lube oil contains some paraffinic wax (generally 5% - 20%). The complete removal of paraffinic wax from lube oil is difficult and expensive; pour point depressants provide an economical means of facilitating the flow property of oil in an engine at low temperature.^{9, 10} At low temperature, the paraffinic wax crystallizes to form a rigid structure that traps the oil molecule and hinders the flow capability. Pour point depressants, otherwise known as lube oil flow improvers (LOFI), are those additives that improve the low temperature fluidity of the fluid. The pour point depressants function by inhibiting the formation of a wax crystal structure that would prevent the oil flow at low temperatures.^{11, 12} The polymeric additives which are used as PPD should have some pendant alkyl groups and there should be an appropriate distances among the pendant groups.^{13, 14} Moreover, there should be a suitable monomer-monomer ratio in the copolymers which are used as PPD.¹⁵



Wax crystal



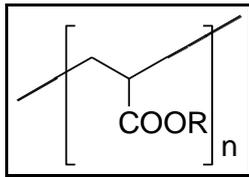
Polymeric additives



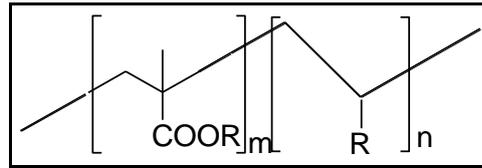
controlled growth of wax

Figure 3 Schematic representation of the action mechanism of additives on wax crystal

Polyalkylacrylates, copolymers of polyalkyl methacrylate,¹⁶ maleic anhydride based polymeric additives, vinyl acetate based polymeric additives¹⁷ and recently polymers of vegetable oils are widely used as PPD in lubricants.¹⁸



Polyalkylacrylate



Copolymer of alkylmethacrylate with α -olefin

Figure 4 Structure of some commonly used pour point depressant

Antiwear additive: The antiwear additives prevent the direct metal to metal contact of the two moving parts of an engine when the oil film is broken down. The antiwear additives enhance the life of the machine. The mechanism action of anti-wear additives is that strong adsorption or chemisorptions takes place between the AW additives and the metal surface and generates a film, which may slide over the friction surface. In case of chemisorptions sometimes electron transfer occurs between additive molecule and metal surface.¹⁹

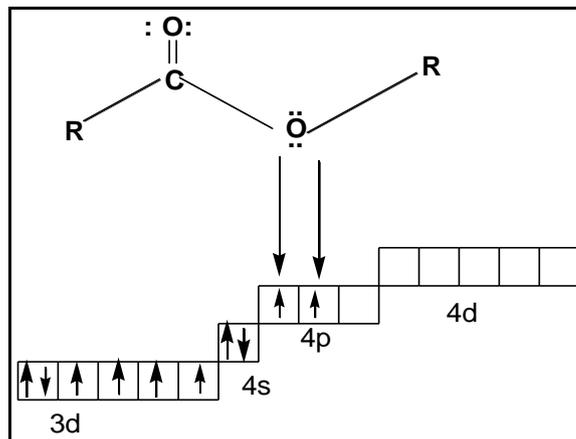
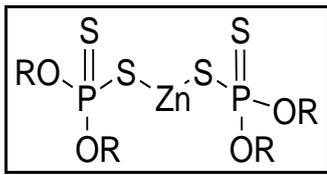
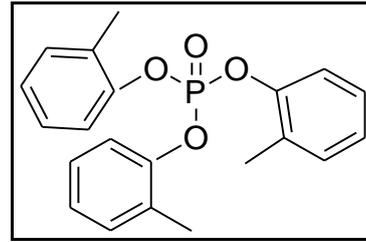


Figure 5 Schematic representation of donor acceptor bond between AW additive and metal (Fe) surface

Organosulfur, organophosphorus compounds are widely used AW and extreme pressure additives. Zinc dialkyl dithio phosphate (ZDDP) is the most widely used AW additive in formulated engine oils.²⁰ It also acts as an antioxidant and corrosion inhibitor. Tricresyl Phosphate (TCP) is used as AW and EP additive in turbine engine lubricants, and also in some crankcase oils and hydraulic fluids. Recently liquid crystals, ionic liquid,²¹ nanoparticles²² and environmentally benign vegetable oils based additives²³ are used as AW for lubricating oils.



Zinc dialkyldithiophosphate



Tricresyl phosphate

Figure 6 Structure of some commonly used antiwear additives

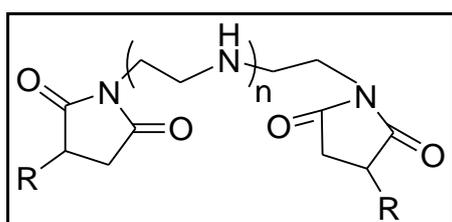
Friction modifier: The additive which reduces the coefficient of friction and hence less fuel consumption is called friction modifiers. Most of FM consists of molecular platelets which may easily slide over each other. The mechanism action of FM is that they generate durable low resistance lubricant films through adsorption on surfaces and association with the oil. Long chain fatty acid and its derivatives, graphite, molybdenum, boron nitride (BN), Tungsten disulphide (WS_2), polytetrafluoroethylene (PTFE) etc. are the lubricants used as FM.

Antioxidant additive: Lubricating oil reacts with oxygen of air or heat forming some organic fatty acids, fatty alcohols, fatty aldehydes and ketones, fatty esters, peroxides etc. The Fe/Cu metal present in internal engine part supports the oxidation process by acting as a catalyst. All oxidized products are solid asphaltic materials. The oxidation products are responsible for the increase of oil viscosity, formation of sludge and varnish, corrosion of internal engine part and reduced fuel economy. For this reason, addition of antioxidants to lubricating oil is necessary to prevent the formation of these products. Alkyl sulphides, aromatic sulphides, aromatic amines, hindered phenols, zinc dithiophosphate (ZDP) etc. are the compounds widely used as antioxidants in lubricating oil. The antioxidant like hindered phenols and aromatics amines transfer hydrogen atom from $-OH$ and $-NH_2$ group respectively that react with alkyl radicals or alkyl alkoxy radicals that was generated during the oxidation of oil. As a result, alkyl radical and alkyl alkoxy radical convert into stable hydrocarbon and alkyl hydro peroxide respectively. After transferring the H-atom, the phenols or amines convert into quinines or quine imines that don't maintain the radical chain mechanism.

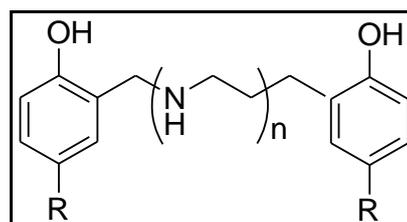
Detergent and dispersant additives: Detergents are the additives which neutralize strong acids present in the lubricant and remove the neutralization products from the metal surface of the engine. The strong acids are generated as a result of combustion process in the internal

combustion engine.²⁴ Detergents are the phenolates, sulphonates or phosphates of alkaline or alkaline earth metals such as Ca, Mg, Na or Ba etc.

The additives which keep the foreign particles present in a lubricant in a finely divided and uniformly dispersed throughout the oil are called dispersant additives.²⁵ The foreign particles are generally sludge and varnish, dirt, products of oxidation, water etc. Long chain polyisobutylene succinimides,²⁶ Mannich bases and phosphosulphurized Mannich bases of hindered phenols,²⁷ amidation products of maleic anhydride and alpha olefin copolymer²⁸ etc. are widely used as dispersants in lubricants.



Succinimide based dispersant



Mannich base type dispersant

Figure 7 Structure of some commonly used dispersant additives

A dispersant molecule consists of a hydrocarbon group, nitrogen or oxygen based polar group and a connecting group, shown in the figure.....

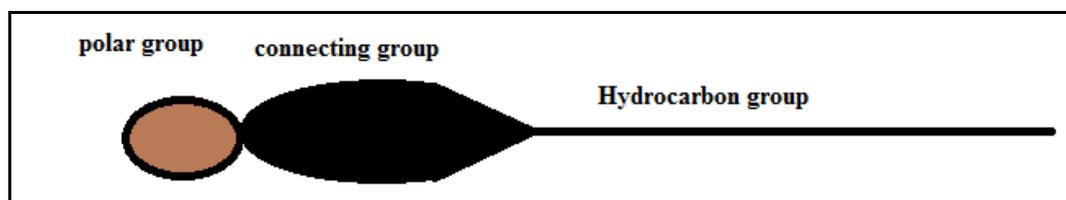


Figure 8 Graphical representation of a dispersant molecule

Dispersants prevents in agglomeration by associating with resins and soot particles. The associated dispersant molecule is incompetent to unite due to steric factors or electrostatic factors. The polar group of the dispersant molecule is associated with the polar particles and the non polar group (hydrocarbon group) keeps such particles suspended in the bulk lubricant.²⁹

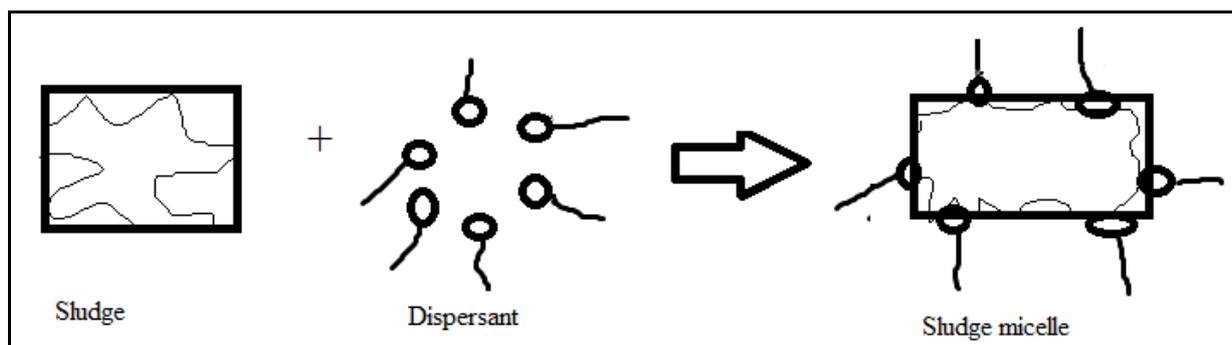


Figure 9 Action mechanism of dispersant

Although many researchers have studied and reported number of additives or polymeric additives functioning either only as a VM³⁰ or PPD³¹ or AW³² additive or some works based on bifunctional properties like VM-PPD³³ or VM-AW³⁴, antioxidants - detergents /dispersants³⁵ etc, but the research based on polymeric additives having multifunctional properties are very scanty till date. With the development of engine technology, the modern engines are demanding high quality, cost effective and environmentally benign additives³⁶⁻³⁸ having multifunctional performance. Keeping these views in mind, the author have made an effort to achieve some multifunctional additives in a single additive system to meet the above demands. Some methacrylate and maleic anhydride based polymeric additives were synthesised and multifunctional additive performance were also evaluated. Keeping the concept of greener technology in mind, the present investigation also comprises the synthesis and performance evaluation of vegetable oil based multifunctional additives. Vegetable oils used in this study are sunflower oil and castor oil. The additive doped lube oils manifested excellent multifunctional additive performance along with very significant biodegradability. In brief, the thesis comprises synthesis, characterization and performance evaluation of a numbers of different additives for lubricating oils. The characterization was carried out by spectroscopic method (FT-IR and NMR). The thermal stability was determined by thermo gravimetric analysis (TGA) method. Molecular weight of the polymers was determined by gel permeation chromatographic method (GPC method) and in some cases by viscometric method. Finally performances of the additives mainly as viscosity index improver (VII) or viscosity modifier (VM), pour point depressant (PPD), in some cases antiwear (AW), antioxidant and detergent/dispersant were evaluated by standard ASTM methods in different base oils. Degradation stability (in terms of shear stability) of some of the prepared additives were also determined and reported. Biodegradability study was carried out by disc diffusion

method and soil burial test method using different fungal pathogens according to ISO 846:1997 rules. Photo micrographic image and powder XRD of some of the PPD were also carried out in base oil to study the mechanism action of pour point. The outcome of our present investigations has some potential additives for lubricating oil which will be dealt with for commercial application and will be taken up by our group in near future. In addition, the investigation has also contributed to the lube oil additive chemistry and will definitely help to grow interest in research among the young scientists in the field of additive chemistry for lubricating oil.

References

References are given in bibliography section under general introduction of present investigation (Page No. 175 - 178).

Part I

Methacrylate based polymeric additives as multifunctional lube oil additives

Chapter I

Background of the present investigation

In recent years, the Original Equipment Manufacturers (OEM) are developing modern and advance engines. The advanced engine technology requires the development of new lubricants and improvement of the existing one. As a result, the productive sector and the regulatory agencies must develop methods and mechanism to monitor cost effectiveness and the performance of the products available in the market. In order to cope up with this present demand it is essential to synthesize some multifunctional lube oil additives that not only increase the lifetime of lubricating oil but also increase the lifetime of engine at a cheaper cost. The use of multifunctional additive in lubricating oil formulation is well known.¹ All commercial lubricants contain some additives to add additional their performances in them. The percentage of additives in lubricants may vary from 1% to 30% or more.² The different types of lubricating oil additives are (a) pour point depressant (PPD)³ which decreases the pour point of lube oil by dissolving the wax present in lube oil, (b) viscosity index improvers (VII)⁴ which increases the viscosity index so that the lube oil does not change its viscosity appreciably with temperature change, (c) antioxidant which increases thermal stability⁵, (d) anti wear which prevents direct metal to metal contact⁶, (e) detergents /dispersants⁷, (f) corrosion inhibitors⁸, (g) extreme pressure additives⁹ etc. These additives when added to lubricating oil enhance the properties already present or add some new properties also. Keeping in view the cost and the harmful nature of the chemicals used in this field, demand for multifunctional additive is increasing. In recent context, multifunctional additives play the major role in the technology of engine oils. Research throughout the world is directed to produce multifunctional lube oil additives.¹⁰

In accordance with the present investigation, it will be very pertinent to include a brief review on VII and PPD property of methacrylate based polymeric additives for lube oil.

As discussed in the general introduction, a viscosity index improver (VII) is explained in terms of viscosity index (VI) which is an arbitrary number¹¹ that indicates the resistance of a lubricant to change in viscosity with increase in temperature. Viscosity index improvers are compounds which increases the viscosity index of lubricant. A higher viscosity index indicates small change in viscosity with rise in temperature and vice - versa. Again productiveness of a VII depends on the type and concentration of the additive. Long chain high molecular weight polymeric additives are generally used as VII. Performance of the VII depends on the behaviour of the polymer molecules in the lube oil in terms of solubility and

resistance to shear degradation.¹² The solubility of polymer molecule increases with increasing temperature and the polymer molecules change from tight coils to an open configuration which has a greater volume. This increase in volume causes increase in viscosity of the oil, which offsets the normal reduction of viscosity with increasing temperature.^{13, 14} The polymer having high molecular weight also increases the effective volume in an oil solution and as a result, a polymer having higher molecular weight also exhibits higher viscosity index than a lower molecular weight polymer of the same type.¹⁵

Pour point depressants are designed to prevent the agglomeration of wax particle present in lube oil. If lubricating oil is not properly protected with pour point depressants, the flow characteristic of lube oil is highly affected which can affect the engine performances. The polymeric additives which are used as pour point depressant must have some pendant alkyl groups and there should be an appropriate distance between the pendant chains and there must be a suitable ratio of monomers if copolymer is used as a PPD.^{16, 17} Pour point depressants used earlier were either alkylated aromatic polymers or comb polymers.¹⁸ Comb polymers have long alkyl chains attached to the backbone of the polymer, with the alkyl group being of different carbon chain lengths. Earlier the mechanism action of PPD was assumed that the alkylated aromatic compounds function by coating the surface of the wax crystals and preventing further growth. More recently, it is believed that PPD function by nucleation, co-crystallization or adsorption and disrupting the formation of three dimensional wax crystals network.¹⁹

The homo and copolymers of alkylmethacrylate or alkylacrylate are widely used as viscosity index improver (VII), commonly known as viscosity modifier (VM) and pour point depressant (PPD). The alkylmethacrylate polymers are more polar than ethylene/propylene or styrene/diene polymers and the long chain alkyl group imparts solubility to the lube oil. A mixture of methacrylates monomer having different alkyl chain can be copolymerized in an identical copolymerization reactivity ratio and in a statistically random distribution regardless of the size of the alkyl groups.²⁰ Most of the additives used as VM and PPD for lubricating oil are methacrylate and acrylate based polymers. The following patents discussed the same. U.S. Patent No. 5834408 described the procedure of synthesis and performance evaluation of acrylate based copolymers as a PPD in lube oil compositions. U.S. Patent No. 4867894 claimed that copolymers of methyl methacrylate having an average molecular weight from 50,000 to 500,000 showed excellent pour point depressants for petroleum oil.

U.S. Patent No. 4073738 described the application of alkyl acrylate or alkyl methacrylate as pour point depressants for lube oil where in the alkyl group can have 8 to 22 carbon atoms. U.S. Patent No. 3897353 disclosed the oil composition comprising lubricating oil and an n-alkyl methacrylate as a pour point depressant. These acrylates may be made from monomers wherein the alkyl group may have 12 to 18 carbon atoms.

Patent No. EP 0140274 described the application of lubricating oil additives which contain n-paraffin based polyalkylmethacrylate and acrylate. U.S. Patent No. 4490267 disclosed the synthesis of alkylmethacrylates based lubricating oil additives having carbon number C_1 - C_{30} .

U.S. Patent No. 4073738 claimed that acrylate and methacrylate based copolymers with conjugated dienes exhibited high shear stability and useful as a VII for lube oil. U.S. Patent No. 5955405 claimed that methacrylate copolymers comprising of 5 to 15 wt% butyl methacrylate, 70-90 wt% C_{10} to C_{15} alkyl methacrylate and 5-10 wt% C_{16} - C_{30} alkyl methacrylate exhibit excellent low temperature properties in lubricating oils. U.S. Patent No. 4968444 described the use of mixed polyacrylates as multifunctional lube oil additives.

U.S. Patent No. 8105990, 3607749 and 4203854 described the application of poly methacrylate as viscosity modifiers for lubricating oil.

A number of literatures are available on efficiency of poly alkyl acrylate and poly alkyl methacrylate as VII and PPD.²¹⁻²³ In 1937, Rohm and Haas Co. patented the first polymeric pour point depressant, poly alkyl methacrylates (PAMAs). Almost 15 years later Ruehrwein reported the action of n- alkyl poly methacrylate as PPD in the series dodecyl, tetradecyl, hexadecyl and octadecyl methacrylate.²⁴

In 1997, El- Gamel et al. reported the synthesis of alkyl methacrylate – C_{18} α -olefin as PPD for waxy residue fuel and concluded that the polymer containing alkyl group consisting of 21 carbon number showed excellent pour point depressant.²⁵ In 2010, Rasha et al. had reported a novel PPD for waxy crude oil based on alkyl acrylates terpolymers.²⁶

In 1949, W. L. Van Horne reported polymethacrylates as VII and PPD in a number of lubricating base stocks.²⁷ In 2010, Jukic et al. studied the thermal stability of n-alkyl methacrylates and styrene based terpolymers. The research group reported that the terpolymer consisting of dodecyl methacrylate (DDMA), octadecyl methacrylate (OCMA) and styrene as monomers has a good thermal stability.²⁸

In 2010, A. M. Nassar reported six copolymers of 2- ethylhexyl methacrylate with vinyl acetate at different molar ratios. The performance of these polymers in lube oil was evaluated as VII and found that efficiency increases with increasing molecular weight of polymers as

well as concentrations in lube oil.²⁹ In 2011, Jung et al. reported twelve copolymers and six terpolymers based on different methacrylates and performance of these polymers in lube oil were evaluated as PPD. The research group reported that the terpolymers made from dodecyl methacrylate, hexadecyl methacrylate and methyl methacrylate at a molar ratio of 3.5:3.5:3 exhibited the best low temperature properties.³⁰

In 2012, Jukic et al. reported the application of polymer made from dodecyl methacrylate (DDMA), octadecyl methacrylate (ODMA), N, N dimethylaminoethyl methacrylate (DMAEMA) with styrene as VII, PPD and detergents/dispersants. The research group reported that by increasing the percentage of DMAEMA in copolymer from 2 to 10 mol%, their M_w values decreases from 120 to 60 kg mol⁻¹.³¹ In 2012, Mohammed et al. reported poly methylmethacrylate as additive for Iraqi lubricating oils in engine condition and performance evaluation was viscosity index improvement.³²

In 2006, Abdel-Azim et al. reported twenty polymeric additives based on different ratios of styrene and different esters of acrylic acid. The efficiency of the polymers in lube oil was evaluated as PPD. The research group reported that the efficiency as PPD decreases by increasing the styrene content in the prepared polymers.³³ In 2007, Jukic et al. reported styrene, dodecylmethacrylate and octadecyl methacrylate based terpolymers as viscosity index improvers for lubricating oil. The research group also cited that the content of styrene in the terpolymer was limited up to 25% by weight and VI increases with increasing molar mass and opposite effect was obtained by increasing the styrene content.³⁴

From the above literature study, it is seen that lot of works already done on polymethacrylate as additive for lubricating oil. Since methacrylate based polymeric additives are widely used as a commercial lube oil additives, therefore, further explorative studies on the methacrylate based additives were felt necessary to obtain still better performance out of this chemistry. Keeping this view in mind, the present investigation comprises the synthesis and characterization of homo and copolymers of decyl and dodecyl methacrylate and evaluation of their performance as VII and PPD in different types of base oils.

References

References are given in bibliography section under Chapter I of Part I (Page No. 178 - 180).

Chapter II

Homo and copolymers of decyl methacrylate – synthesis, characterization and performance evaluation for lube oil

1.2.1 Introduction

Base oil is the major component of lubricating oil. Some additives are to be added to the base oil to meet the requirement of modern lubricating oil. Additives are the chemical substances which when added to the base oil they can enhance the properties already present or add some new properties. Some of the important additives added in lube oil are viscosity index improver (VII),¹ pour point depressant (PPD),² antiwear,³ antioxidant, dispersant⁴ etc.

Viscosity index improvers are long chain, high molecular weight polymers and are used to resist the change of viscosity and function by increasing the relative viscosity of oil more at high temperatures than at low temperatures.⁵ It is believed that polymer molecules in cold oil adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the polymer molecules tend to straighten out and the interaction between these long molecules and the oil produces a proportionally greater thickening effect. As the temperature increases, the solubility improves and the polymer coils expand to some maximum size and in so doing donate more and more viscosity. The process of coil expansion is entirely reversibly as coil contraction occurs with decreasing temperature.^{6, 7} The viscosity index is an indicator which indicates the change in viscosity when the temperature is changed. A higher viscosity index indicates the less change in viscosity of oil for a given temperature changes.⁸

Shear stability is an indicator which indicates the amount of viscosity of oil may lose during operation. Lube oil experiences very high stresses in certain areas of engine such as in the oil pump, piston rings and any other areas where two mating surface areas compress the oil film out momentarily. Most of the lubricating oils contain viscosity modifier which are composed of very large viscosity- controlling molecules.⁹

The pour point of oil is the lowest temperature at which the oil stops its flowing. Most of base oil contains some dissolved paraffinic wax. The complete removal of wax from oil is difficult and expensive. Pour point depressants provide an economical alternative way of facilitating the proper flow of the oil in an engine at low temperature.^{10, 11} At low temperature, the wax crystallizes to form a rigid structure that traps the oil in small packets in the structure. With sufficient formation of these crystal structures, the oil will no longer capable to flow. To overcome this problem some high molecular weight polymers are used as pour point depressant (PPD). The high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent the oil flow at low temperature.^{12, 13}

In this present work, author has prepared homopolymers of decylmethacrylate and its copolymers with styrene at different percentage composition by using two types of initiators (BZP and AIBN) and investigated the efficiency of the polymers as viscosity index improver and pour point depressant in two types of base oil. Shear stability, which is an indicator to indicate the amount of viscosity of oil, may lose during operation, of each of the polymer have also been investigated. Finally a comparison of the efficiency of the polymers in terms of their performances in lube oil is investigated and reported in this chapter.

1.2.2 Experimental section

1.2.2.1 Chemicals used

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), styrene (99%, Sigma-Aldrich), decyl alcohol (DA, 98%, SRL Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), hexane (99.5%, S. d Fine Cheme Ltd.) and methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.), benzoyl peroxide (BZP, 98% Thomas Baker Pvt. Ltd.) and azobisisobutyronitrile (AIBN, 98%, Spectrochem Pvt. Ltd.) were purified by recrystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. Base oil was collected from IOCL and BPCL, India. Physical properties of the base oils are given in **table 1.2.1**.

1.2.2.2 Preparation of ester (monomer)

Decylmethacrylate (DMA) was prepared by reacting methacrylic acid with n-decyl alcohol in the molar ratio of 1.1:1 in the presence of conc. H₂SO₄ as a catalyst, 0.25% (w/w) hydroquinone with respect to the reactants as polymerization inhibitor, and toluene as solvent by using Dean Stark apparatus. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen. The reactants were mixed with toluene and heated gradually from room temperature to 130° C using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester.

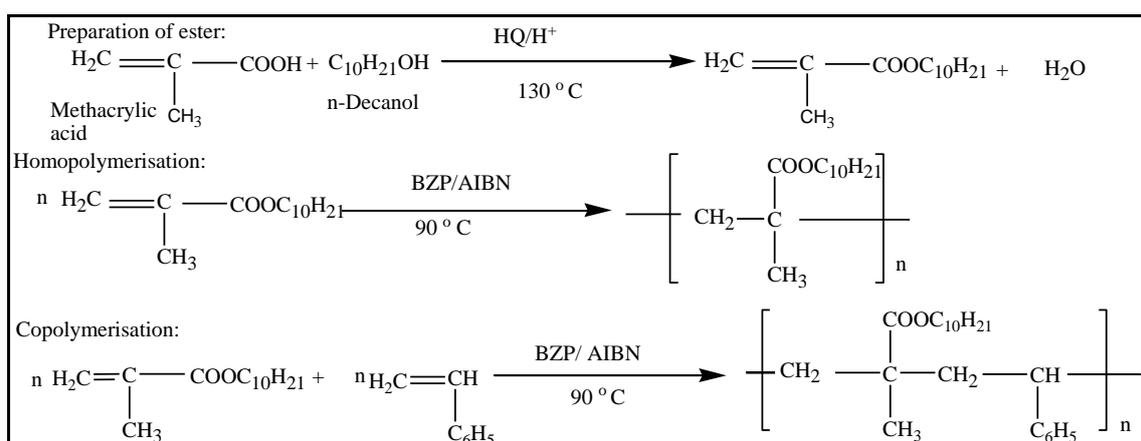
1.2.2.3 Purification of prepared ester

A suitable amount of charcoal was added to the prepared ester. It was allowed to reflux for 2 ½ h and then filtered off. The filtrate was washed with 0.5 N sodium hydroxide solution in a separating funnel and then shaken well. This process was repeated several times to ensure the complete removal of unreacted acid and hydroquinone. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide. The ester was then dried by Na₂SO₄ and distillation under reduced pressure and was used in the polymerization process.

1.2.2.4 Preparation of copolymers and homopolymers

The polymers were prepared by free radical polymerization of different percentage ratios of styrene with DMA in presence of different initiators (BZP and AIBN). The polymerization was carried out in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. In the flask, the desired amounts of DMA and styrene in toluene solvent were heated to 90 °C for half an hour. AIBN/BZP (0.5% w/w, with respect to the total monomer) was then added and heated for 6 hours keeping the temperature constant at 90°C. At the end of the reaction time, the mixture was poured into cold methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K temperature. The homopolymer of DMA was also prepared and purified in the same procedure.

By the above process, the author had prepared five polymers by using initiator BZP (one homopolymer and four copolymers) and another five polymers by AIBN (one homopolymer and four copolymers) at different percentage composition, shown in **table 1.2.2**.



Scheme 1 Preparation of ester, homopolymer and copolymer

1.2.3 Measurements

1.2.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

1.2.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (polystyrene calibration) equipped with a 2414 detector, waters 515 HPLC pump and 717 plus auto sampler. Sample solutions (0.4% w/v in HPLC grade THF) are prepared by dissolving ~4 mg of polymer per ml THF and filtering (0.45- μ m Millipore PTFE) to remove suspended particulates. The pump flow rate is 1.0 mL/min with THF as the carrier solvent, and injection volumes are set to 20 μ L. The polydispersity index¹⁴ which indicates the nature of the distribution of the molecular weights in the polymers was also calculated.

1.2.3.3 Determination of Thermo gravimetric analysis (TGA) data

The thermo-oxidative stability of all the polymers was determined by a thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating of rate of 10 °C/min.

1.2.3.4 Determination of shear stability

Shear stability of the polymer blended lube oil is one of the essential criteria that determine the suitability of the additive in a lubricant formulation. The shear stability of the doped VM's has a strong influence on multigrade engine oil's ability to retain its viscosity under shearing conditions, experienced by the lubricant when it is used. The loss of viscosity of a lubricant under shearing condition can be of two types, temporary viscosity loss (TVL) and permanent viscosity loss (PVL). The PVL values are generally expressed in terms of permanent shear stability index (PSSI). The PVL/PSSI value was determined as per ASTM D-3945 method by the following relation.¹⁵

$$\text{PVL (\%)} = (V_i - V_s) / V_i \times 100 \quad (1)$$

$$\text{PSSI (\%)} = (V_i - V_s) / (V_i - V_o) \times 100 \quad (2)$$

Where V_i = Kinematic viscosity of lube oil with polymer before shearing at 100 °C

V_s = Kinematic viscosity of lube oil with polymer after shearing at 100 °C

V_o = Kinematic viscosity of lube oil at 100 °C

Higher the PVL/PSSI value, lower is the shear stability of the polymer.

1.2.3.5 Performance evaluation as viscosity index improver

Viscosity index was calculated by dissolving prepared polymer in two different base oils (BO1 and BO2) using an Ostwald Viscometer (size 200, No 3205), thoroughly cleaned, dried and calibrated at the experimental temperatures (313K and 373K) with distilled water and purified methanol.¹⁶ It was then filled with experimental solution and placed vertically in a

glass sided thermostat. After reaching thermal equilibrium, the time flow of solutions was recorded with a digital stopwatch. In all the determinations an average of three measurements was taken into account and precautions were taken to minimize the losses due to evaporation. The kinematic viscosity (ν) of the sample solution, which was used to calculate Viscosity index (VI), was determined at 313K and 373K temperatures from the following equation¹⁷

$$\nu = (Kt - L/t) d \quad (3)$$

Where K and L are the viscometric constants and their values are $0.06853\text{cm}^2\text{s}^{-2}$ and 5.2706cm^3 respectively, are determined by taking toluene as a solvent, t and d are the time of flow and density of the experimental solution respectively. The densities were measured with a density meter (Anton Paar, DMA 4500M). Before measurements, the density meter was calibrated with distilled water and acetone at the experimental temperature and atmospheric pressure. VI was calculated from the following empirical equation¹⁷

$$VI = 3.63 (60 - 10^n) \quad (4)$$

Where n is given by

$$n = (\ln \nu_1 - \ln \nu_2) / \ln v_2 \quad (5)$$

Where ν_1 and ν_2 are the kinematic viscosities at lower and higher temperatures respectively, K is a constant which is equal to 2.714 for the temperature range performed and n is the characteristic constant for each oil.¹⁷

Different concentrations ranging 1% - 5% (w/w) were used to study the effect of additive concentration on VI.

1.2.3.6 Performance evaluation as pour point depressant

Pour point was determined in polymer doped different base oils (BO1 and BO2) through the pour point test according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging 1% - 5% (w/w).

1.2.4 Results and discussion

1.2.4.1 Spectroscopic analysis

The IR and NMR spectra of the two homopolymers (P-1 and P-6) of decylmethacrylate are similar. IR absorption band at 1736cm^{-1} represents the ester carbonyl group. The peaks at 2854.5cm^{-1} and 2924cm^{-1} represent the CH_3CH_2- group. The peaks at 1466cm^{-1} , 1404cm^{-1} , 1229cm^{-1} , 1211cm^{-1} and 1149.5cm^{-1} due to CO stretching vibration and absorption bands at 1064.6cm^{-1} , 710cm^{-1} and 690cm^{-1} were due to bending of C-H bond (**figure 1.2.1**). In the ^1H NMR of homopolymer, the methyl protons appear in the range of 0.890 to

1.29 ppm, the methylene protons appear in the range of 1.62 to 1.93 ppm for all alkyl groups. A broad peak at 3.93 ppm indicates the protons of $-\text{OCH}_2$ group. Absence of any peak in the range of 5-6 ppm confirms the polymerisation (**figure 1.2.2**). In the ^{13}C NMR of homopolymer, the peak at 177.54 ppm indicates the presence of ester carbon. The peaks at 65.03 ppm and 64.88 ppm confirm the presence of $-\text{OCH}_2$ carbon. Peaks in the range of 14.16 - 45.12 ppm represent all sp^3 carbon atoms of alkyl groups. No peak in the range of 120-150 ppm indicates the absence of sp^2 carbons and confirms the polymerization (**figure 1.2.3**).

The IR and NMR spectra of all copolymers are similar. The ester carbonyl group at 1736 cm^{-1} of homopolymer shifted to 1728 cm^{-1} in the copolymer. Peaks at 750.4 cm^{-1} , 722 cm^{-1} and 702 cm^{-1} were attributed to the C-H bond of the phenyl group of styrene (**figure 1.2.4**). In the ^1H NMR of copolymer, a broad peak in the range of 3.933 - 4.15 ppm indicates the $-\text{OCH}_2$ protons. A broad peak at 7.01 - 7.33 ppm appears due to the protons of phenyl group. All the sp^3 protons appear in the range of 0.9 - 1.94 ppm. Absence of peaks in the range of 5-6 ppm indicates that the polymerisation was carried out successfully (**figure 1.2.5**). In the ^{13}C NMR of copolymer, the peaks in the range of 176.8 - 177.79 ppm confirm the presence of ester carbons. The phenyl carbons appear in the range of 125.04 - 128.56 ppm. The $-\text{OCH}_2$ carbon peaks appear at 64.86 ppm and 65.02 ppm. Peaks in the range 14.12 - 54.41 ppm represent all the sp^3 carbons (**figure 1.2.6**).

1.2.4.2 Analysis of molecular weight

The experimental values of M_n and M_w for the polymer P-1 to P-10 (determined by GPC) are given in **table 1.2.3**. The data indicated that molecular weight of homopolymer prepared by BZP (P-1) initiator is higher than homopolymer prepared by AIBN initiator (P-6). But the copolymers prepared by BZP have lower molecular weight than the copolymers prepared by AIBN. Moreover, it is also seen that with increasing the percentage of styrene in copolymers the molecular weight as well as PDI values increase.

1.2.4.3 Analysis of TGA data

The TGA values of all the polymers are given in **table 1.2.4**. From the experimental data, it is found that the homopolymer prepared by BZP initiator (P-1) is thermally less stable than homopolymer prepared by AIBN initiator. It may be due to higher molecular weight and higher PDI value of P-1. From the values, it is also observed that thermal stability of copolymers (P-2, P-3, P-4 and P-5) is more than homopolymer, P-1. Similarly, the copolymers P-7, P-8 and P-9 are thermally more stable than homopolymer, P-6 except P-10, which is thermally less stable than P-6. It may be because of the higher PDI value P-10, that

may lead to more degradation. The higher thermal stability of copolymers may be due to the presence of phenyl group. On the other hand, the homopolymer containing only the ester group may easily undergo degradation by producing gaseous products.^{18, 19} Moreover, it is also observed that with increasing the styrene content in the feed of copolymers, the thermal stability decreases which is also reflected in their higher PDI value.

1.2.4.4 Analysis of permanent shear stability index (PSSI) data

PSSI values were calculated in polymer doped base oil (BO2) at 2% (w/w) and 5 % (w/w) concentrations at 100 ° C. The experimental values are given in **figure 1.2.7**. From the figure, it is found that homopolymer P-1 is less shear stable (higher PSSI value) than homopolymer P-6. It may be due to higher molecular weight of P-1. The copolymer P-2, P-3, P-4 and P-5 are more shear stable than P-1 at low concentration but at higher concentration P-4 and P-5 is less shear stable. In case of copolymers prepared by AIBN initiator, P-7 and P-8 are more shear stable than homopolymer P-6 but P-9 and P-10 are less shear stable than P-6. It may be due to higher PDI value of P-9 and P-10. Moreover, it is also found that at a higher concentration polymer - base oil blend is less shear stable than at lower concentration. From the figure 1.2.7, it also is observed that with increasing the styrene content in copolymers the shear stability decreases (higher PSSI value) which may be due to their increased PDI values.²⁰

1.2.4.5 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers at the concentrations of 1% - 5 % (w/w) to the two types of base oil (BO1 and BO2). The experimental values of VI are given in **table 1.2.5**. From the experimental data, it is found that for all the polymers VI values increase with increasing the concentration of polymer in base oils. With increasing temperature, the lube oil viscosity decreases but the expansion of polymer molecules take place at high temperature due to increase in solvation power and increased size of micelle. This increased in micelle size minimize the reduction of the viscosity of the polymer doped lube oil. Therefore, with increasing the concentration of polymer in lube oil leads to an increase in the total volume of polymer micelle in lube oil, thus exerting higher thickening effect and improves the VI property.^{21, 22} Between the two homopolymers (P-1 and P-6), P-1 (prepared by BZP initiator) has greater effect on VI for both the base oils than P-6 (prepared by AIBN initiator). It may be due to higher molecular weight of P-1. From the experimental values, it is also found that the performance of the prepared copolymers as VI increases by increasing the styrene content. It may be due to increase of the molecular weight with

increasing styrene content. In case of P-5 and P-10 (% of styrene 10), the molecular weight has increased but VI remain approximately same with P-4 and P-9 respectively. It may be due to higher PDI value and hence reduces the solubility.^{23, 24} The VI value is somewhat better in case of copolymers prepared by AIBN initiator than copolymers prepared by BZP initiator. The lower decomposition temperature of AIBN compared to BZP may be responsible for giving higher molecular weight and hence the VI.²⁵ All the polymers are more effective in BO1 (lower viscous) than BO2 as VM.

1.2.4.6 Analysis of pour point data

The polymer doped base oils (BO1 and BO2) at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **table1.2.6**. From the values, it is observed that all the polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oils. It may be due to decrease in solvation power. The efficiency as PPD of homopolymer, P-1(prepared by BZP initiator) is better than homopolymer, P-2 (prepared by AIBN initiator). It may be due to higher PDI value of P-1.²⁶ The copolymers P-2, P-3, P-4 and P-5 are less efficient as PPD than the homopolymer, P-1. It may be due to presence of phenyl group in the copolymers that reduces the adsorption of the polymer molecule on the wax crystals.²⁷ From the experimental values, it is clear that there is no significant change of pour point with increasing the styrene content among the copolymers of P-2, P-3, P-4 and P-5 (prepared by BZP initiator). The copolymers P-7 and P-8 (prepared by AIBN initiator) are more efficient as PPD than homopolymer P-6 (prepared by AIBN initiator) but P-9 and P-10 are less efficient compare to homopolymer. With increasing the styrene content among the copolymers P-7, P-8, P-9 and P-10, it is found that PPD property gradually decreases and may be due to increase of percentage of phenyl group. By comparing the PPD property of copolymers, prepared by BZP initiator and AIBN initiator, it is seen that copolymers prepared by AIBN initiator are more effective as PPD. The lower decomposition temperature of AIBN compare to BZP may be responsible for this observation.

1.2.5 Conclusions

From the above study, it is found that all the prepared decyl methacrylate based polymers are effective as VII and PPD. The homopolymer prepared by BZP initiator is more effective as VII and PPD than the homo polymer prepared by AIBN initiator. The efficiency of the copolymers as VII increases with increasing the styrene content up to 7.5% of styrene but at 10% of styrene, it does not increase. The performance as VII of the copolymers prepared by

AIBN initiator is better than the copolymers prepared by BZP initiator. The efficiency of the copolymers as PPD prepared by AIBN initiator decreases with increasing styrene content. Therefore, a critical observation can be made from the above study that initiator and percentage of styrene has a significant role in relation to the performance of the additive as VII and PPD.

1.2.6 References

References are given in bibliography section under Chapter II of Part I (Page No. 180 - 182).

1.2.7 Tables and figures

Table 1.2.1 Physical properties of the base oils

Base oil properties	Base oil	
	BO1	BO2
Density (g cm ⁻³) at 40 ° C	0.83	0.84
Viscosity at 40 °C in c St	7.102	23.502
Viscosity at 100 °C in c St	1.850	3.98
Viscosity index	84.56	85.15
Pour point (° C)	-3	-6
Cloud point (° C)	-1	-4

Table 1.2.2 Different percentage composition of the prepared polymers

Polymer code	% of DMA	% of styrene	Initiator	Polymer code	% of DAMA	% of styrene	Initiator
P-1	100	-	BZP	P-6	100	-	AIBN
P-2	97.5	2.5	BZP	P-7	97.5	2.5	AIBN
P-3	95	5	BZP	P-8	95	5	AIBN
P-4	92.5	7.5	BZP	P-9	92.5	7.5	AIBN
P-5	90	10	BZP	P-10	90	10	AIBN

DMA = Decyl methacrylate; BZP = Benzoyl peroxide; AIBN = Azobisisobutyronitrile

Table 1.2.3 M_n , M_w and PDI values of the polymers, P-1 to P-10

Polymer	M_n	M_w	PDI	Polymer	M_n	M_w	PDI
P-1	21,112	58,917	2.7906	P-6	20,482	49,682	2.43
P-2	19,121	40,571	2.1217	P-7	21,592	58,982	2.73
P-3	19,842	39,918	2.0117	P-8	27,457	77,688	2.83
P-4	22,982	56,121	2.4419	P-9	28,946	81,556	2.82
P-5	23,245	68,712	2.9559	P-10	30,345	93,842	3.09

M_n = Number average molecular weight; M_w = Weight average molecular weight;

PDI = Polydispersity index;

Table 1.2.4 TGA values of the polymers (P-1 to P-10)

Polymer	Decom. temp. /° C	PWL	Polymer	Decom. temp. /° C	PWL
P-1	170/350	28/82	P-6	248/315	20/76
P-2	250/412	16/81	P-7	280/382	20/78
P-3	250/410	15/81	P-8	275/350	18/82
P-4	210/360	14/85	P-9	275/336	19/88
P-5	190/362	31/90	P-10	172/300	20/92

Decom. temp = Decomposition temperature; PWL = Percent weight loss

Table 1.2.5 Viscosity Index (VI) of polymer doped base oils

Polymer code	VI in BO1					VI in BO2				
	Conc. of the polymer (% in w/w)					Conc. of the polymer (% in w/w)				
	1	2	3	4	5	1	2	3	4	5
P-1	96	114	123	144	153	96	104	109	118	128
P-2	91	96	98	107	122	92	98	110	112	107
P-3	96	108	115	126	128	108	116	118	120	126
P-4	112	120	128	138	162	104	105	119	128	136
P-5	112	122	134	156	162	108	114	116	124	138
P-6	103	105	123	130	136	98	102	112	114	118
P-7	99	102	106	116	125	106	110	108	119	126
P-8	101	104	115	122	132	106	108	114	122	132
P-9	99	118	128	148	163	105	122	138	142	143
P-10	102	124	124	142	160	102	115	132	142	142

Table 1.2.6 Pour point of polymer doped base oils

Polymer code	Pour point ($^{\circ}\text{C}$) in BO1					Pour point ($^{\circ}\text{C}$) in BO2				
	Conc. of the polymer (% in w/w)					Conc. of the polymer (% in w/w)				
	1	2	3	4	5	1	2	3	4	5
P-1	-10	-10	-8	-7	-7	-12	-12	-10	-9	-9
P-2	-7.4	-7.4	-6	-5.5	-5.5	-8.8	-8.8	-7.5	-7.5	-7.5
P-3	-7.8	-7.8	-6.8	-6.8	-6	-9.6	-9.6	-9	-9	-9
P-4	-9.4	-9.4	-7.5	-7	-7	-10	-10	-9	-9.5	-9
P-5	-9	-9	-8	-8	-8	-8	-8	-7.5	-7.5	-7.5
P-6	-9	-9	-8	-7	-7	-10	-11	-10	-10	-10
P-7	-15	-15	-13	-10	-10	-12	-12	-10	-10	-9.5
P-8	-12	-12	-10	-10	-10	-12	-12	-10	-10	-10
P-9	-9.4	-9.4	-8.5	-7.5	-7.5	-10	-9.5	-9.5	-9.5	-8.5
P-10	-9	-10	-8	-7	-7	-9.4	-9	-8.5	-8	-8

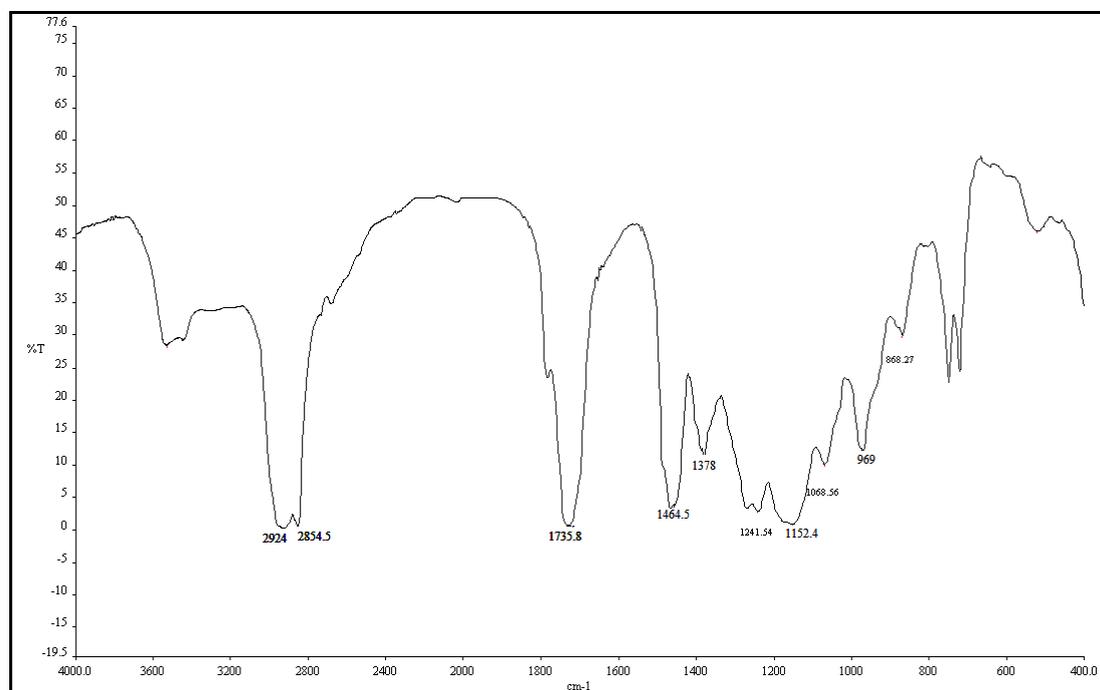


Figure 1.2.1 IR spectra of homopolymer (P-1)

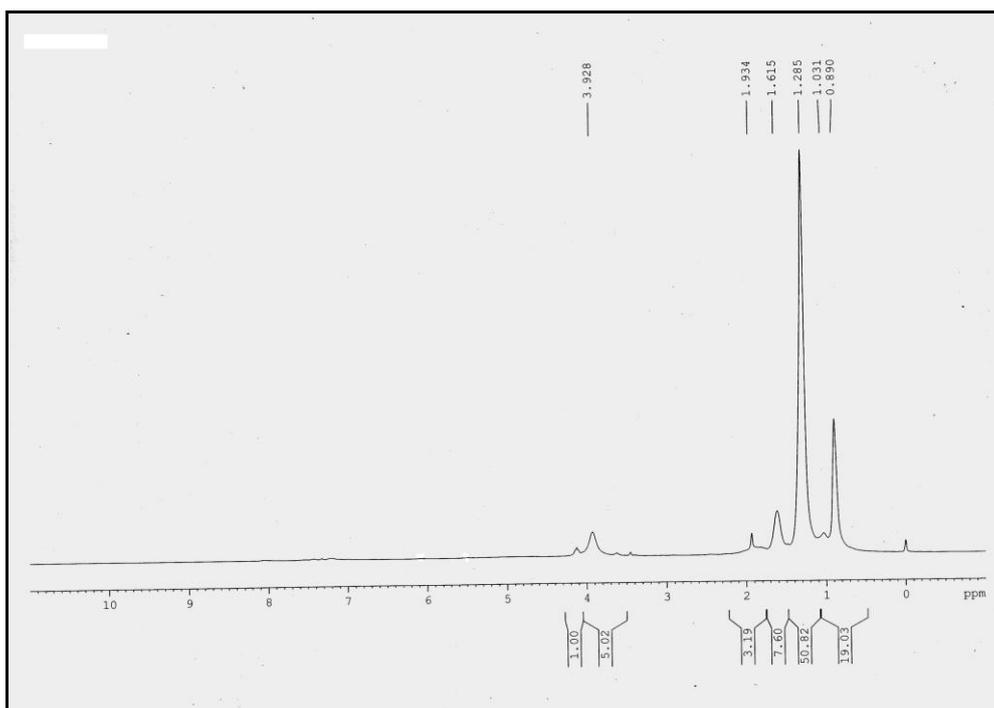


Figure 1.2.2 ^1H NMR spectra of homopolymer (P-1)

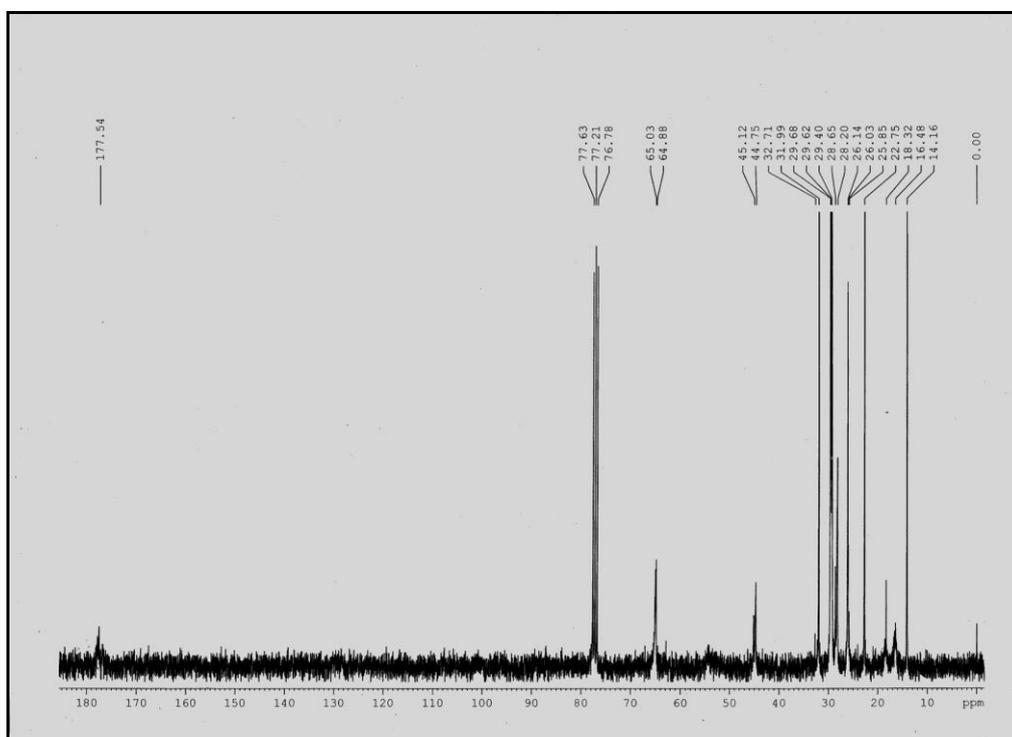


Figure 1.2.3 ^{13}C NMR spectra of homopolymer (P-1)

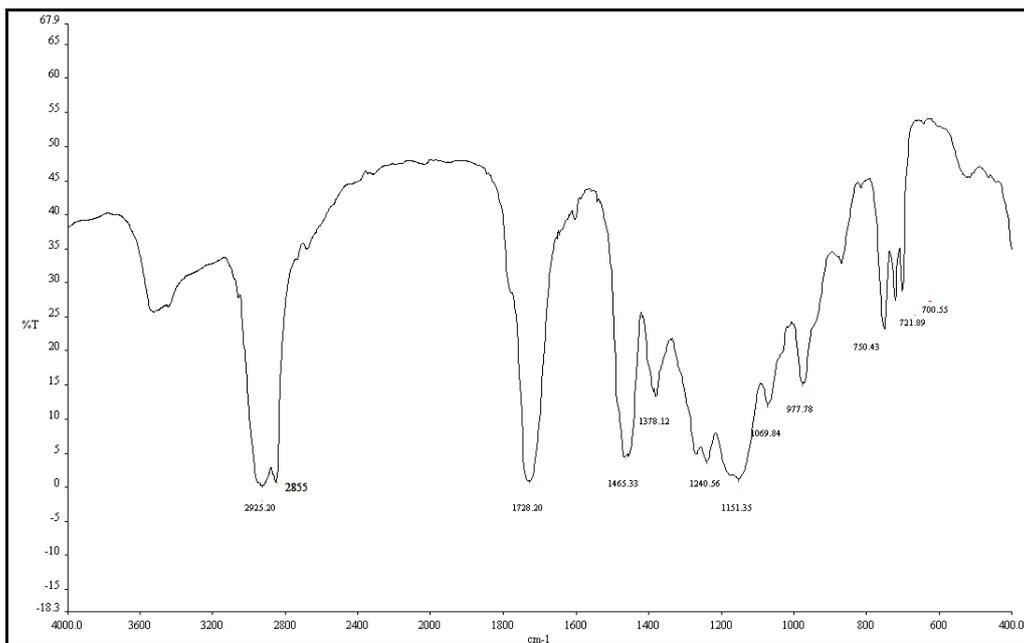


Figure 1.2.4 IR spectra of copolymer (P-2)

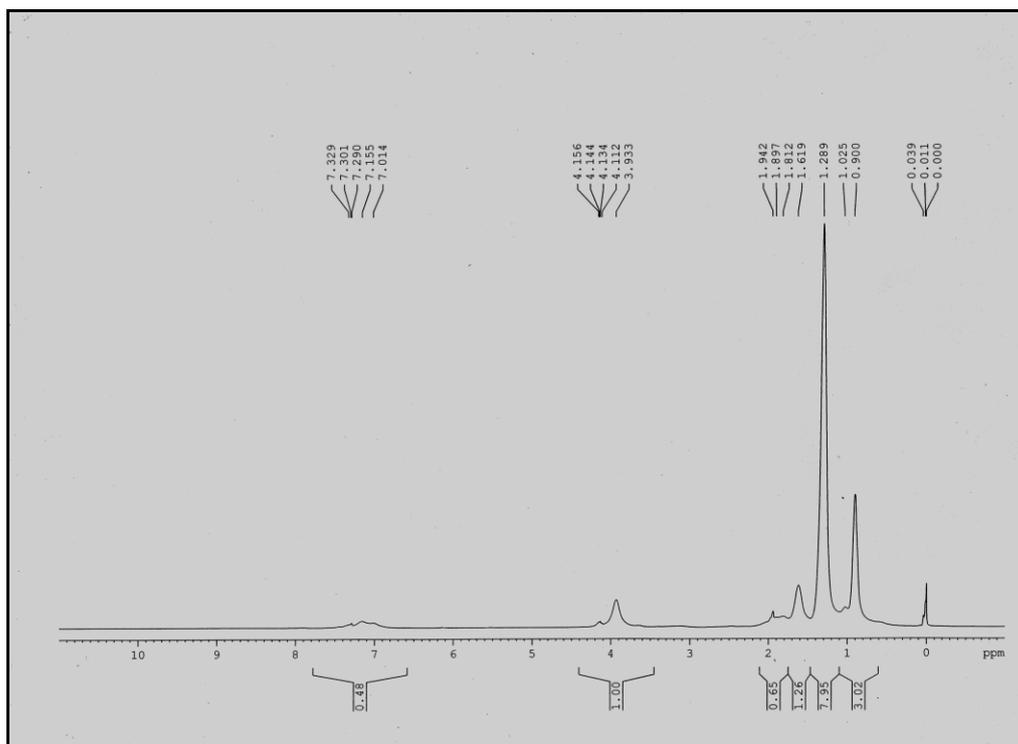


Figure 1.2.5 ¹H NMR spectra of copolymer (P-2)

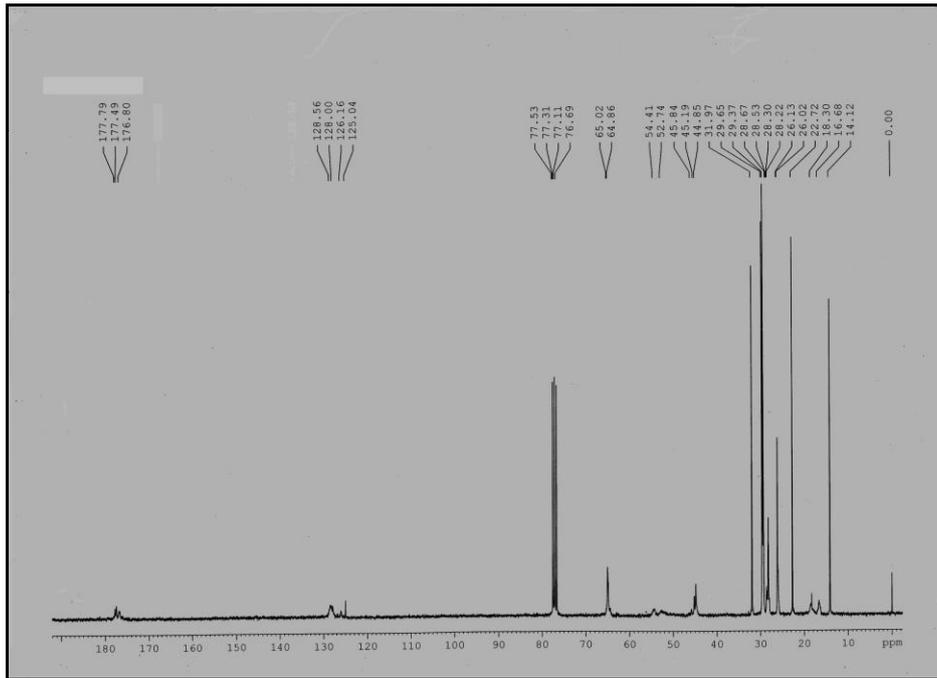


Figure 1.2.6 ¹³C NMR spectra of copolymer (P-2)

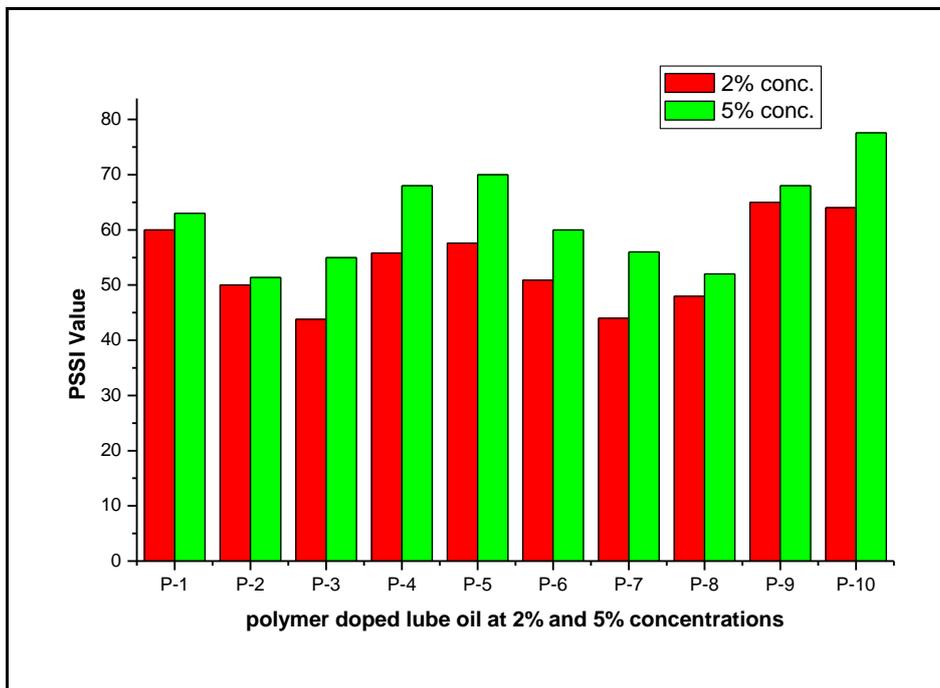


Figure 1.2.7 Variation of PSSI values of polymer doped base oil (BO2) at 2% and 5% concentrations

Chapter III

Dodecyl methacrylate based polymeric additives as viscosity modifier and pour point depressant for lube oil

1.3.1 Introduction

Lubricating oil plays a very important role in automobile industry. It keeps the moving parts lubricated and protects against rust and corrosion. Lubricating oil alone cannot satisfy the all requirements of modern engine. Therefore, some additives are to be blended with the lube oil. Lubricating oil containing a package of additives is called lubricant.¹ The role of additives in lubricant is very significant. They optimize the performance of lubricant. They fall into two major categories viz. surface active additive and performance enhancing additive.² The first one protects the metal surfaces in the engine, such as antiwear, anti-rust and extreme pressure additives.³ The second type reinforces the base stock performance, such as viscosity index improver (VII)^{4, 5} pour point depressant (PPD),^{6, 7} antioxidant⁸, detergent- dispersant⁹ etc.

Generally, in the formulation of a high performance lubricant different types of additives at different percentages are blended with the base oils. This would increase the overall cost of the furnished lubricant. The addition of additives having multifunctional character to the base fluid may lead to formulate a cost effective as well as better performance lubricant. Therefore, research in this area has attracted much attention today. In this work we have synthesized multifunctional additives which showed as excellent VII and PPD performances. Lot of works on acrylate polymers as multifunctional PPD and VII additive was carried out so far. Kamal et al.¹⁰ in their work have shown the application of copolymers of vinyl acetate (VA) with esters of acrylic acid as a viscosity index improver for lubricating oil. They also studied the rheological properties of lube oil without and with polymeric additives. Al-Sabagh et al.¹¹ have mentioned the application of copolymers of VA with n-alkyl itaconate as a pour point depressants in lubricating oil. The rheological properties were also studied by the research group. Abdel-Azim et al.¹² synthesized the copolymers of dialkyl fumarates with vinyl acetate and they recognized that the copolymer of didodecyl fumarate with VA is the most effective pour point depressant for lubricating oil.

The potential application of copolymer of vinyl acetate (VA) as pour point depressant for crude oil is also well documented. VA – α olefin copolymers¹³, VA – methacrylate (MA) copolymers¹⁴ were used as pour point depressant for crude oil. The copolymers of vinyl acetate, styrene and n- butyl acrylate having different monomer ratios were used to study the rheological behaviours of Mexican crude oil¹⁵. Borthakur et al.¹⁶ have shown the application of alkyl fumarate and vinyl acetate copolymer in combination with alkyl acrylate as a flow improver for high waxy Borholla crude oil.

However reports regarding the application of acrylate copolymers of VA as VII and PPD for lube oil are scanty. Therefore, in this work homo polymer of dodecylmethacrylate (DDMA) and copolymers of DDMA with VA at different molar ratio were synthesized by thermal free radical polymerization method. After purification and characterization, investigation of their efficiency as viscosity index improver and pour point depressant additive in two different types of mineral base oils were carried out according to ASTM standards. Photo micrographic images were taken to study their mechanism of action as pour point depressant. Rheological properties of the lubricants were also studied during the work by a rheometer.

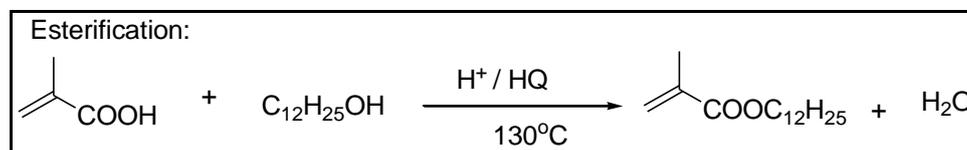
1.3.2 Experimental section

1.3.2.1 Chemicals used

Methacrylic acid (MA, 99%, LOBA Cheme Pvt. Ltd.), vinyl acetate (VA, 99%, S. d Fine Cheme Ltd.), dodecyl alcohol (DA, 98%, SRL Pvt. Ltd.) were used without purification. Toluene (99.5%, Merck Specialties Pvt. Ltd.), hexane (99.5%, S. d Fine Cheme Ltd.) and methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialties Pvt. Ltd.) and azobisisobutyronitrile (AIBN, 98%, Spectrochem Pvt. Ltd.) were purified by recrystallization before use. Conc. H₂SO₄ (98%, Merck Specialties Pvt. Ltd.) was used as received. Base oils were collected from IOCL and BPCL, India. Physical properties of base oils are given in **table 1.3.1**.

1.3.2.2 Preparation of ester and its purification

Dodecylmethacrylate (DDMA) was prepared by reacting methacrylic acid with dodecyl alcohol in 1.1:1 molar ratio in presence of conc. H₂SO₄ as a catalyst, 0.25% (w/w) hydroquinone with respect to the reactants as polymerization inhibitor, and toluene as solvent in a Dean Stark apparatus. The process of esterification and its purification were carried out by the procedure as reported in the chapter II of part I (**1.2.2.2 &1.2.2.3**).

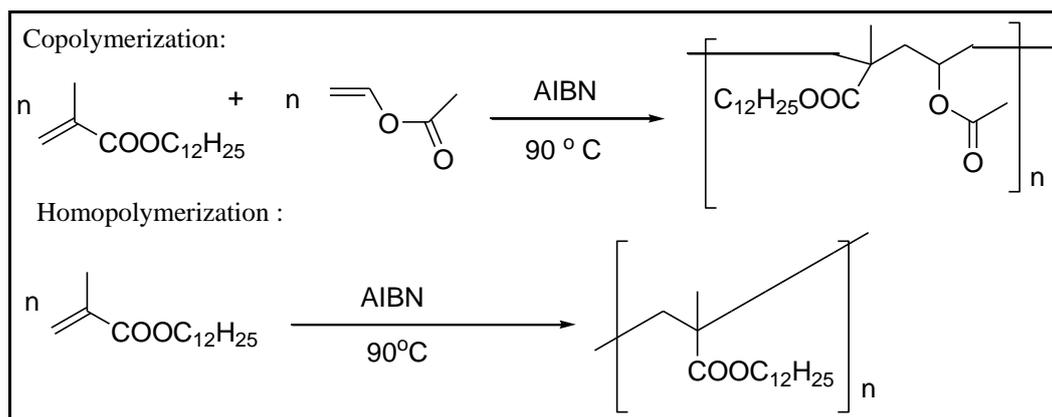


Scheme 1 Preparation of DDMA from methacrylic acid and dodecyl alcohol

1.3.2.3 Preparation of copolymers and homopolymer

The monomers, vinyl acetate and DDMA, at different molar ratios (**table 1.3.2**) were subjected to free radical copolymerization (**scheme 2**) by AIBN radical initiator. The polymerization was carried out in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. In the flask, the

mixture of DDMA and vinyl acetate (VA) at a definite molar ratio in toluene was heated to 90 °C for half an hour. AIBN (0.5% w/w, with respect to the total monomer) was then added and heated for 6 hours keeping the temperature constant at 90°C. At the end of the reaction time, the mixture was poured into cold methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K temperature. The homopolymer of DDMA was also prepared and purified in the same procedure.



Scheme 2 Preparation of copolymer and homopolymer

1.3.3 Measurements

1.3.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

1.3.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (polystyrene calibration) equipped with a 2414 detector, waters 515 HPLC pump and 717 plus auto sampler. Sample solutions (0.4% w/v in HPLC grade THF) are prepared by dissolving ~4 mg of polymer per ml THF and filtering (0.45- μm Millipore PTFE) to remove suspended particulates. The pump flow rate is 1.0 mL/min with THF as the carrier solvent, and injection volumes are set to 20 μL . The polydispersity index¹⁷ which indicates the nature of the distribution of the molecular weights in the polymers was also calculated.

1.3.3.3 Determination of Thermo gravimetric analysis (TGA) data

The thermo-oxidative stability of all the polymers was determined by a thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating rate of 10 °C/min. A comparison of thermal stability of the homo polymer of DDMA with their copolymers was explained by this study.

1.3.3.4 Performance evaluation as viscosity index improver (VII)

Viscosity index was calculated by dissolving the prepared polymer in two types of base oils (SN150 and SN500) through the viscosity index test according to ASTM D 2270-10. The kinematic viscosity of the lubricant compositions was determined at 40° C and 100° C. Different concentrations of additives [ranging from 1% - 5% (w/w)] were blended to the base oils to study the effect of additive concentration on VI.

1.3.3.5 Performance evaluation as pour point depressant (PPD)

Pour points were determined using the cloud and pour point tester (model WIL-471, India) according to ASTM D 97-09 method. The performance of additives as PPD was investigated through the variation of concentration of the blended polymers [ranging from 1% - 5% (w/w)] in the base fluids.

1.3.3.6 Photographic analysis

The photomicrograph showing wax behaviour of lube oil (SN150, pour point = - 6 ° C) without and with 4% (w/w) polymers has been recorded at 0° C. A Banbros polarizing microscope model BPL-400B was used for photographic analysis. The adopted magnification was 200X.

1.3.3.7 Rheological study

Rheological study of the homo polymer and copolymers at 5% (w/w) concentration in SN150 oil was performed using Brookfield Rheometer (Model DV-III ultra). Dynamic viscosity (cp) and shear rate (sec⁻¹) were measured at two temperatures (40 ° C and 100 ° C).

1.3.4 Results and discussion

1.3.4.1 Spectroscopic data analysis

The homopolymer of dodecylmethacrylate exhibited IR absorption band at ν 1722 cm⁻¹ for the ester carbonyl group. The peaks at 2853.5 cm⁻¹ and 2924 cm⁻¹ are the characteristic of CH₃CH₂- group. The peaks at 1456 cm⁻¹, 1377 cm⁻¹, 1296 cm⁻¹ and 1164 cm⁻¹ due to CO stretching vibration and absorption bands at 1013.5 cm⁻¹, 937 cm⁻¹, 813 cm⁻¹, 749 cm⁻¹, and 719.5 cm⁻¹ were due to bending of C-H bond (**figure1.3.1**). In the ¹H NMR of homopolymer, the methyl protons appears in the range of δ_H 0.88 to 1.03 ppm, the methylene

protons in the range of 1.28 to 1.81 ppm for all alkyl groups. A broad peak at 3.93 ppm indicates the protons of $-\text{OCH}_2$ group. Absence of any peak in the range of 5-6 ppm confirms the polymerisation. In ^{13}C NMR, the peak at 176.70 ppm indicates the presence of ester carbonyl group. The peaks at 64.66 - 65.01 ppm indicate the presence of $-\text{OCH}_2$ carbons. The peaks ranging from 14.08 – 45.09 ppm represent all other sp^3 carbons. No peak in the range of 120 -150 ppm indicates the absence of sp^2 carbons and confirms the polymerization (**figures 1.3.2 and 1.3.3**).

The spectroscopic data (IR and NMR) of all the five copolymers (P-2 to P-6) are similar. In the IR spectra, peaks at ν 1733-1735 cm^{-1} and 1716.5-1720 cm^{-1} indicate the presence of ester carbonyl group in the copolymer due to vinyl acetate and DDMA moiety respectively. The peaks at 2853.6-2854 cm^{-1} and 2923-2925.4 cm^{-1} are the characteristic of CH_3CH_2- group. The peaks at 1456 -1457 cm^{-1} , 1377-1378 cm^{-1} , 1368.4-1369 cm^{-1} , 1321-1322 cm^{-1} , 1296-1296.8 cm^{-1} , 1238 -1238.6 cm^{-1} , 1163.0-1164.2 cm^{-1} , 1065.5-1066 cm^{-1} , and 1011.6-1012 cm^{-1} due to CO stretching vibration and absorption bands at 814.9-816 cm^{-1} and 721.3-722 cm^{-1} were due to bending of C-H bond. It is observed from the IR data of the five copolymers that with increasing the percentage of vinyl moiety in the copolymer the peak intensity gradually decreases (**figure 1.3.4**). In the ^1H NMR of copolymer, a broad peak δ 3.93 ppm indicates the protons of $-\text{OCH}_2$ and $-\text{OCH}_3$ groups. The hydrogen attached to sp^3 carbons appear in the range of 0.87 ppm to 2.350 ppm. Absence of any peak in the range of 5-6 ppm indicates the disappearance of C=C bond and confirms the polymerisation. In the ^{13}C NMR of homopolymer, the peaks at δ_{C} 176.73 - 177.84 ppm indicate the presence of ester carbons. The peaks at 63.06 - 65.40 ppm confirm the presence of $-\text{OCH}_2$ carbons. Peaks in the range of 14.13 – 45.22 ppm represent all sp^3 carbon atoms of alkyl groups. No peak in the range of 120-150 ppm indicates the absence of sp^2 carbon atoms and confirms the polymerization (**figures 1.3.5 &1.3.6**).

1.3.4.2 Analysis of molecular weight

The experimental values of M_n and M_w of the prepared homo and copolymers are given in **table 1.3.2**. From the values, it is found molecular weight of homopolymer is less than copolymers. The molecular weight of copolymers increases with increasing the percentage of vinyl acetate moiety in the prepared copolymers. The PDI values of P-4 and P-6 copolymer are almost unity. Hence these two polymers are expected to be more linear than others.

1.3.4.3 Analysis of TGA data

From the experimental TGA values (**figure 1.3.7**), it is found that homo polymer of DDMA (P-1) is thermally less stable than the copolymers. The copolymer having vinyl acetate (VA) as a monomer has a head to tail structure and may be due to fact that VA monomer molecule adds on to the growing chain by free radical through its $-\text{CH}_2-$ group and such type of addition involves less steric effect.¹⁸ The less steric effect free radical polymers always have a higher molecular weight and become thermally more stable.¹⁹ In case of P-1, decomposition starts at 150°C and another major decomposition is found at 400° C with 75% weight loss. Among the copolymers, the polymer P-6 has higher thermal stability in which decomposition starts at 220 ° C and another major decomposition is found at 400° C with 50% weight loss. It may be due to higher molecular weight and lower PDI value.²⁰ The order of thermal stability of the prepared polymers is P-1 < P-2 < P-3 < P-5 < P-4 < P-6.

1.3.4.4 Analysis of viscosity index data

Viscosity index (VI) values of the lubricant composition prepared by blending the copolymers at different concentration levels [1% - 5% (w/w)] to the two types of base oils were determined from the kinematic viscosity values of the blends at 40 ° C and 100 ° C. The experimental values of VI are given in **figures 1.3.8** and **1.3.9**. From the experimental data, it is found that for all the polymers VI values increase with increasing the concentration of polymer in base oils. With increasing temperature, the lube oil viscosity decreases but the expansion of polymer molecules take place at high temperature due to increase in solvation power and increased size of micelle. This increased in micelle size minimize the reduction of the viscosity of the polymer doped lube oil. Therefore, with increasing the concentration of polymer in lube oil leads to an increase in the total volume of polymer micelle in lube oil, thus exerting higher thickening effect and improves the VI property.²¹⁻²³ From the experimental values, it is found that the VI values of homo polymer (P-1) are less than copolymers. It may be due to low molecular weight of P-1. The performance of the prepared copolymers as VI increases by increasing the percentage of vinyl acetate. It may be due to increase of the molecular weight of the copolymers²⁴ (P-2 to P-6).

1.3.4.5 Analysis of pour point data

The base oils blended with the polymers at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **figures 1.3.10** and **1.3.11**. From the values, it is observed that all the polymers can be effectively used as pour point depressant and the efficiency as pour point depressant (PPD) increases with increasing

the concentration of polymer in base oil up to 4%. This means that at this concentration, the polymer may interact with the paraffinic wax and change their crystals size.²⁵ The homo polymer P-1 has greater efficiency as PPD than copolymer. It may be due to lower molecular weight of P-1. The lower molecular weight polymers are highly adsorbed on the wax crystal present in lube oil and efficiency as PPD improves.²⁶ Among the five copolymers, the polymer P-2, P-3 and P-5 have greater efficiency as PPD. It may be due to higher PDI values of the polymers.²⁷

1.3.4.6 Analysis of Rheological study

Rheological study was carried out with lube oil (SN150) without and with 5% (w/w) of polymers. For lube oil without any polymer, the viscosity approximately constant with increasing shear rate. This indicates that pure lube oil behaves like a Newtonian fluid at any shear rate.²⁸ For lube oil with polymer, it is found that at low shear rate ($5-30 \text{ S}^{-1}$), the viscosity gradually decreases and hence the sample behaves like a non-Newtonian fluid.²⁹ But at high shear rate the viscosity of all polymer blended samples approximately remain constant and behaves like a Newtonian fluids.³⁰ Viscosity modifiers at low temperature in lube oil exist in the spherical coils form having random orientation exert high viscosity in absence of shear. When shear is applied the polymer starts rearranging itself in the direction of flow and viscosity decreases.³¹ At high shear rate all the polymers are arranged in the direction of flow and there is a negligible change in viscosity. Viscosity modifiers at high temperature exist in the expanded form and hence polymers are easily arranged in the direction of flow under shear and viscosity approximately remains constant under high shear rate for all polymer blended lube oil. In this way the copolymers counterbalance decrement of lube oil viscosity under high temperature. The decrease of viscosity was caused due to presence of shear and by changing the temperature from 40° C to 100° C (**figures 1.3.12 and 1.3.13**).

1.3.4.7 Analysis of photo micrographic images

Photo micrographic analysis was used to study the pour point and its mechanism of the lube oil (SN150) without and with 4% (w/w) polymeric additives. The photograph of lube oil without and with different additives is shown in the **figure 1.3.14(a-g)**. The figure 1.3.14a is the photograph of lube oil (pour point = -6° C) without any additives where there is large number of cyclic crystalline and some needle shaped wax. When lube oil is treated separately with 4% (w/w) of P-1 (figure 1.3.14b), 4% (w/w) of P-2 (figure 1.3.14c), 4% (w/w) of P-3 (figure 1.3.14d), 4% (w/w) of P-4 (figure 1.3.14e), 4% (w/w) of P-5 (figure 1.3.14f) and 4%

(w/w) of P-6 (figure 1.3.14g), it is seen that greater wax modification is found in case of lube oil with 4% of P-1(homo polymer) and least wax modification is observed in case of 4% of P-6. This indicates that homo polymer of DDMA is a better PPD than copolymer of DDMA with VA for lube oil. This is in agreement with the pour point values determined by ASTM D97-09 method.

1.3.5 Conclusions

From the above study it is found that the prepared copolymers are effective as viscosity index improver and pour point depressant for lube oil. The viscosity index property of homo polymer is lower than copolymer and VI property increases with increasing the percentage of vinyl acetate in the copolymer. The efficiency as pour point depressant was found higher in case of homo polymer than copolymers. Among the copolymers, the polymer which has higher PDI value, results better PPD property. From rheological study, it was found that pure lube oil is a Newtonian fluid at any shear rate but polymer doped lube oil is non-Newtonian at low shear rate but at high shear rate it behaves like a Newtonian fluid.

1.3.6 References

References are given in bibliography section under Chapter III of Part I (Page No. 182 - 185).

1.3.7 Tables and figures

Table 1.3.1 Base oil properties

Base oil properties	Base oils	
	SN150	SN500
Density (g cm ⁻³) at 40 ° C	0.84	0.87
Viscosity at 40 °C in c St	23.502	107.120
Viscosity at 100 °C in c St	3.98	10.322
Viscosity index	85.15	81.5
Pour point (° C)	-6	-0.5
Cloud point (° C)	-4	+2

Table 1.3.2 Molar ratio and molecular weight (M_n , M_w , PDI) of the prepared polymers

Polymer code	Molar ratio of DDMA	Molar ratio of VA	M_n	M_w	PDI
P-1	1	0	17824	24588	1.38
P-2	1	0.075	21575	33018	1.53
P-3	1	0.150	24013	35842	1.49
P-4	1	0.225	56866	66210	1.16
P-5	1	0.300	61990	81219	1.31
P-6	1	0.375	81070	88008	1.09

M_n = Number average molecular weight; M_w = Weight average molecular

Weight; PDI = Polydispersity index; DDMA = Dodecylmethacrylate; VA = Vinyl acetate;

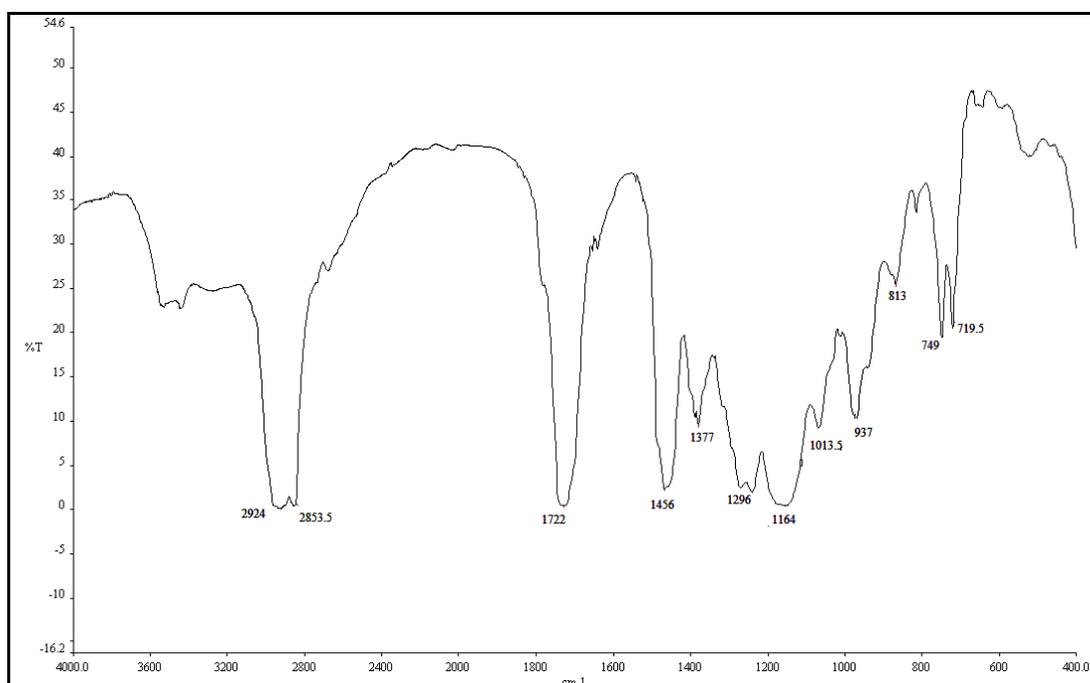


Figure 1.3.1 IR spectra of homopolymer, (P-1)

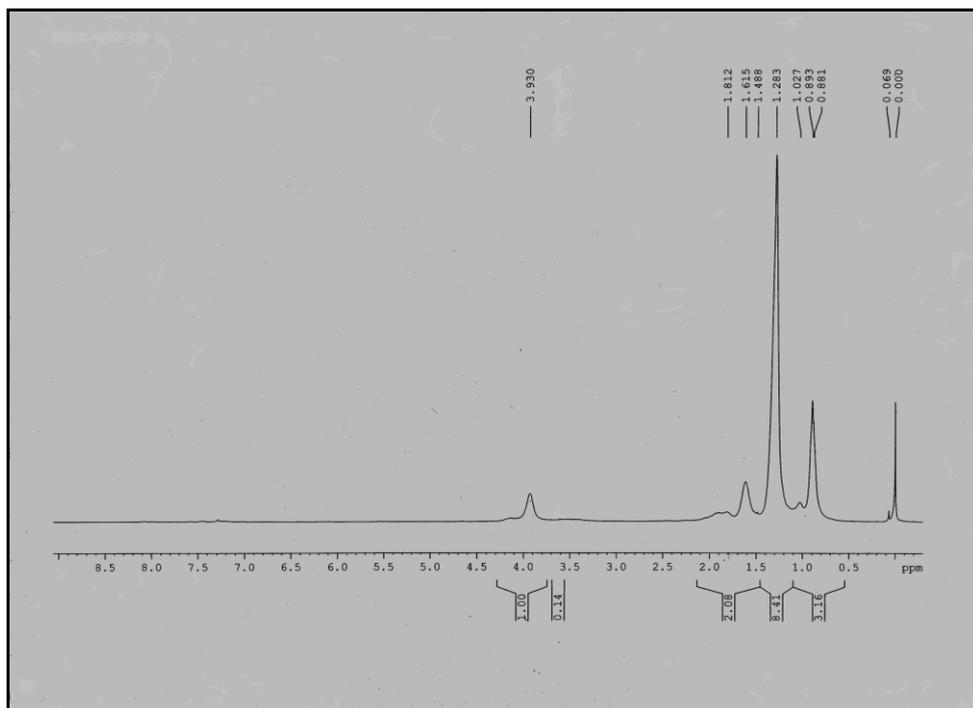


Figure 1.3.2 ^1H NMR spectra of homopolymer, (P-1)

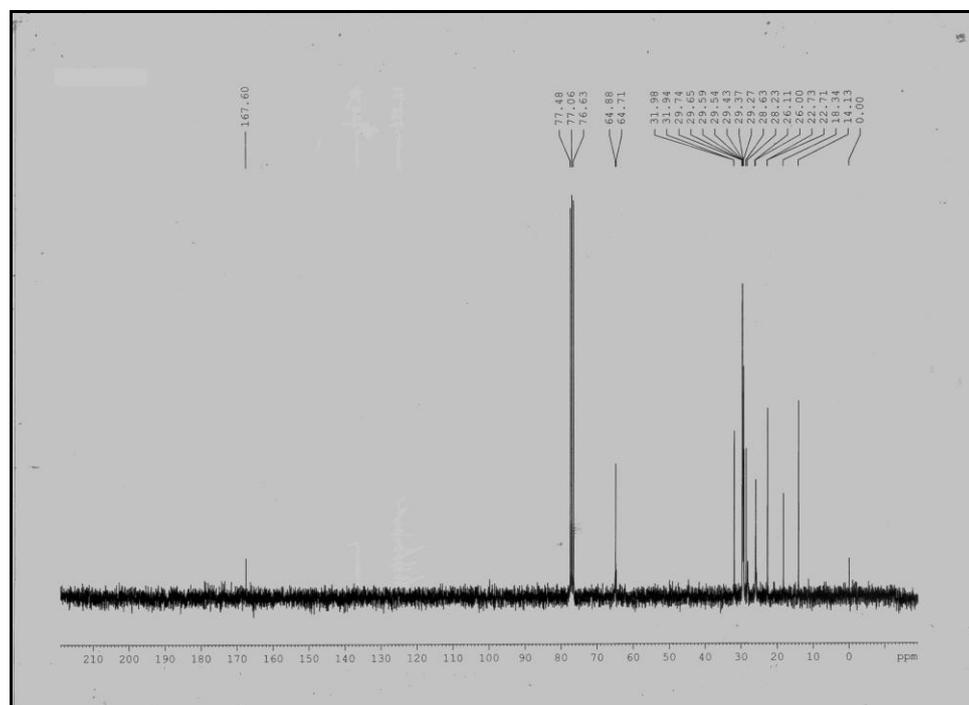


Figure 1.3.3 ^{13}C NMR spectra of homopolymer (P-1)

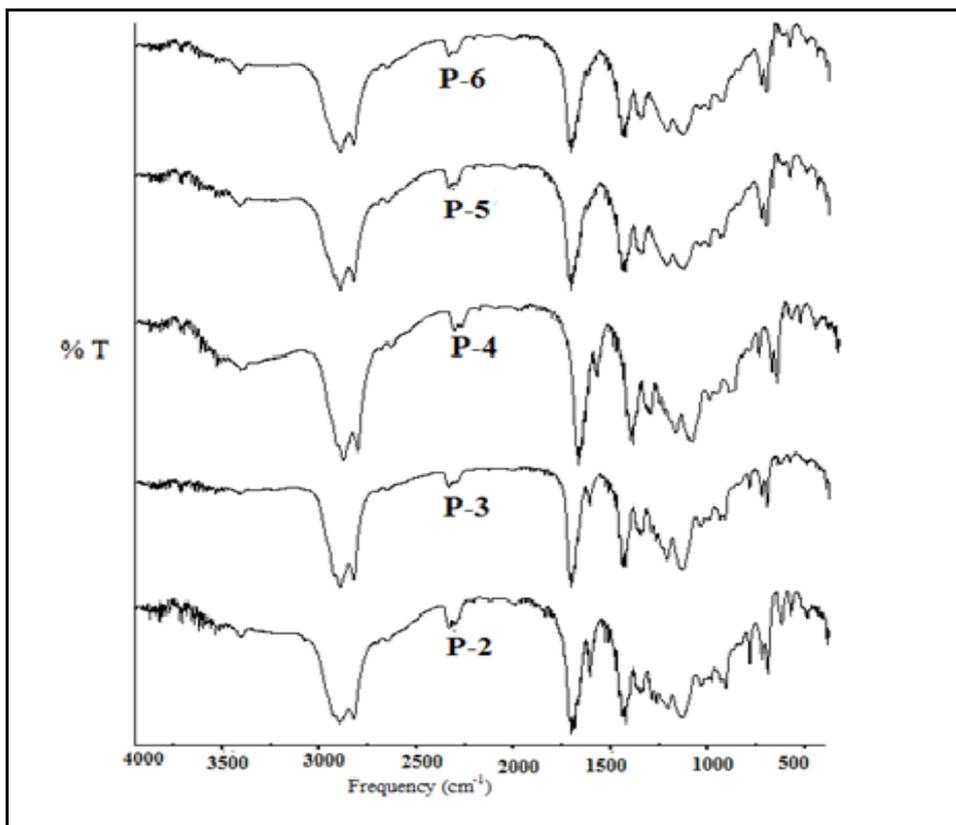


Figure 1.3.4 IR spectra of copolymers (P-2 to P-6)

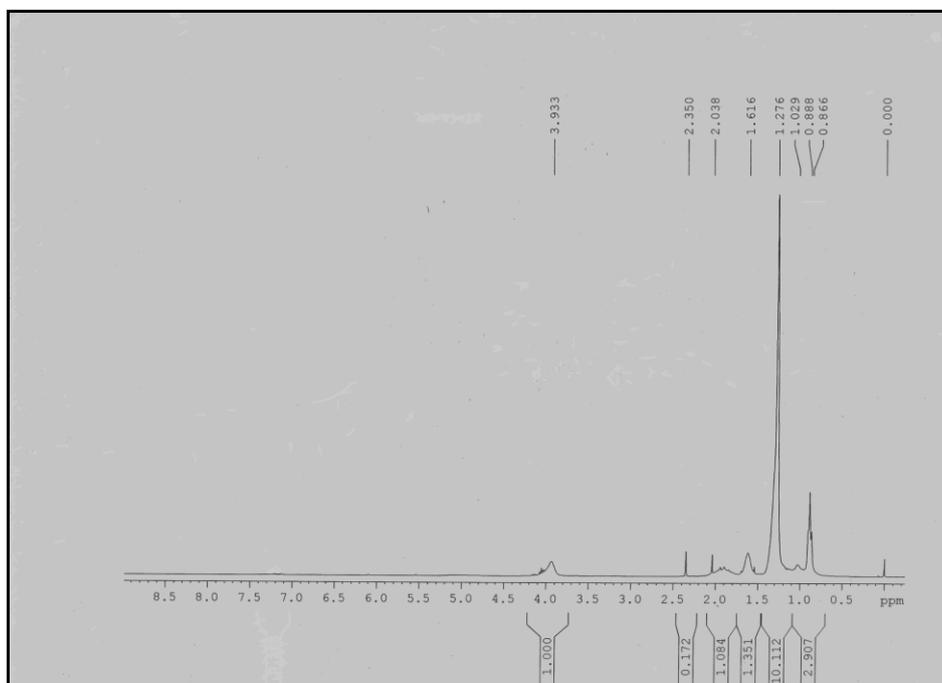


Figure 1.3.5 ¹H NMR spectra of copolymer (P-2)

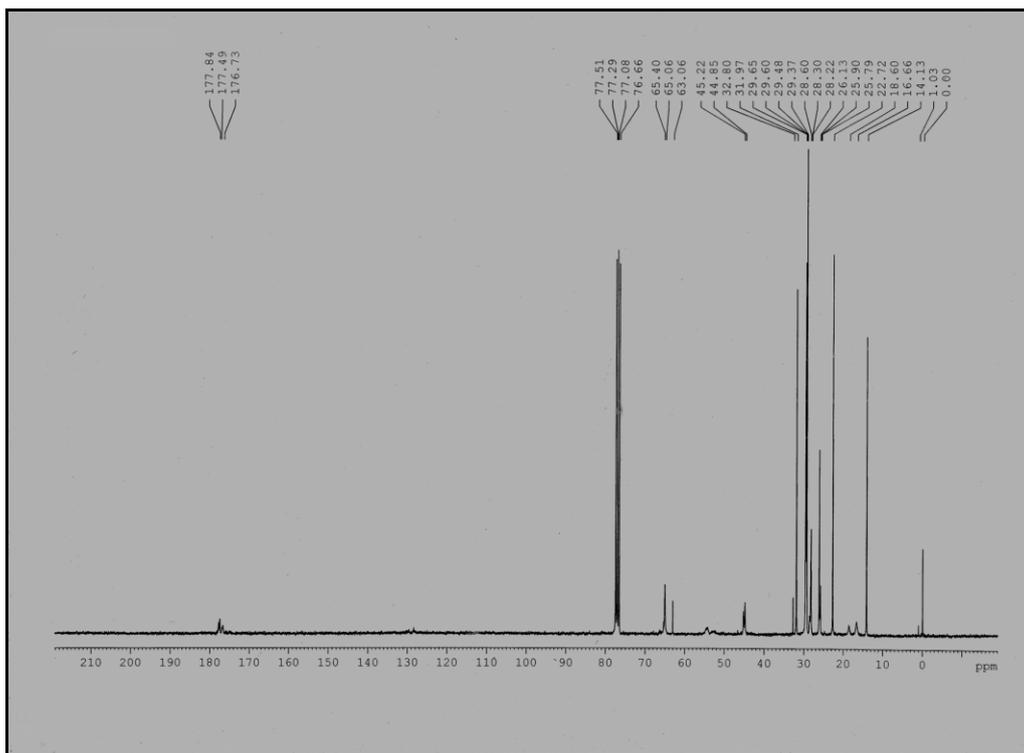


Figure 1.3.6 ^{13}C NMR spectra of copolymer (P-2)

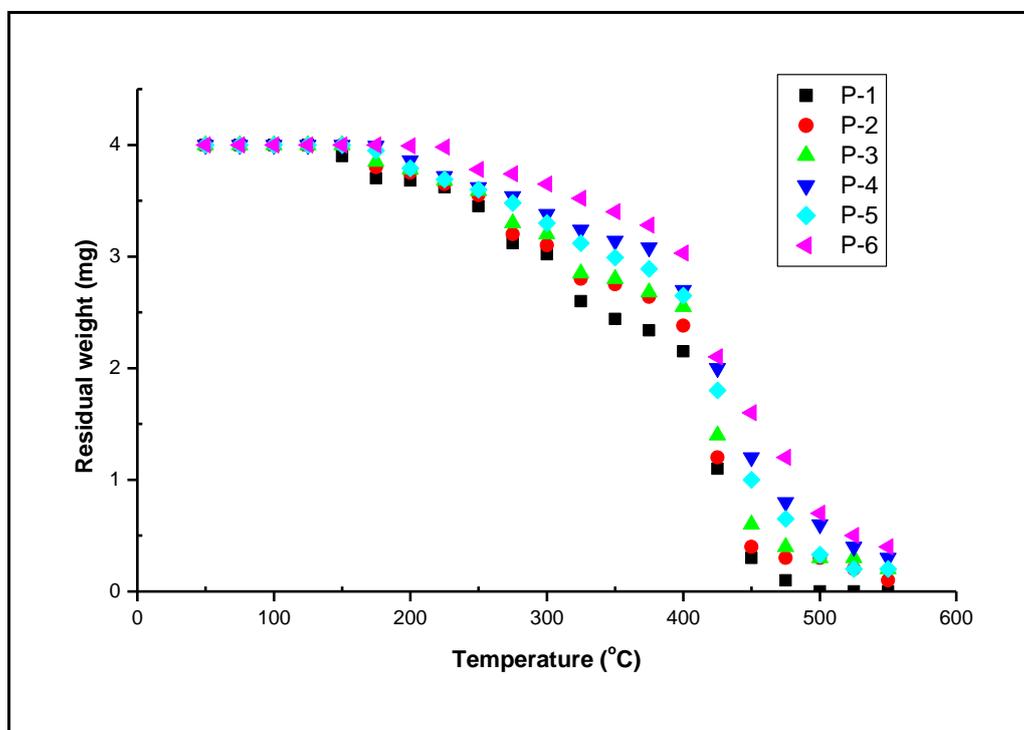


Figure 1.3.7 Thermal degradation of polymers P-1, P-2, P-3, P-4, P-5 and P-6

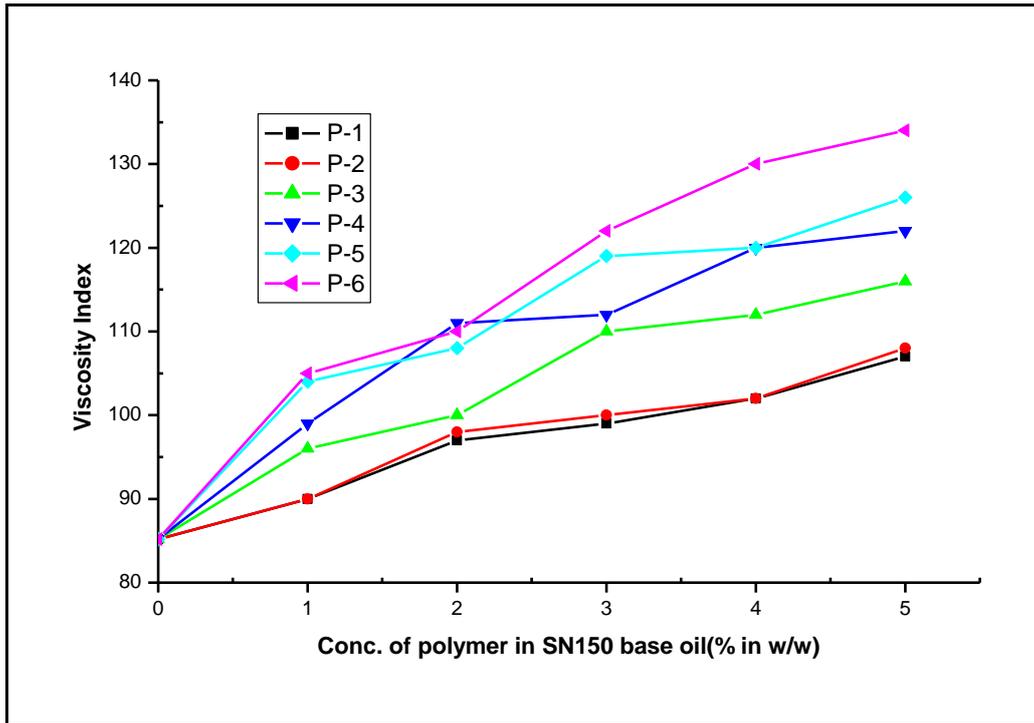


Figure 1.3.8 Variation of viscosity index of polymer doped base oil (in SN150) at different concentrations

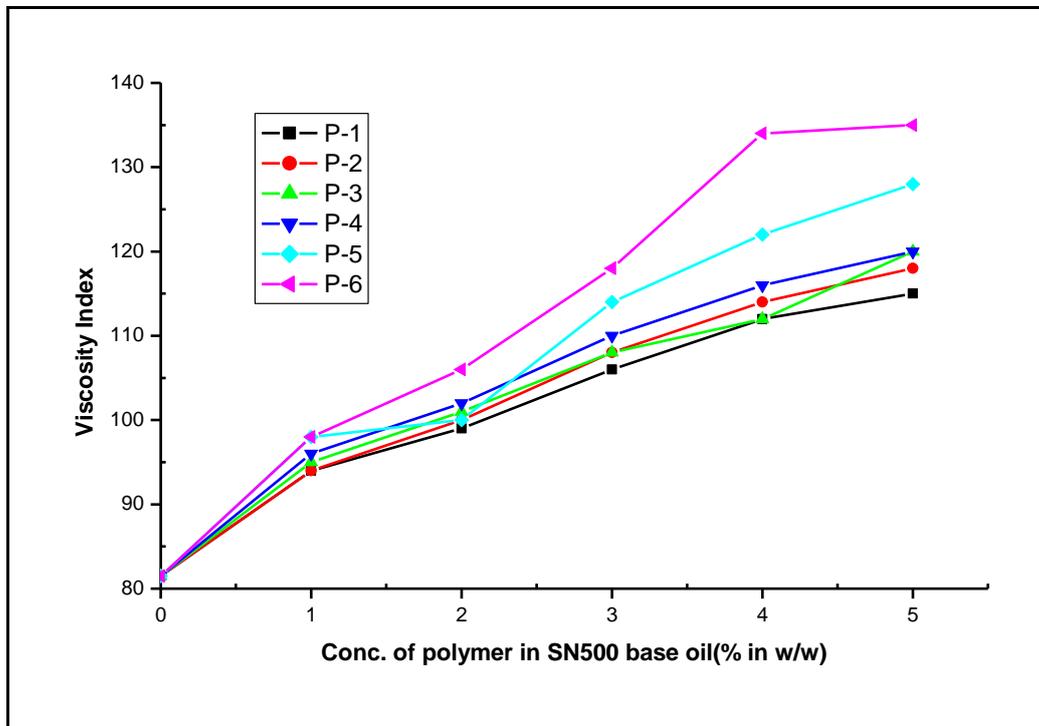


Figure 1.3.9 Variation of viscosity index of polymer doped base oil (in SN500) at different concentrations

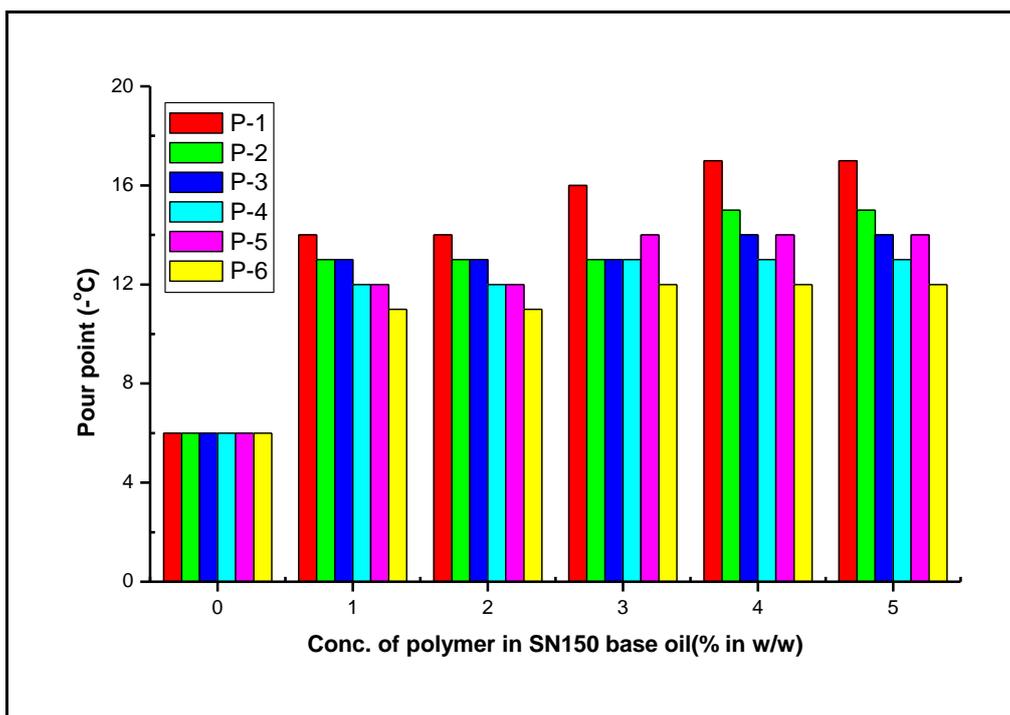


Figure 1.3.10 Variation of pour point of polymer doped base oil (in SN150) at different concentrations

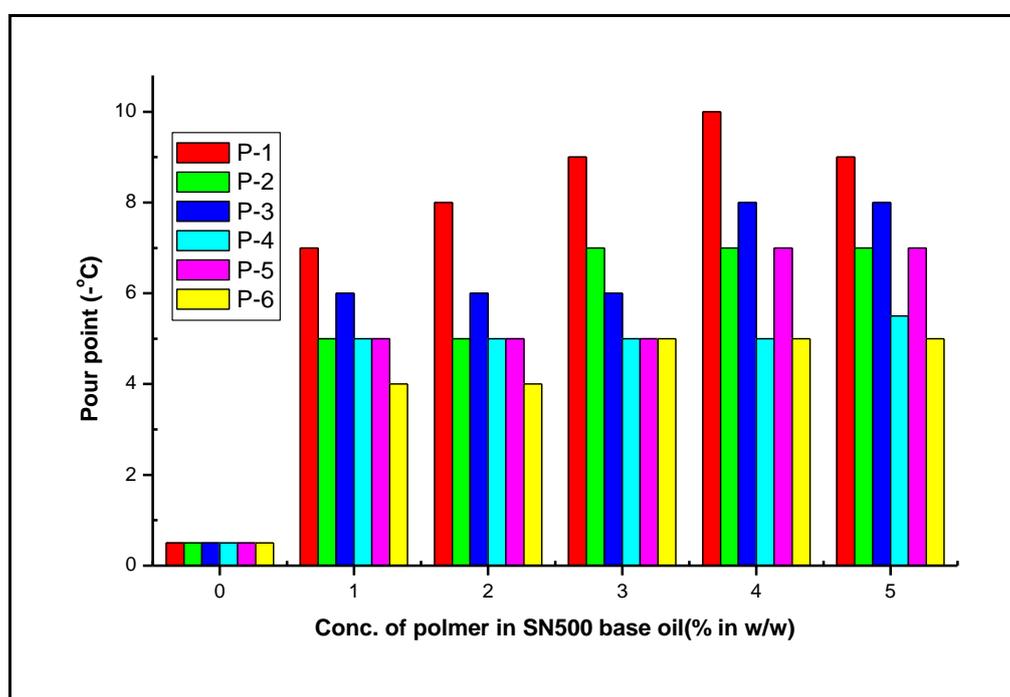


Figure 1.3.11 Variation of pour point of polymer doped base oil (in SN500) at different concentrations

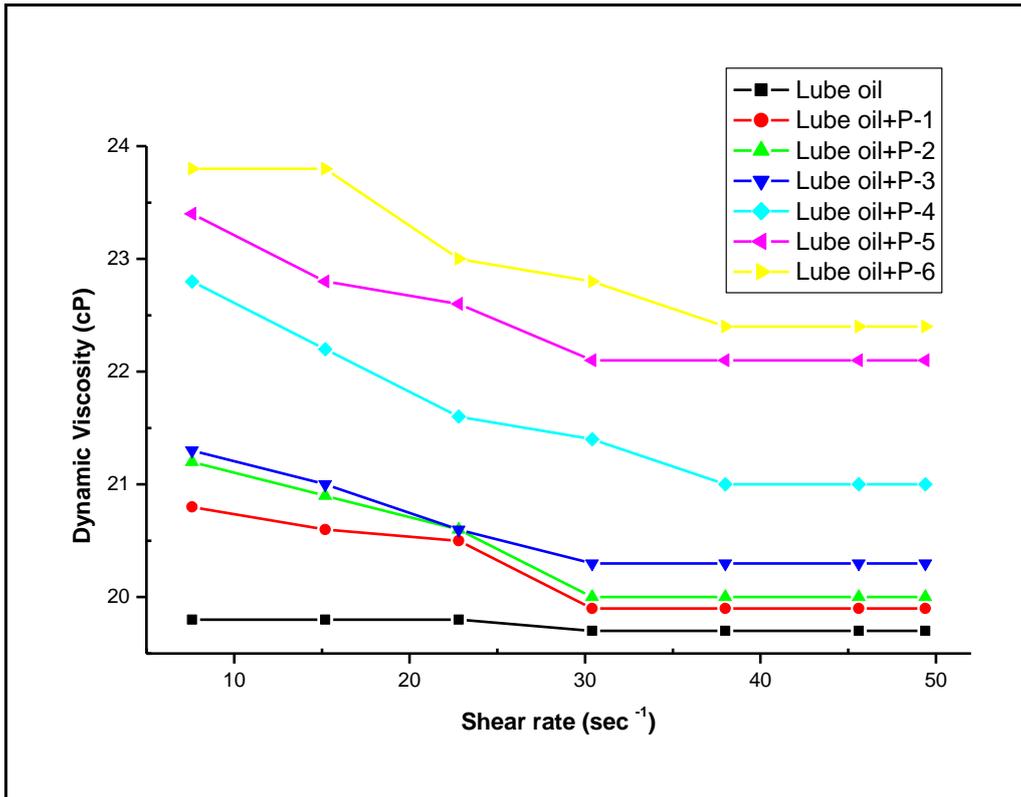


Figure 1.3.12 Variation of dynamic viscosity with shear rate at 40 ° C

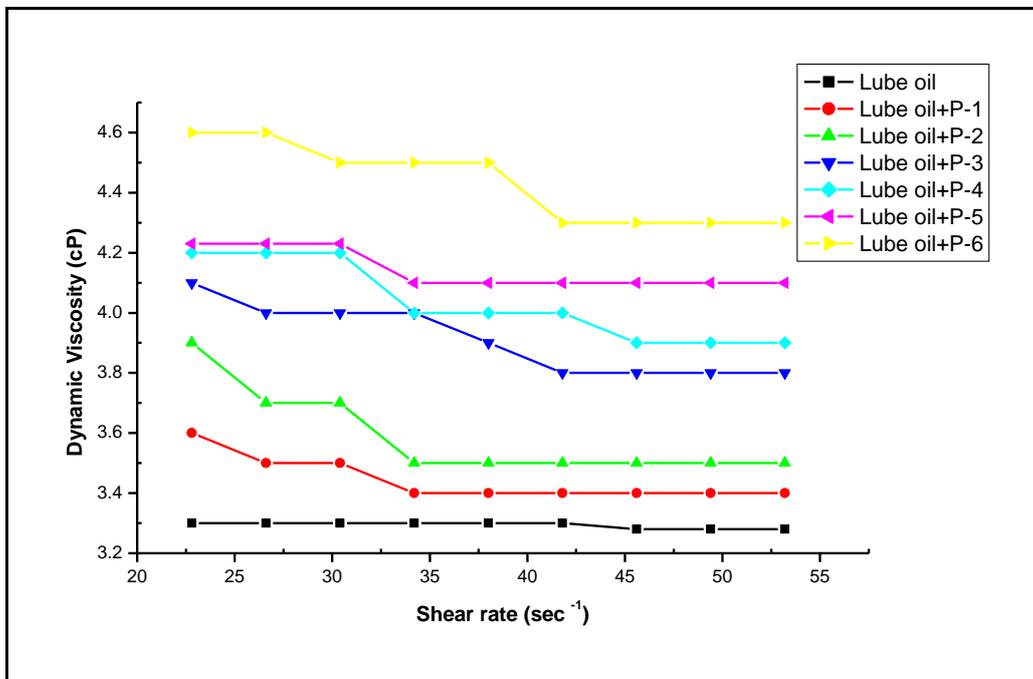
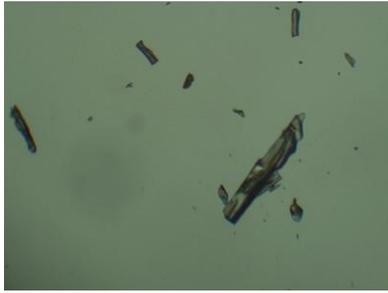


Figure 1.3.13 Variation of dynamic viscosity with shear rate at 100 ° C



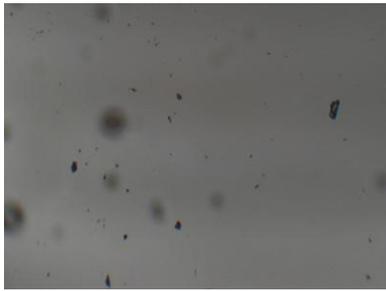
a. (Pour point= -6 °C)



b. (Pour point= -17 °C)



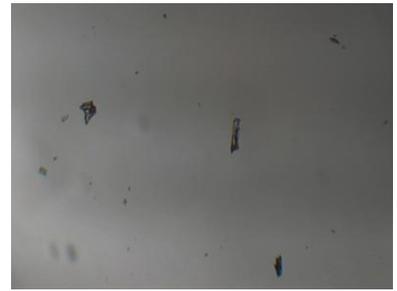
c. (Pour point= -15 °C)



d. (Pour point= -14 °C)



e. (Pour point= -13 °C)



f. (Pour point= -14 °C)



g. (Pour point= -12 °C)

Figure 1.3.14 Photomicrograph images of a) Pure lube oil (SN150) b) Lube oil + 4% (w/w) of P-1 c) Lube oil + 4% (w/w) of P-2 d) Lube oil + 4% (w/w) of P-3 e) Lube oil + 4% (w/w) of P-4 f) Lube oil + 4% (w/w) of P-5 g) Lube oil + 4% (w/w) of P-6

Part II

Maleic anhydride based additives - synthesis, characterization and performance evaluation as multifunctional additive for lube oil

Chapter I

Background of the present investigation

The primary function of a lubricant is to create a film barrier between the moving two engine parts to reduce friction and wear. It also acts as a coolant, suppresses harmful deposit formation, controls corrosion and oxidation. Since the base oil alone cannot meet these challenging demands, performance-enhancing additives formulations are added to the lubricant formulation. These packages can include pour point depressant (PPD), viscosity modifier (VM), antiwear, antioxidant, corrosion inhibitor, detergent and dispersant components. Not only these additives can improve overall efficiency in the engine, they also extend the lifetime of the lubricant and engine parts.¹

In recent context multifunctional additives play the major role in the technology of engine oils. Research throughout the world is increasing to produce multifunctional additives.²⁻⁴ Again, according to the literature, in case of multifunctional additive more than one additive performance can be found in a single system.^{5, 6} Thus introduction of multifunctionality in single system has become very relevant now a days. With this background the present investigation comprises the incorporation of three major additive performances (VM and PPD or VM, PPD and dispersant or antioxidant and detergents/dispersants) in single additive system.

In the general introduction section, we have discussed in details about VM, PPD, antioxidant and detergent/dispersant. In this present investigation, we will discuss about maleic anhydride based polymeric additives and Mannich base type additives and their multifunctional activity in lube oil. In accordance with the present investigation, it will be very pertinent to include a brief review on VM, PPD, antioxidant and detergents/dispersants additives for lubricating oil. The review of the foregoing researchers regarding on multifunctional lube oil additives is being presented, in a selective manner, in the following paragraphs.

U. S. Patent No. 3087893 described the preparation of copolymers of maleic anhydride and unsaturated esters of carboxylic acid. The prepared copolymers act as a multifunctional (VM and PPD) lube oil additives. U. S. Patent No. 4514314 claimed for the preparation of copolymer of 1- olefin having carbon number C_{14} to C_{18} and maleic anhydride esterified with 1.2 to 2.0 moles of 2- alkyl alkanol having carbon number C_{32} to C_{36} per molar proportion of maleic anhydride moiety and used as a pour point depressant for lubricating oil.

U.S. Patent No. 4668412 has described the synthesis of a terpolymer of maleic anhydride and lauryl methacrylate and stearyl methacrylate which has been formulated with dimethyl amino propyl amine and Mannich base of N- amino ethyl piperazine, paraformaldehyde and 2, 6-di-

t- butyl phenol. The prepared terpolymers act as dispersant, VII and PPD for lube oil. U. S. Patent No. 4707285 has claimed the synthesis of VM, PPD and dispersant copolymers which can be prepared by solutions of ethylene – propylene copolymers grafted with vinyl containing monomers, maleic anhydride or ethylenically unsaturated acids and finally formulated with polyols, polyamines and hydroxylamine as well as hydrogenated isoprene or butadiene copolymers.

U. S. Patent No. 4089794 claimed that copolymers of ethylene and one or more α - olefin having carbon number C_3 to C_{28} are grafted under an inert atmosphere and at elevated temperature with an ethylenically unsaturated carboxylic acid in the presence of free radical initiator and finally reacted with polyamine or hydroxyl amine to form a carboxy – grafted polymeric derivatives which have good engine sludge and varnish control behaviour in lubricating oil and fuels. If molecular weight of the polymeric derivatives is above 10000, then these are useful as viscosity index improver also.

U. S. Patent No. 4292185 claimed that the polymeric additives comprising a diene – modified olefinic backbone polymer functionalized with chloro sulphonyl isocyanate and post reacted with a nitrogen compound having at least one 1° or 2° amino group. The additives impart detergent, VII and other useful properties to lubricating oils and motor fuels.

U. S. Patent No. 5271856 described the synthesis of novel polymers prepared by reacting with a heterocyclic nitrogen compounds containing at least one –NH– group in the ring, an aldehyde and amino substituted polymer to form an oil soluble Mannich base derivative which are useful as antioxidant additive for lubricating oils and fuels.

In 2009, Abdel- Azim et al. reported the maleic anhydride based polymeric additives as multifunctional lube oil additives. They prepared the copolymer of maleic anhydride and styrene. The copolymer was esterified separately with different alcohols (dodecyl, hexadecyl, octadecyl and docosanol) to prepare four co polymeric additives and the performance was evaluated as viscosity modifiers and pour point depressants for lube oil. Another three polymeric additives were prepared by amidation of maleic anhydride – styrene copolymer with different long chain amines (dodecyl amine, hexadecyl amine and octadecyl amine) and performance was evaluated as viscosity modifiers, pour point depressants and dispersants for lube oil. They found that efficiency as VII or VM increases with increasing the molecular weight of the prepared polymers and the aminated products have a good dispersancy for sludge and solid particles.⁷ In 2011, Abdel-Azim et al. reported another similar type of work based on maleic anhydride and 1- octadecene copolymer and the copolymer was esterified

with different alcohols and aminated with different long chain amines and performance was evaluated as VM, PPD and dispersants for lube oil.⁸

In 2012, T. Du et al. had reported the synthesis of copolymers of ester of methacrylic acid and maleic anhydride at different molar ratios (1:1, 1:2, 1:3, 1:4, 2:1, 3:1, 4:1) and performance was evaluated as pour point depressant for lube oil. The best result obtained by the research group when the molar ratio was 3:1.⁹ In 2015, Atta et al. reported the synthesis of copolymers of vinyl acetate and maleic anhydride at different molar ratios (1:1, 1:2 and 2:1) followed by esterification with different types of n- alkanol (dodecyl, stearyl or behenyl alcohol). The esterified product was used as PPD for crude oil. The best performance as PPD was found when the molar ratio of copolymer is 1:2 and esterified by stearyl alcohol.¹⁰

In 2007, T. T. Khidr reported some maleic anhydride based polymeric additives as PPD for waxy crude oil. The copolymers were prepared by α -olefin (C₈ or C₁₄) with maleic anhydride and esterified with different alcohols (dodecyl or NAFOL 1822B alcohol). The prepared esters of the copolymers with average weights in the range of 26,300 to 38,200 were found to be more effective as pour point depressants for waxy crude oil.¹¹ In 2011, T. T. Khidr again reported some maleic anhydride based copolymers and terpolymers to study the flow properties for paraffin gas oil.¹²

In 2009, Zhang et al. reported the synthesis of copolymers of maleic anhydride and vinyl acetate and finally copolymer was aminated with long chain amine. The aminated polymeric additive was used as cold flow improver for diesel fuel.¹³ In 2014, Feng et al. had reported the synthesis of terpolymer based on alkyl acrylate, vinyl acetate and maleic anhydride in the molar ratio of 1:1:1 and the terpolymer was used as cold flow improver for diesel fuel.¹⁴ In 2001, Aleman-Vazquez had synthesized polyalkenylsuccinimides and their detergency and dispersancy properties evaluated in an internal combustion engine. Polyalkenylsuccinimides were prepared from polyisobutene with maleic anhydride and finally treated with primary amines. They found that polyalkenylsuccinimides obtained from ethylenediamine and tetraethylenepentamine were the best detergents/dispersants additives in fuel.¹⁵

In 2013, Kamal et al. had reported the Mannich base type additives for lubricating oil. The additives were prepared by p- dodecyl phenol, HCHO and different polyethylene polyamines and finally the additives were modified with P₂S₅. They investigated the efficiency of the prepared additives as antioxidant and detergents/dispersants for lubricating oil. They found that the efficiency increases with increasing the number of –NH groups in the amines used.¹⁶

In 2008, Ahmed et al. had reported some additives based on preparation of polyisobutylene

succinic anhydride (PIBSA) and then reaction of PIBSA with different polyethylene glycol and the products were aminated with different polyamines. They investigated the efficiency of the prepared compounds as antioxidants and detergents/dispersants for lube oil. They found that the efficiency of the prepared compounds increases with increasing the number of –NH groups in the prepared compounds and by increasing the molecular weight of the polyethylene glycols.¹⁷

From the above literature survey, it is appeared that multifunctional lube oil additives have greater importance than those having single or dual property, and in this direction chemistry of maleic anhydride showed potential application although the study is limited with this material. Thus considering the present need and emphasis as given by the original equipment manufacturers (OEMs), it was felt necessary to undertake some maleic anhydride based polymeric additives and Mannich base type additives towards the development of efficient multifunctional lube oil additives.

References

References are given in bibliography section under Chapter I of Part II (Page No. 185 - 186).

Chapter II

Synthesis and performance evaluation of maleic anhydride –

1- decene copolymer for lubricating oil

2.2.1 Introduction

Lubricating oil is a complex mixture of paraffinic wax, aromatic and naphthenic hydrocarbons with high molecular weights, very low volatility and with high viscosity index. The proportions of different hydrocarbon components determine the characteristic of the base oil.¹ However, the base oil alone cannot satisfy the requirements of lubricating oil without addition of additives. These additives, commonly known as lube oil additives are oil soluble substances that can improve the properties already present or add some new properties in the base oils. Some additives act to reduce the rate at which undesirable changes take place in the finished product during its service life. Some of the important commonly used additives are viscosity modifier or viscosity index improver,² pour point depressant,³ antiwear,⁴ detergents/ dispersants and antioxidants.⁵

The viscosity index is an indicator which indicates the change in viscosity when the temperature is changed. A higher viscosity index indicates the less change in viscosity of an oil for a given temperature change.⁶ Viscosity index improvers (VII) or viscosity modifiers (VM) are the polymeric additives that resist the change of viscosity of oil with change in temperature. They are long chain, high molecular weight polymers.⁷ It is believed that polymer molecule in lube oil solution exists as a random coil, which is swollen by lube oil solvent at high temperature and produces a network with lube oil and cause a minimal increase of viscosity in engine oil at low temperature but considerable increase at high temperature.⁸

Most of the base oil contains some dissolved paraffinic wax. At low temperature, the wax crystallizes to form a rigid structure that trap the oil in small packets in the structure. With sufficient formation of these crystal structures, the oil will no longer capable to flow.⁹ The lowest temperature at which the lube oil just stops its flowing is called pour point. To overcome this problem some high molecular weight polymers are used as pour point depressant (PPD). Pour point depressants, otherwise known as lube oil flow improvers (LOFI), are those additives that improve the low temperature fluidity of the fluid. The pour point depressants function by inhibiting the formation of a wax crystal structure that would prevent the oil flow at low temperatures.¹⁰

In the present work, author has prepared 1-decene-maleic anhydride copolymer and due to insolubility of the copolymer in lube oil, it was esterified with three different long chain alcohols (isooctanol, n- decanol and n- dodecanol). The efficiency of the prepared polymers

has been investigated as viscosity index improver and pour point depressant in three types of base oil through standard test methods.

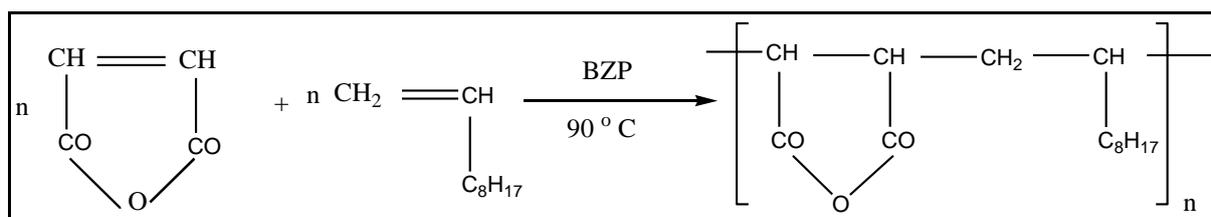
2.2.2 Experimental section

2.2.2.1 Chemicals used

Maleic anhydride (99%, LOBA Chemie, India) and 1-decene (95%, Acros organics) were used without further purification. Benzoyl peroxide (98%, LOBA chemie, India) was used after recrystallisation from chloroform- methanol mixture. Toluene (98%, Sd. fine chemicals, India) was purified by distillation and used as solvent for polymerisation as well as esterification of polymer. P-toluene sulphonic acid (98%, LOBA chemie) was used as catalyst after complete drying. Isooctanol (99%, LOBA chemie, India), 1- decanol (99.1%, Sd. fine chemicals, India) and 1-dodecanol (98%, Sd. fine chemicals, India) were used in esterification without further purification. Base oils were collected from IOCL and BPCL, India. Physical properties of the three base oils are given in **table 2.2.1**.

2.2.2.2 Preparation of 1-decene-maleic anhydride copolymer

The copolymerization of 1-decene and maleic anhydride was carried out in a three necked round bottom flask fitted with a magnetic stirrer and an inlet for the introduction of nitrogen. 1-Decene and maleic anhydride was mixed in the molar ratio of 1:1 in the presence of benzoyl peroxide (0.5% w/w, with respect to the monomer) as an initiator and toluene used as a solvent. The reactants were mixed and temperature was kept constant at 90° C and then benzoyl peroxide was added and heated for 8 hours. After the reaction is over, the product was put into cold methanol and filtered to obtain the copolymer.

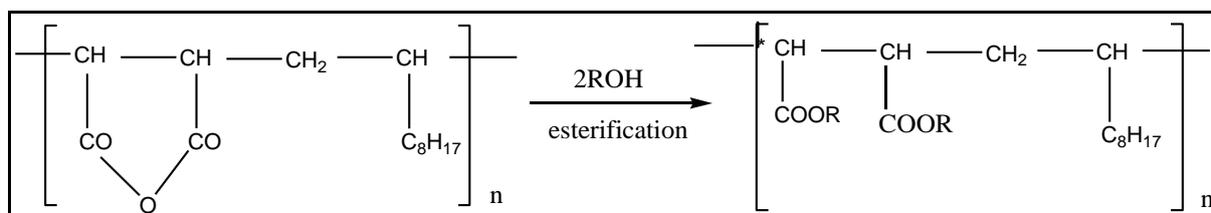


Scheme 1 Preparation of copolymer of maleic anhydride and 1- decene

2.2.2.3 Esterification of the copolymer with different alcohols

The esterification of the prepared copolymer was reacted separately with isooctanol, n-decanol and n- dodecanol to prepare three esters of the copolymer. In a four necked round bottom flask fitted with a mechanical stirrer, an efficient condenser with Dean Stark apparatus, a thermometer and a nitrogen gas inlet. The dry copolymer was esterified with

different alcohols in the presence of p-toluene sulphonic acid as a catalyst and toluene as a solvent. The copolymer and alcohol were taken in 1:1(w/w) ratio. Reaction mixture was slowly heated up to 130°C until all water of esterification is removed. The esterified product is dried by passing through solid Na₂SO₄ and finally methanol was added to precipitate the polymer and filtered to obtain the product. The designation of the prepared compounds is listed in **table 2.2.2**.



Scheme 2 Esterification of the copolymer

2.2.3 Measurements

2.2.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl₃ was used as solvent and tetramethylsilane (TMS) as reference material.

2.2.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (polystyrene calibration) equipped with a 2414 detector, waters 515 HPLC pump and 717 plus auto sampler. Sample solutions (0.4% w/v in HPLC grade THF) are prepared by dissolving ~4 mg of polymer per ml THF and filtering (0.45-µm Millipore PTFE) to remove suspended particulates. The pump flow rate is 1.0 mL/min with THF as the carrier solvent, and injection volumes are set to 20 µL. The polydispersity index¹¹ which indicates the nature of the distribution of the molecular weights in the polymers was also calculated.

2.2.3.3 Determination of Thermo gravimetric analysis (TGA) data

The thermo-oxidative stability of all the polymers was determined by a thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating of rate of 10 °C/min.

2.2.3.4 Performance evaluation as viscosity index improver

Viscosity index (VI) was calculated by dissolving prepared polymer in three different base oils (BO1, BO2 and BO3) using an Ostwald Viscometer (size 200, No 3205), thoroughly cleaned, dried and calibrated at the experimental temperatures (313K and 373K) with distilled water and purified methanol.^{12, 13} It was then filled with experimental solution and placed vertically in a glass sided thermostat. After reaching thermal equilibrium, the time flow of solutions was recorded with a digital stopwatch. In all the determinations an average of three measurements was taken into account and precautions were taken to minimize the losses due to evaporation. The kinematic viscosity (ν) of the sample solution, which was used to calculate viscosity Index (VI), was determined at 313K and 373K temperatures from the following equation¹⁴

$$\nu = (Kt - L/t) d \quad (1)$$

Where K and L are the viscometric constants and their values are $0.06853 \text{ cm}^2 \text{ s}^{-2}$ and 5.2706 cm^3 respectively, are determined by taking toluene as a solvent, t and d are the time of flow and density of the experimental solution respectively. The densities were measured with a density meter (Anton Paar, DMA 4500M). Before measurements, the density meter was calibrated with distilled water and acetone at the experimental temperature and atmospheric pressure. VI was calculated from the following empirical equation¹⁴

$$VI = 3.63 (60 - 10^n) \quad (2)$$

Where n is given by

$$n = (\ln \nu_1 - \ln \nu_2) / \ln 2 \quad (3)$$

Where ν_1 and ν_2 are the kinematic viscosities at lower and higher temperatures respectively, K is a constant which is equal to 2.714 for the temperature range performed and n is the characteristic constant for each oil.¹⁴

Different concentrations ranging 1% - 6% (w/w) were used to study the effect of additive concentration on VI.

2.2.3.5 Performance evaluation as pour point depressant

Pour point depressants were calculated in polymer doped different base oils (BO1, BO2 and BO3) through the pour point test according to the ASTM D 97-09 method¹⁵ using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging 1% - 6% (w/w).

2.2.4 Results and discussion

2.2.4.1 Analysis of molecular weight and TGA data

The experimental values of M_n and M_w for the polymer A, B and C (determined by GPC) are given in **table 2.2.3**. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the M_w values decrease but PDI value increases.

From TGA values of all the three polymers (**table 2.2.4**), it is seen that polymer C is thermally less stable than polymer A and B. Thermal stability of polymer A and B are almost same. Therefore, it is expected that polymer A and B are more linear than polymer C.¹⁶

2.2.4.2 Spectroscopic data analysis

The spectroscopic data of the three polymers A, B and C are similar. In the IR spectra (**figure 2.2.1**), the peak at 1736 cm^{-1} indicates presence of ester carbonyl group. The peak at 2854.5 cm^{-1} and 2924 cm^{-1} is the characteristic of CH_3CH_2- group. The peaks at 1465.8 , 1404 , 1373 , 1211.2 and 1165 cm^{-1} due to CO stretching vibration and absorption bands at (810 cm^{-1} and 725 cm^{-1}) were due to bending of C-H bond. The disappearance of two anhydride peaks indicates that the esterification of copolymer was carried successfully.

In the ^1H NMR (**figure 2.2.2**), the methyl protons appear in the range of 0.88 to 0.92 ppm, the methylene protons in the range of 1.27 to 1.30 ppm for all alkyl groups. A broad peak at (4.17 ppm and 4.19 ppm) indicates the protons of $-\text{OCH}_2$ group. Absence of peak in the range of 5-6 ppm indicates the disappearance of C=C bond and confirms the polymerisation. In the ^{13}C NMR (**figure 2.2.3**), the peak at 165.27 ppm indicates the presence of ester carbonyl carbon. The peak at 65.35 ppm confirms the presence of $-\text{OCH}_2$ carbon. The peaks ranging from 14.03 – 32.62 ppm represents all sp^3 carbon atoms of alkyl groups. No peak in the range of 120-150 ppm indicates the absence of sp^2 carbons and confirms the polymerization.

2.2.4.3 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers at a concentration range of 1% - 6% (w/w) in different base oils. The values are given in **table 2.2.5**. From the experimental data, it is found that VI values increase with increasing the concentration of polymer in base oil. The higher concentration of polymer increases the total volume of polymer micelles in the oil solutions and hence increases the VI.¹⁷ The VI value of polymer A is higher than polymer B and C in all the three base oils. The lube oil viscosity decreases with increasing temperature but expansion of polymer molecules increase with increasing temperature. As a result, the hydrodynamic volume increases and micelle size of the solvated polymer molecule also increase and resists the reduction of the viscosity of lube oil with temperature.^{18, 19} This effect is greater in case of polymer A and may be due to its higher molecular weight. From the

figures 2.2.4, 2.2.5 and 2.2.6, it is found that all the polymers are more effective in BO2 and least effective in BO3 as VII.

2.2.4.4 Analysis of pour point data

The polymer doped base oils (BO1, BO2 and BO3) at different concentration ranging from 1% - 6% (w/w) were tested for pour point and experimental values are given in **table 2.2.6**. From the values, it is observed that all the three polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oil. It may be due to decrease in solvation power.^{20, 21} Among the three polymers (A, B and C), the polymer C is more efficient as PPD in all the three base oil. It may be due to decrease in molecular weight and increase in polydispersity index.^{22, 23} Pour point of polymer A and B are not so much different in BO1 but in BO2 and BO3, the pour point of polymer B is higher than polymer A (**figures 2.2.7, 2.2.8 and 2.2.9**). From the values of ΔPP , a critical observation can be taken that in most of the concentrations ΔPP value is higher in case of base oil BO1. This indicates that the polymers are more effective in case of BO1 i.e. in the lower viscous base oil.

2.2.5 Conclusions

From the above study, it is found that all the prepared polymers are effective as VI and PPD. In case of VI, polymer A is more effective than B and B is more effective than C. This indicates that with decreasing the alkyl chain length in alcohols used for esterification, the VI property increases. The polymer C has highest PPD property than A and B, therefore, with increasing the alkyl chain length in alcohols used in esterification, the PPD property improves. Therefore, carbon chain length in polymer has a significant role when added in the lube oil to act as a VII and PPD.

2.2.6 References

References are given in the bibliography section under Chapter II of Part II (Page No. 186 - 188).

2.2.7 Tables and figures

Table 2.2.1 Physical properties of the base oils

Base oil properties	Base oils		
	BO1	BO2	BO3
Density (g cm ⁻³) at 40 ° C	0.83	0.84	0.87
Viscosity at 40 °C in c St	7.102	23.502	107.120
Viscosity at 100 °C in c St	1.850	3.98	10.322
Viscosity index	84.56	85.15	81.5
Pour point (° C)	-3	-6	-0.5
Cloud point (° C)	-1	-4	+2

Table 2.2.2 Polymer code of the prepared compounds (esters)

Copolymer + Alcohol	Code
1-Decene-maleic anhydride copolymer + Isooctanol	A
1-Decene-maleic anhydride copolymer + n- decanol	B
1-Decene-maleic anhydride copolymer + n- dodecanol	C

Table 2.2.3 Molecular weight of A, B and C (determined by GPC)

Polymer code	M _n	M _w	PDI
A	19,327	19,496	1.02
B	15,883	18,056	1.14
C	9,105	14,472	1.59

M_n = Number average molecular weight, M_w = weight average molecular weight,

PDI = Polydispersity index

Table 2.2.4 TGA data for the polymers A, B and C

Polymer	Decomposition temperature/ ° c	Percent weight loss(PWL)
A	203/365	26/44
B	195/ 360	27/48
C	183/309	32/53

Table 2.2.5 Viscosity index of polymer of A, B and C at different concentrations in different base oil (BO1, BO2 and BO3)

Polymer	Base oil	VI of Polymer doped base oil						
		0%	1%	2%	3%	4%	5%	6%
A	BO1	84.6	94	97	99	102.6	104.5	114
	BO2	85.2	102.3	106	108	112.4	124	124
	BO3	81.5	87.5	93.4	98.5	104	109	109
B	BO1	84.6	92.3	95	98.7	102.7	104.7	109.8
	BO2	85.2	92.5	106	106	112	120	124
	BO3	81.5	88	88	94	104	107	108
C	BO1	84.6	89	94.6	94	99	103	103.7
	BO2	85.2	93	94	100.5	110	116	117
	BO3	81.5	87	90	91	98	103	106

Table 2.2.6 Pour point (PP) and difference in pour point of pure lube oil and polymer doped lube oil (Δ PP) of polymer A, B and C at different concentrations (w/w) in base oils (BO1, BO2 and BO3

Polymer code	Base oil	PP	Δ PP	PP	Δ PP	PP	Δ PP	PP	Δ PP	PP	Δ PP	PP	Δ PP
		1%		2%		3%		4%		5%		6%	
A	BO1	-10	7	-10	7	-8	5	-8	5	-6	3	-6	3
	BO2	-10	4	-10	4	-9	3	-8	2	-7.5	1.5	-7.5	1.5
	BO3	-6	5.5	-5.5	5	-5	4.5	-5	4.5	-3.5	3	-3.5	3
B	BO1	-10	7	-8	5	-8	5	-7.5	4.5	-5.5	2.5	-5.5	2.5
	BO2	-12	6	-11	5	-11	5	-11	5	-8	2	-8	2
	BO3	-6	5.5	-8	7.5	-6	5.5	-5.5	5	-4	3.5	-4	3.5
C	BO1	-14	11	-12	9	-12	9	-9	6	-9	6	-8.5	5.5
	BO2	-12	6	-14	8	-14	8	-11	6	-10	4	-10	4
	BO3	-9	8.5	-8.8	8.3	-8.8	8.3	-7	6.5	-6	5.5	-6	5.5

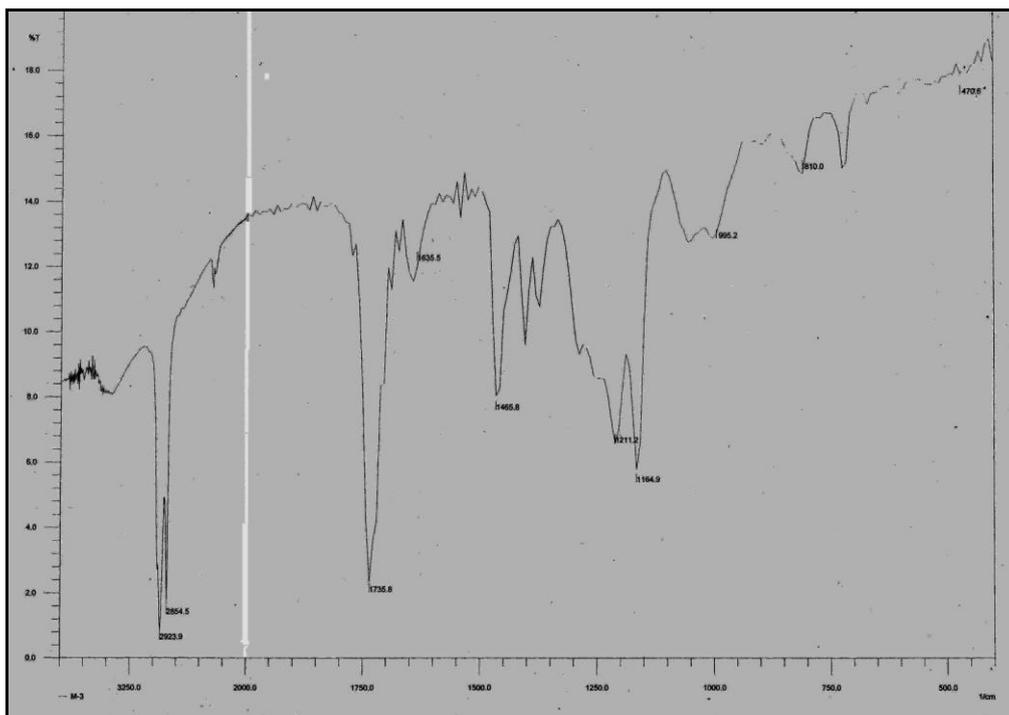


Figure 2.2.1 IR spectra of polymer C

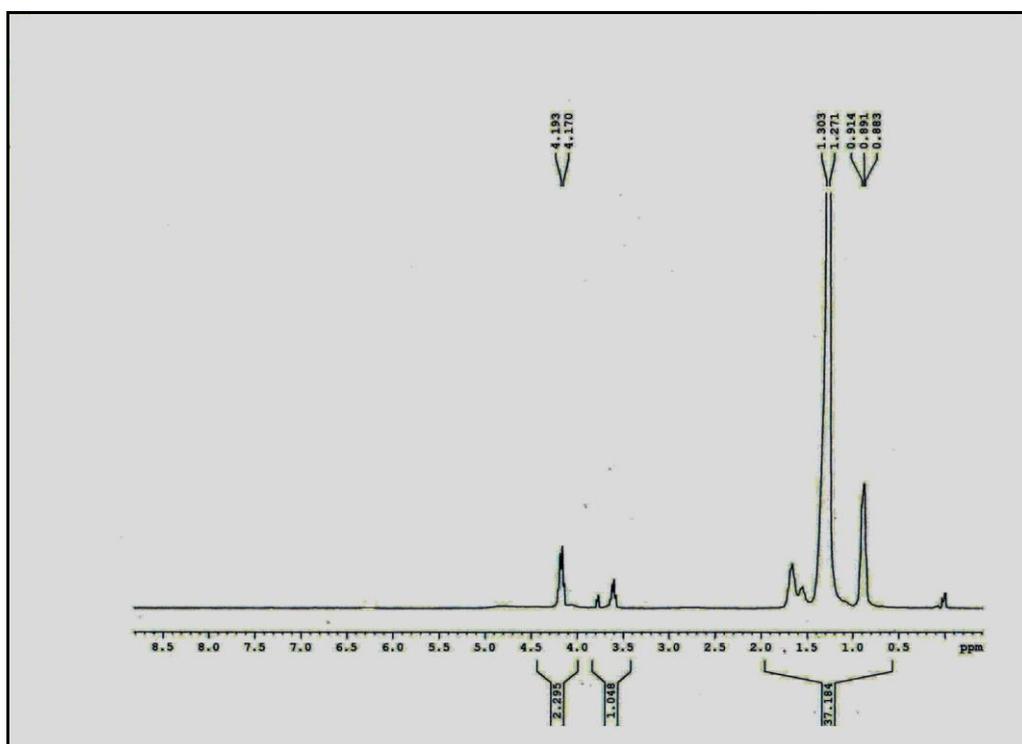


Figure 2.2.2 ¹H NMR of polymer C

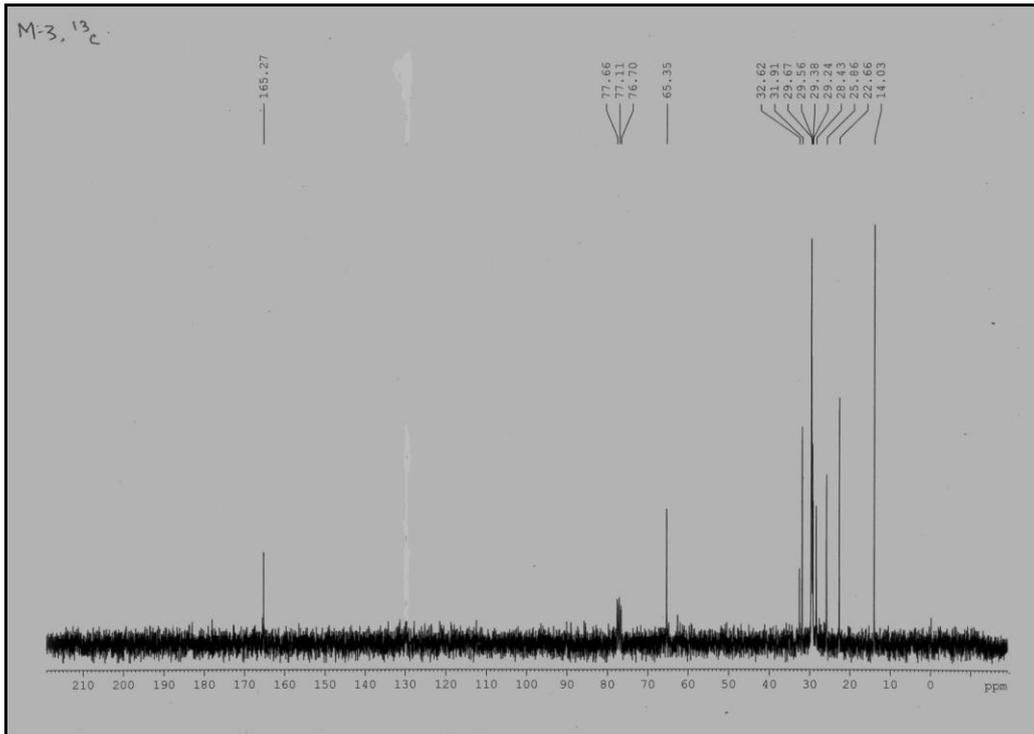


Figure 2.2.3 ¹³C NMR of polymer C

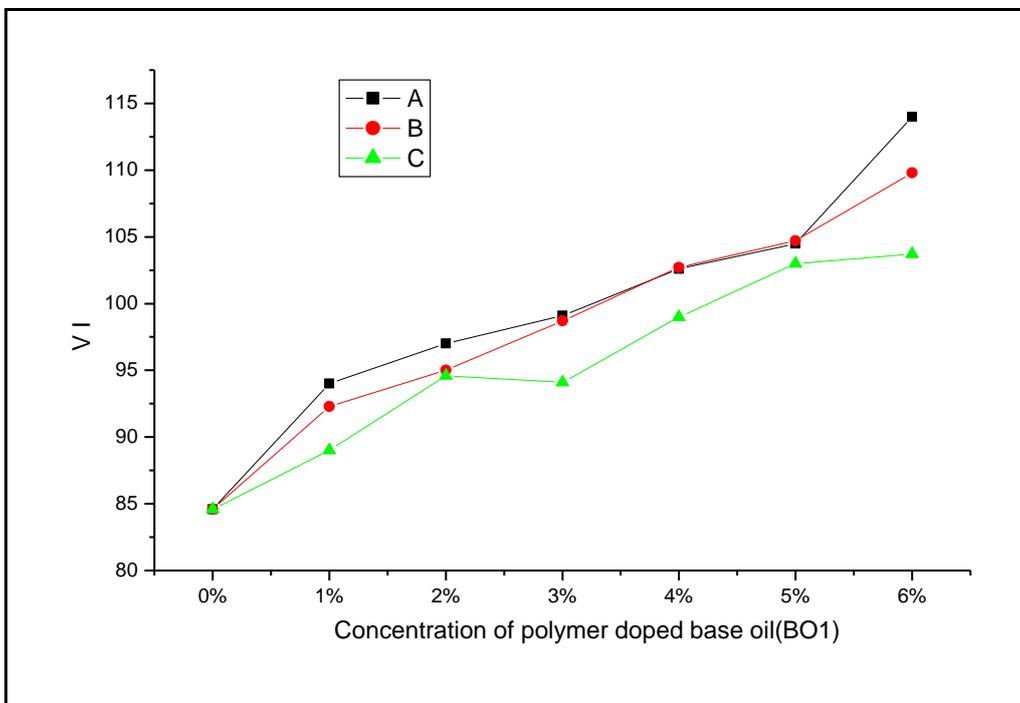


Figure 2.2.4 Comparison of VI values of three polymers in base oil, BO1

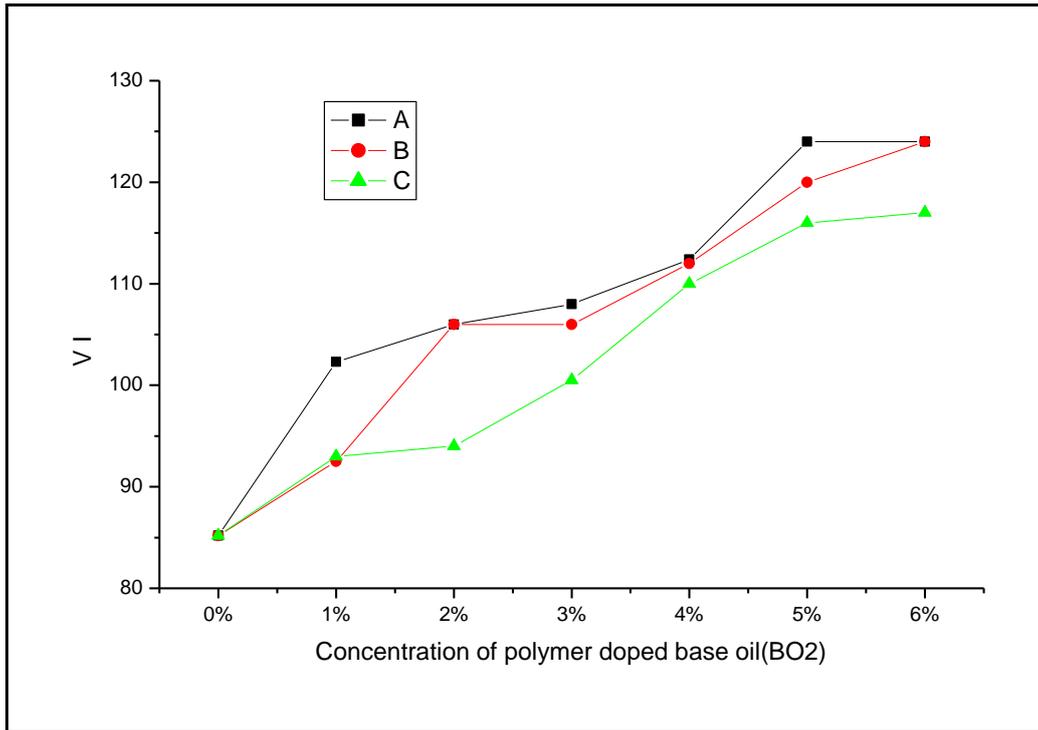


Figure 2.2.5 Comparison of VI values of three polymers in base oil, BO2

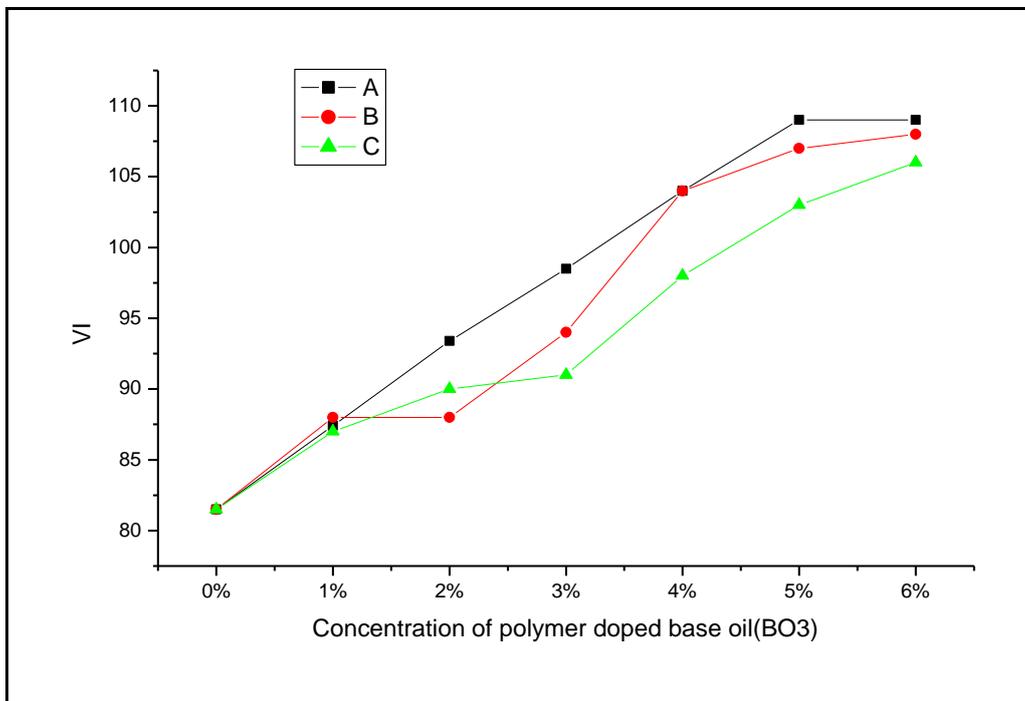


Figure 2.2.6 Comparison of VI values of three polymers in base oil, BO3

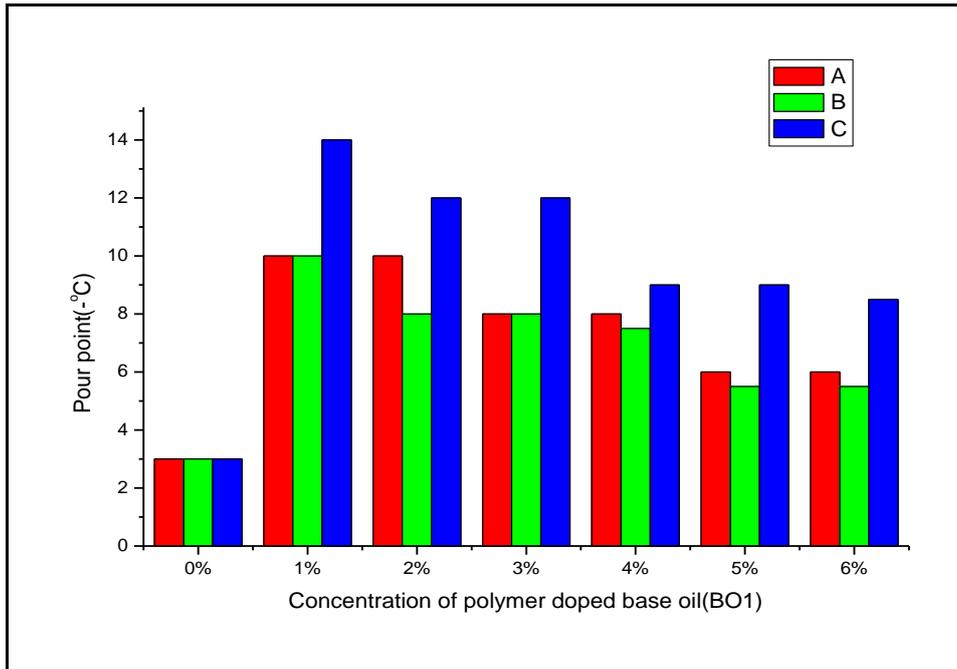


Figure 2.2.7 Comparison of pour point values of three polymers in base oil, BO1

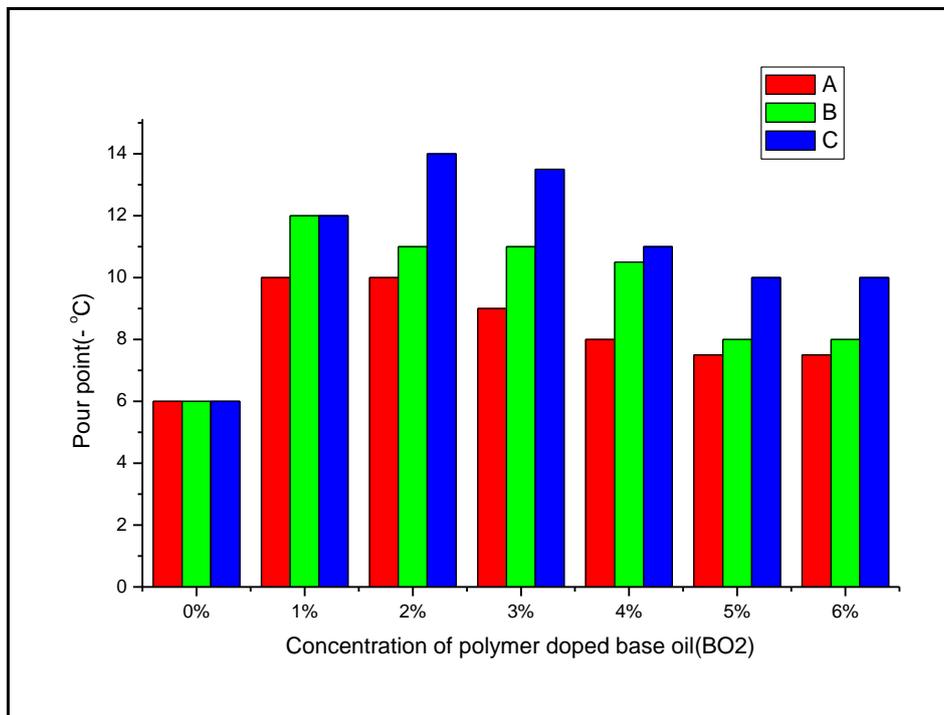


Figure 2.2.8 Comparison of pour point values of three polymers in base oil, BO2

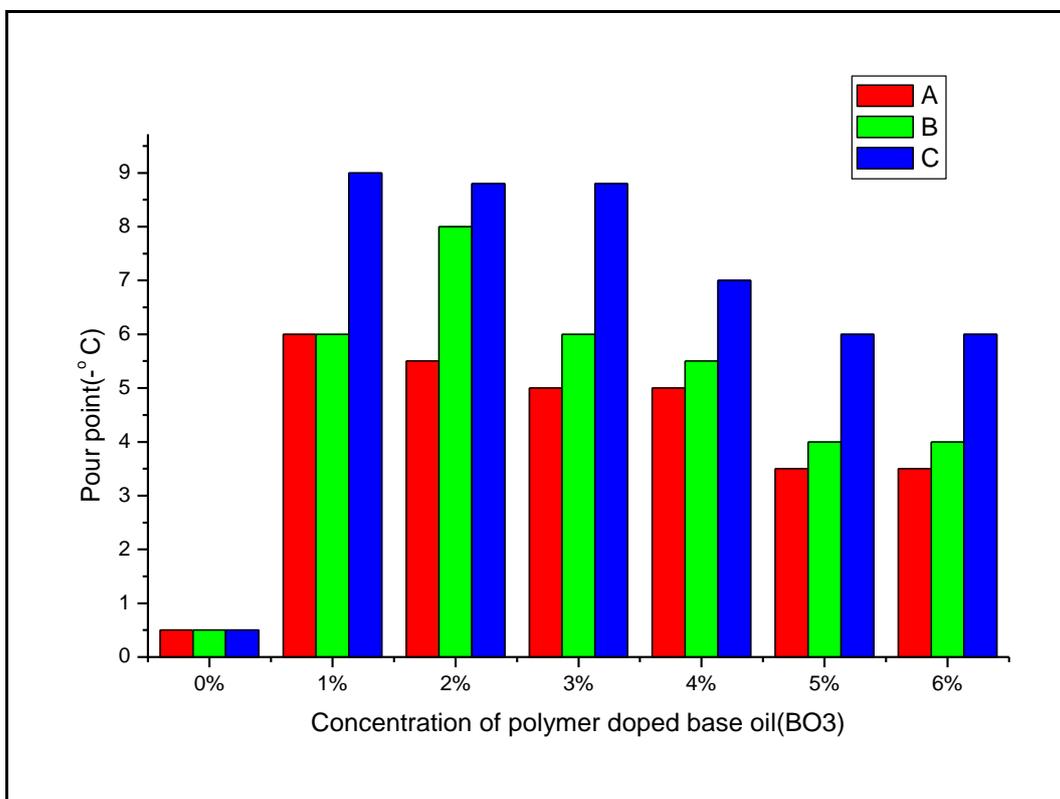


Figure 2.2.9 Comparison of pour point values of three polymers in base oil, BO3

Chapter III

Synthesis and performance evaluation of vinyl acetate maleic anhydride based polymeric additives for lubricating oil

2.3.1 Introduction

Lubricant comprises a base fluid and a package of additives.^{1, 2} The basic function of lubricant is to lubricate modern engines to prolong its lifetime. Base fluids also known as base oils, the basic building block of a lubricant, are a complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with low volatility and high viscosity index.^{3, 4} The percentage of different hydrocarbon components determines the characteristics of the base oils.⁵ Additives are the specific chemical compounds when added to base oil, impart new and useful properties to the oil. Some additives enhance the properties already present and some act to reduce the rate at which undesirable changes take place in the product during its service life.⁶ The most important additive is viscosity index improver (VII). The degree of susceptibility of viscosity of a fluid with rise in temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI). A higher VI value signifies a lesser effect of temperature on viscosity. Viscosity index improvers (VII) or viscosity modifiers (VM) are additives that resist the change of viscosity of oil with change in temperature.⁷⁻¹⁰ The performance of VII mainly depends on the behaviour of polymer molecule in the base stock, polymer solubility, molecular weight, resistance to shear degradation.¹¹

Pour point is the lowest temperature at which the lube oil loses its flow ability. The freezing of lube oil is caused by the formation of crystal network of paraffinic wax present in the lube oil. The pour point of lube oil can be lowered with additives, called pour point depressants (PPDs), also known as cold flow improvers. The PPD additive works by destroying the wax crystal network and thereby lowering the pour point. The flow property at low temperature is thus maintained.^{12,13} The additives which are used as pour point depressants should have some pendant alkyl groups and there should be an appropriate distance between the pendant alkyl group and there should be a suitable ratio of monomers when a copolymer is used.^{14, 15}

In this present work, author prepared maleic anhydride - vinyl acetate copolymer. Due to insolubility of the copolymer in lube oil, it was esterified with three types of long chain alcohol (1-octanol, 1-decanol and 1-dodecanol) to get the corresponding esterified polymeric products. The author have investigated the efficiency of each of them as viscosity index improver or viscosity modifier and pour point depressant in three types of base oils.

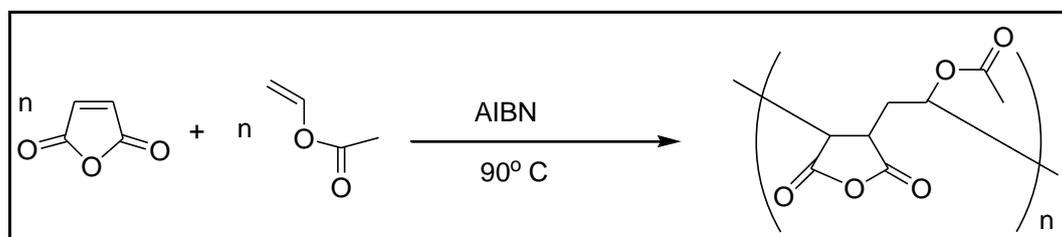
2.3.2 Experimental section

2.3.2.1 Chemicals used

Maleic anhydride (99%, LOBA Chemie, India) and vinyl acetate (99%, Sd. fine chemicals, India) were used without further purification. Azobisisobutyronitrile (AIBN, 98%, Spectrochem Pvt. Ltd. India) was used without purification. Toluene (98%, Sd. fine chemicals, India) was purified by distillation and used as solvent for polymerisation as well as esterification of polymer. P-toluene sulphonic acid (98%, LOBA chemie) was used as catalyst after complete drying. 1-Octanol (99%, LOBA chemie, India), 1-decanol (99%, Sd. fine chemicals, India) and 1-dodecanol (98%, Sd. fine chemicals, India) were used in esterification without further purification. Base oils were collected from IOCL and BPCL, India. Physical properties of the base oils are given in **table 2.3.1**.

2.3.2.2 Preparation of maleic anhydride-vinyl acetate copolymer

The copolymerization of maleic anhydride and vinyl acetate was carried out in a three necked round bottom flask fitted with a magnetic stirrer and an inlet for the introduction of nitrogen. Vinyl acetate and maleic anhydride was mixed in the molar ratio of 1:1 in the presence of azobisisobutyronitrile (AIBN, 0.5% w/w, with respect to the monomer) as an initiator and toluene was used as a solvent. The reactants were mixed and temperature was kept constant at 90° C for half an hour and then AIBN was added and heated for 6 hours. After the reaction is over, the product was put into cold methanol and filtered to obtain the copolymer.

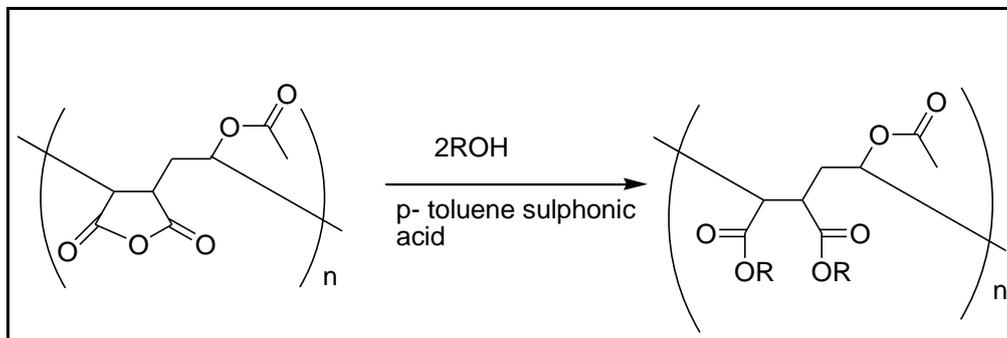


Scheme 1 Preparation of copolymer of maleic anhydride and vinyl acetate

2.3.2.2 Esterification of the copolymer with different alcohols

The prepared copolymer was reacted separately with 1-octanol, 1-decanol and 1-dodecanol in presence of catalytic amount of p-toluene sulphonic acid to prepare three esterified product A, B and C respectively of the copolymer. In a four necked round bottom flask fitted with a mechanical stirrer, an efficient condenser with Dean Stark apparatus, a thermometer and a nitrogen gas inlet. The dried copolymer was esterified with different alcohols in the presence of p-toluene sulphonic acid as a catalyst and toluene as a solvent. The copolymer and alcohol

were taken in 1:1(w/w) ratio. Reaction mixture was slowly heated up to 130°C until all water of esterification is removed. The ester was purified by washing with distilled water and drying over Na₂SO₄. Finally methanol was added to precipitate the product and was filtrated and dried.



Scheme 2 Esterification of copolymer by three types of alcohols.

ROH = C₈H₁₇OH (octyl alcohol) gives polymeric additive **A**, ROH = C₁₀H₂₁OH (decyl alcohol) gives polymeric additive **B**, ROH = C₁₂H₂₅OH (dodecyl alcohol) gives polymeric additive **C**

2.3.3 Measurements

2.3.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the range of 400 to 4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl₃ was used as solvent and tetramethylsilane (TMS) as reference material.

2.3.3.2 Determination of intrinsic viscosity and viscometric average molecular weight of the prepared polymeric additives

Viscometric properties were determined at 40°C in toluene solution using an Ubbelohde OB viscometer. The time flow was counted at eight different concentrations (g/c.c) of the polymer solution. Intrinsic viscosity and viscometric molecular weight were determined by Huggins (equation-1) and Mark- Houwink- Sukurda equation (equation-2) respectively.¹⁶

$$\text{Huggins equation (H), } \eta_{sp}/C = [\eta]_h + K_h [\eta]_h^2 C \quad (1)$$

Where, C is the mass concentration, $\eta_{sp} = \eta_r - 1$, η_{sp} is the specific viscosity, $\eta_r = t/t_0$, η_r is the relative viscosity or viscosity ratio, where t is the flow of time of the polymer solution and t₀ is the flow of time of the pure solvent. $[\eta]_h$ = intrinsic viscosity, respective to Huggins equation, K_h is the Huggins coefficient. According to Mark- Houwink–Sukurda (equation-2),

the value of intrinsic viscosity changes with the molecular weight of the additive in a solvent as: $[\eta] = KM^a$ (2)

Where $[\eta]$, the intrinsic viscosity can be calculated by using Huggins equation, parameter 'K' and 'a' depends on the type of polymer, solvent and temperature. For the determination of viscosity average molecular weight, the constants, $K = 0.00387$ dl/g and $a = 0.725$ were used in Mark Houwink- Sukurda equation.¹⁷

2.3.3.3 Determination of Thermo gravimetric analysis (TGA) data

The thermo-oxidative stability of all the polymers was determined by a thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating rate of 10°C/min.

2.3.3.4 Performance evaluation of the polymers as viscosity index improver

Viscosity index (VI) was calculated by dissolving prepared polymer in three different base oils (BO1, BO2 and BO3) through the viscosity index test according to ASTM D 7042 method.¹⁸ The kinematic viscosity of the polymer doped base oil was determined at 40°C and 100°C. Different concentrations ranging 1% - 5% (w/w) were used to study the effect of additive concentration on VI.

2.3.3.5 Performance evaluation of the polymers as pour point depressant

Pour point of the additive doped base oils (BO1, BO2 and BO3) were recorded through the pour point test according to the ASTM D 97-09 method¹⁹ using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging 1% - 5% (w/w).

2.3.4 Results and discussion

2.3.4.1 Spectroscopic data analysis

In the IR spectra of copolymer of maleic anhydride and vinyl acetate (**figure 2.3.1**), the peaks at 1782 cm^{-1} and 1851.5 cm^{-1} indicate the presence of anhydride group. The peak at 1728 cm^{-1} indicates the presence of ester carbonyl group in the copolymer due to vinyl acetate moiety. The peaks at 2862 cm^{-1} and 2920 cm^{-1} are the characteristic of CH_3 - group. The peaks at 1458 cm^{-1} , 1365.5 cm^{-1} , 1219 cm^{-1} and 1033.8 cm^{-1} due to CO stretching vibration and absorption bands at 933.5 cm^{-1} and 725 cm^{-1} were due to bending of C-H bond.

The spectroscopic data (IR and NMR) of the three polymers A, B and C are similar. In the IR spectra of polymer A (**figure 2.3.2**), peak at 1735.8 cm^{-1} indicates the presence of ester carbonyl group. The peaks at 2854.5 cm^{-1} and 2925 cm^{-1} are the characteristic of CH_3CH_2 - group. The peaks at 1466 cm^{-1} , 1404 cm^{-1} , 1373 cm^{-1} , 1211 cm^{-1} and 1156 cm^{-1} due to CO stretching vibration and absorption bands at 818 and 725 cm^{-1} were due to bending of C-H

bond. The disappearance of two anhydride peaks at 1782 cm^{-1} and 1851.5 cm^{-1} indicate that esterification of copolymer was carried out successfully.

In the ^1H NMR (**figure 2.3.3**), a broad peak in the range of 3.37 ppm to 3.98 ppm indicates the protons of $-\text{COCH}_3$ group. Another broad peak ranging from 4.002 ppm to 4.185 ppm indicates the protons of $-\text{OCH}_2$ groups. The hydrogens attached to sp^3 carbons appear in the range of 0.90 ppm to 2.43 ppm. Absence of any peak in the range of 5-6 ppm indicates the disappearance of $\text{C}=\text{C}$ bond and confirms the polymerisation.

In ^{13}C NMR (**figure 2.3.4**), the peak at 165.53 ppm indicates the presence of ester carbonyl group. The peak at 62.56 ppm indicates the presence of $-\text{COCH}_3$ methyl carbon. The peaks at 64.83 ppm and 65.56 ppm confirm the presence of all $-\text{OCH}_2$ carbons. The peaks ranging from 14.18 – 32.65 ppm represents all other sp^3 carbons. No peak in the range of 120 -150 ppm indicates the absence of sp^2 carbons and confirms the polymerization.

2.3.4.2 Molecular weight and TGA data analysis

The experimental values of intrinsic viscosity and viscometric molecular weight of polymer A, B and C are given in **table 2.3.2**. From the values, it is seen that with increasing the alkyl chain length of the alcohol used in esterification, the molecular weight increases. From TGA values of all the three polymers (**table 2.3.2**), it is seen that polymer A is thermally less stable than polymer B and C. Polymer B and C are thermally almost equal stable.

2.3.4.3 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers at a concentration range of 1% - 5% (w/w) in different base oils. The values are given in **table 2.3.3**. From the experimental data, it is found that VI values increase with increasing the concentration of polymer in base oils. The higher concentration of polymer increases the total volume of polymer micelles in the oil solutions and hence increases the VI.^{20, 21} The VI value of polymer C is higher than polymer B and B is higher than A in all the three base oils. The lube oil viscosity decreases with increasing temperature but expansion of polymer molecules increase with increasing temperature. As a result, the hydrodynamic volume increases and micelle size of the solvated polymer molecule also increase and resists the reduction of the viscosity of lube oil with temperature.^{22, 23} This effect is greater in case of polymer C which may be due to its higher molecular weight.

2.3.4.4 Analysis of pour point data

The polymer doped base oils (BO1, BO2 and BO3) at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **table 2.3.4**.

From the values, it is observed that all the three polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oil. It may be due to decrease in solvation power.^{24, 25} Among the three polymers (A, B and C), the polymer A is more efficient as PPD in all the three base oils. It may be due to presence of short alkyl chain in polymer A. The interaction between the short alkyl chain length and paraffin in the lube oil is more effective than long alkyl chain length and wax crystal formation is inhibited.^{26, 27} From the experimental pour point values, it is also observed that all the three polymers are more effective in base oil, BO1 i.e. in the lower viscous base oil.

2.3.5 Conclusions

From the above study, it is found that all the prepared three polymers are effective as VII and PPD. Among the three polymers, polymer C is more efficient than B and B is more efficient than A as VII. This indicates that with increasing the alkyl chain length of alcohols used in esterification, the VI property increases. The PPD property of polymer A is higher than polymer B and C, it indicates that with decreasing the alkyl chain length of alcohols used in esterification, the PPD property improves. Therefore, alkyl chain length has a significant role in polymerization to enhance the property of VII and PPD for lube oil polymeric additives.

2.3.6 References

References are given in the bibliography section of Chapter III of Part II (Page No. 188 - 190).

2.3.7 Tables and figures

Table 2.3.1 Physical properties of the base oils

Base oil properties	<u>Base oil</u>		
	BO1	BO2	BO3
Density (g cm ⁻³) at 40 ° C	0.83	0.84	0.87
Viscosity at 40 °C in c St	7.102	23.502	107.120
Viscosity at 100 °C in c St	1.850	3.98	10.322
Viscosity index	84.56	85.15	81.5
Pour point (° C)	-3	-6	-0.5
Cloud point (° C)	-1	-4	+2

Table 2.3.2 Intrinsic viscosity, Viscometric molecular weight and thermo gravimetric analysis (TGA) values of polymer A, B and C

Polymer	$[\eta]_h$	$[M]_h$	Deco.tem/°C	PWL
A	4.12	14,973	180/306	32/91
B	4.38	16,220	198/ 355	26/88
C	4.52	16,916	203/365	25/87

A = esterified product of copolymer of maleic anhydride-vinyl acetate with 1-octanol; B = esterified product of copolymer of maleic anhydride-vinyl acetate with 1-decanol; C = esterified product of copolymer of maleic anhydride-vinyl acetate with 1-dodecanol; $[\eta]_h$ = intrinsic viscosity respective to Huggins; $[M]_h$ = Viscometric molecular weight according to Mark Houwink–Sukurda equation; Deco.tem = decomposition temperature; PWL = percentage weight loss.

Table 2.3.3 Viscosity index (VI) of polymer of A, B and C at different concentrations (% in w/w) in different base oil (BO1, BO2 and BO3)

Polymer	Base oil	<u>VI of Polymer doped base oil</u>					
		0%	1%	2%	3%	4%	5%
A	BO1	84.6	90	96	96	100	104
	BO2	85.2	92	95	95	100	103
	BO3	81.5	87	92	92	98	105
B	BO1	84.6	93	97	97	104	106
	BO2	85.2	95	98	100	106	108
	BO3	81.5	88	90	96	96	105
C	BO1	84.6	96	96	99	108	112
	BO2	85.2	98	98	102	110	112
	BO3	81.5	89	94	94	102	107

Table 2.3.4 Pour point of polymer A, B and C at different concentrations (% in w/w) in different base oil (BO1, BO2 and BO3)

Polymer	Base oil	<u>Pour point of Polymer doped base oil</u>					
		0%	1%	2%	3%	4%	5%
A	BO1	-3	-10	-12	-9	-9	-9
	BO2	-6	-12	-12	-10	-10	-10
	BO3	-0.5	-6	-7	-6	-5	-5
B	BO1	-3	-10	-10	-9	-8	-8
	BO2	-6	-10	-10	-10	-9	-9
	BO3	-0.5	-6	-6	-5	-5	-5
C	BO1	-3	-9	-9	-7	-7	-7
	BO2	-6	-9	-10	-8	-8	-8
	BO3	-0.5	-6	-4	-4	-4	-3

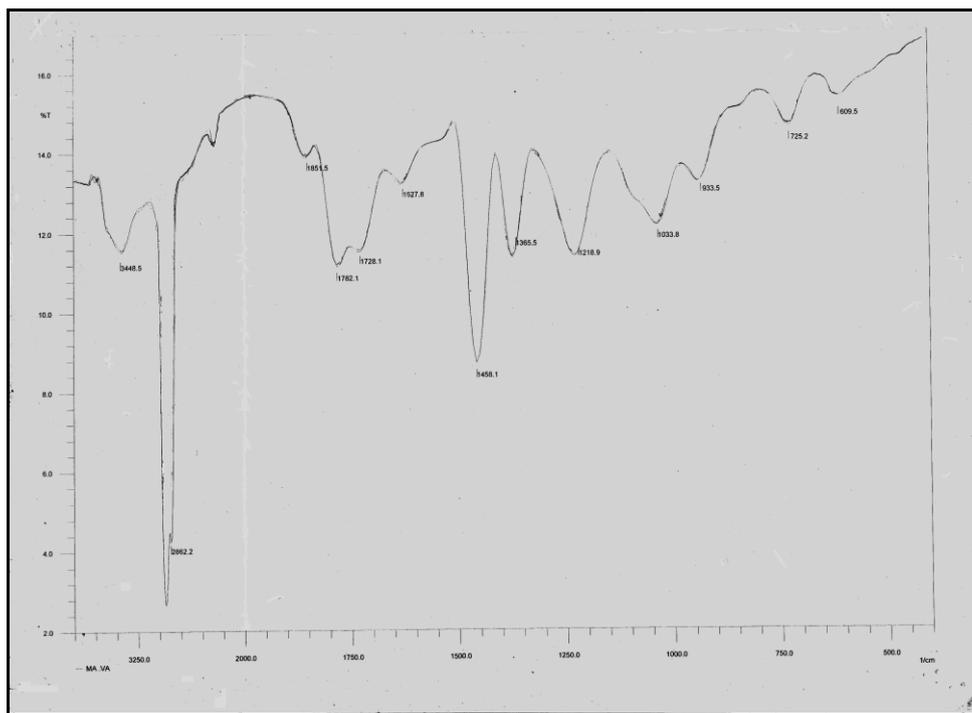


Figure 2.3.1 IR spectra of copolymer of maleic anhydride and vinyl acetate

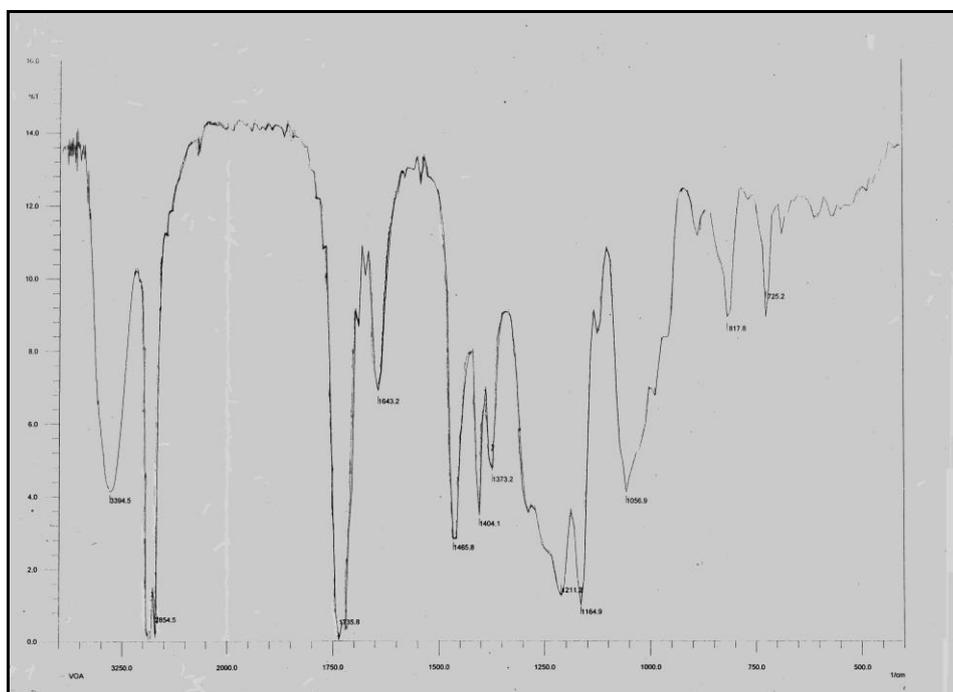


Figure 2.3.2 IR spectra of polymer A

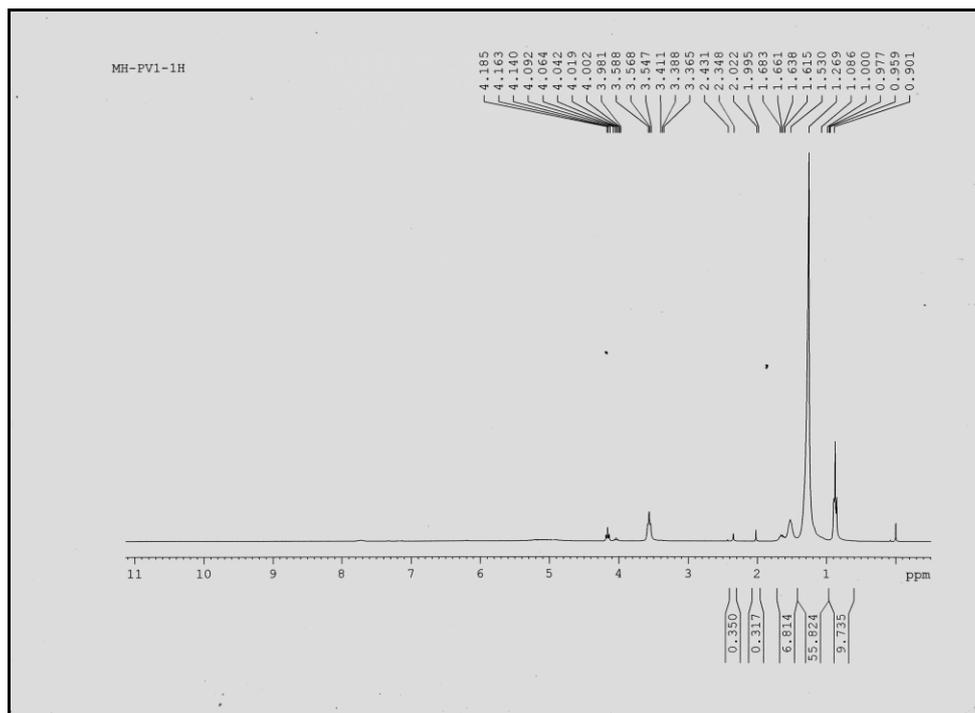


Figure 2.3.3 ^1H NMR spectra of polymer A

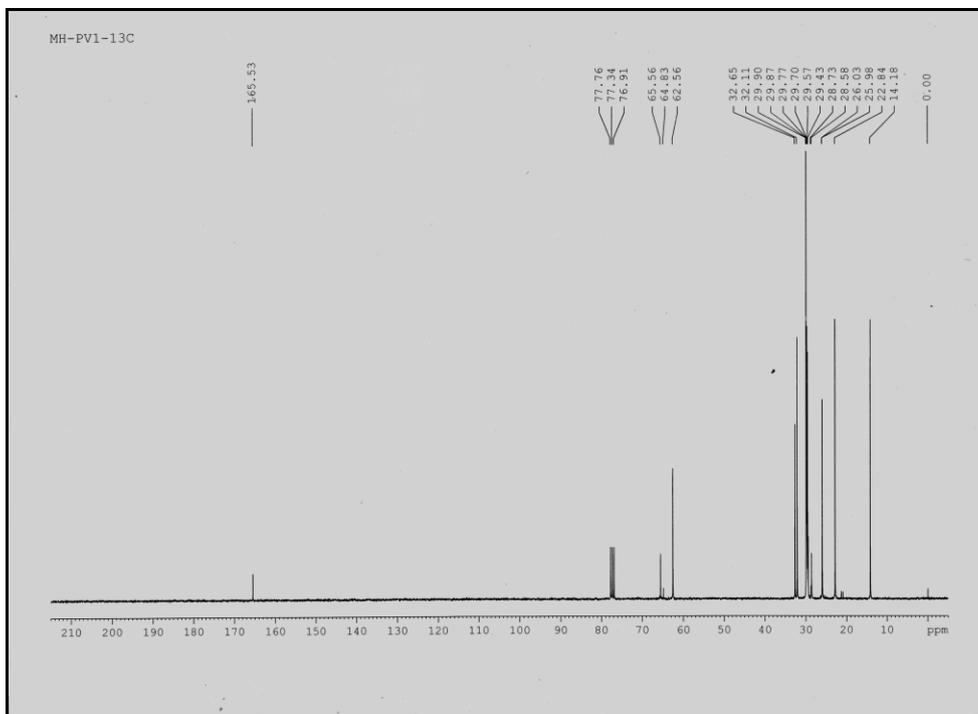


Figure 2.3.4 ^{13}C NMR spectra of polymer A

Chapter IV

Multifunctional lube oil additives based on maleic anhydride and 1-decene

2.4.1 Introduction

Engine oils are used to reduce the metal to metal contact of the moving parts in internal combustion engine. With the development of modern engine technology, the demands are being placed to modify engine oils or lubricating oils for automotive engines. Hence much research effort has been committed to develop the lubricating oil. The petroleum based lubricating oil can't satisfy all the requirements of modern engines. Hence, to enhance the characteristic properties, those already present or to impart some new additional properties, a large number of additives are to be added to the lubricating oil.¹

The most important single property of lubricating oil is its viscosity. Lubricating oils are used in different fields depending on their viscosity and viscosity index (VI) is an important affecting factor on the field of application of lubricant.² The variation of viscosity of a lubricant with change in temperature is determined by its viscosity index (VI), which is an arbitrary number calculated from the observed kinematic viscosities at two widely separated temperatures (generally at 40 ° C and 100 ° C).^{3,4} VI improver is added to the base oil to get better VI.⁵ Viscosity index improver or viscosity modifier increases the thickness of the base oil and develop the viscosity – temperature characteristic of base oil.⁶ A higher viscosity index indicates the less change in viscosity of an oil for a given temperature change.⁷

The pour point of lubricating oil is the lowest temperature at which it cannot flow. Lube oil contains some paraffinic waxes. The solubility of waxes decreases with decreasing temperature. The temperature at which first crystal appears is called cloud point or wax appearance temperature.⁸ Below this point, the wax crystals grow up and form three dimensional network. This network traps the oil molecules around it and a gel like structure is made.⁹ This gel on further cooling becomes sufficiently dense and the movement of the lube oil get stopped. But when pour point depressants (PPD), also known as lube oil flow improvers (LOFI), are added, they modify the crystal structure of waxes by adsorption and produces smaller and more isotropic crystals which have higher solubility and hence pour point decreases.¹⁰

Lubricating oils are subjected to oxidation at high temperature in the presence of air or metal and due to oxidation; lube oil decomposes to form some oxidation products, sludge and varnish, dirt etc. and as a result viscosity increases. The oxidation products, sludge particles deposit on the engine parts. Dispersants keep these particles in a dispersed form. Dispersant additive contains a polar head group with an oil soluble hydrocarbon tail, keeps metal

surfaces clean by preventing deposition of oxidation products of internal combustion engines.^{11, 12} The mechanism of dispersancy is generally described on the basis of adsorption of the additive through its polar ends on the sludge materials.^{13, 14}

In the present work, author prepared maleic anhydride -1-decene copolymer by using AIBN as an initiator in toluene solvent and due to insolubility of the copolymer in lube oil, it was aminated with three different long chain amines (n-octyl amine, n-decyl amine and n-dodecyl amine). The efficiencies of the prepared polymers as viscosity index improver, pour point depressant and dispersant in three types of base oils through standard test methods were investigated.

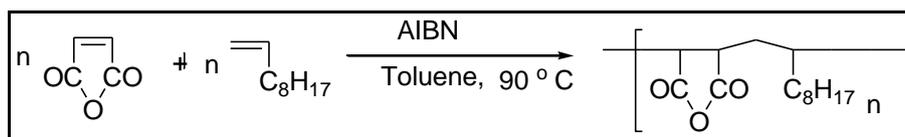
2.4.2 Experimental section

2.4.2.1 Chemicals used

Maleic anhydride (99%, LOBA Chemie, India) and 1-decene (95%, Acros organics) were used without further purification. AIBN (98%, Spectrochem Pvt. Ltd.) was used after recrystallisation from chloroform - methanol mixture. Toluene (Thomas Baker, 99%) was purified by distillation and used as solvent for polymerisation as well as amination of polymer. Octyl amine (Spectrochem Pvt. Ltd., 99%), n- decyl amine (Acros Organics, 99%) and n- dodecyl amine (Sigma – Aldrich, 99%) were used without purification. Methanol (Thomas Baker, 98%) was used after purification by distillation method. Base oils were collected from IOCL and BPCL, India and their properties are given in **table 2.4.1**.

2.4.2.2 Preparation of maleic anhydride - 1-decene Copolymer

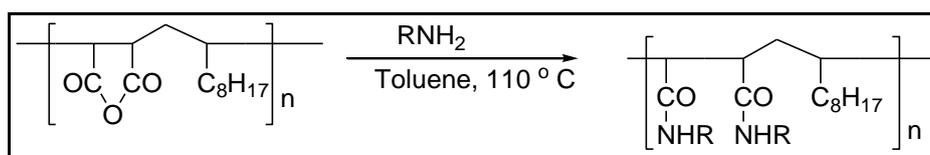
The copolymerization of 1-decene and maleic anhydride was carried out in a three necked round bottom flask fitted with a magnetic stirrer and an inlet for the introduction of nitrogen. Maleic anhydride and 1-decene was mixed in the molar ratio of 1:1 in the presence of AIBN (0.5% w/w, with respect to the monomer) as an initiator and used toluene as a solvent. The reactants were mixed and temperature was kept constant at 90° C and then AIBN was added and heated for 8 hours. After the reaction is over, the product was put into cold methanol and filtered to obtain the copolymer.



Scheme 1 Copolymerization of maleic anhydride and 1-decene

2.4.2.3 Reaction of maleic anhydride – 1-decene copolymer with different amines

The prepared copolymer was reacted with different amines (n-octyl amine, n-decyl amine and n-dodecyl amine) separately in a ratio of 1:1 (w/w) to prepare three polymeric additives designated by A₁, A₂ and A₃ respectively. The reaction was carried out in a three necked round bottom flask fitted with a condenser, a magnetic stirrer and a thermometer and heated for 6 hours in toluene solvent at 110° C. After the reaction time is over, cold methanol was added to the reaction mixture. The amidated copolymer appears as precipitate and finally filtered and dried to obtain the product.



Scheme 2 Amidation of copolymer with different amines. $\text{RNH}_2 = \text{C}_8\text{H}_{17}\text{NH}_2$ (octyl amine) gives polymeric additives A₁; $\text{RNH}_2 = \text{C}_{10}\text{H}_{21}\text{NH}_2$ (decyl amine) gives polymeric additives A₂; $\text{RNH}_2 = \text{C}_{12}\text{H}_{25}\text{NH}_2$ (dodecyl amine) gives polymeric additives A₃

2.4.3 Measurements

2.4.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

2.4.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (Waters 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 35 °C at a flow rate of 1ml/min.

2.4.3.3 Determination of Thermo gravimetric analysis (TGA) data

The thermo-oxidative stability of all the polymers was determined by a thermo gravimetric analyzer (Shimadzu TGA-50) in air using an alumina crucible at a heating of rate of 10 °C/min.

2.4.3.4 Performance evaluation as viscosity index improver (VII)

Viscosity index was calculated by dissolving prepared polymer in three types of base oils (BO1, BO2 and BO3) through the viscosity index test according to ASTM D 2270-10. The kinematic viscosity of the polymer doped base oil was determined at 40° C and 100° C.

Different concentrations of additives [ranging from 1% - 5% (w/w)] were used, to study the effect of additive concentration on VI.

2.4.3.5 Performance evaluation as pour point depressant (PPD)

Pour point was determined in polymer doped three types of base oils (BO1, BO2 and BO3) through the pour point test according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging from 1% - 5% (w/w).

3.4.3.6 Photomicrographic image

The photomicrograph showing wax behaviour of lube oil (BO2, pour point = - 6) without and with 3% (w/w) polymers has been recorded at 0° C temperature. A Banbros polarizing microscope model BPL-400B was used for photographic analysis. The adopted magnification was 200X.

3.4.3.7 Performance evaluation as dispersant

Spot method was applied to determine dispersancy¹⁵. A few drops of oxidized product of pure lube oil and lube oil containing 3% additive (w/w) were taken from the Indiana oxidation apparatus where samples are oxidized at 165.5 ° C in presence of Fe and Cu strips and after each 24 h intervals of oxidation and up to 72 h to make spots on filter paper (Durieux 122) and dispersancy of the sample was calculated as follows:

$$\% \text{ Dispersancy} = \frac{\text{Diameter of the black spot}}{\text{Diameter of the total spot}} \times 100$$

An additive having higher value of dispersancy will act as a good dispersant for lube oil.

3.4.4 Results and discussion

3.4.4.1 Spectroscopic analysis

The spectroscopic data of the three polymers A₁, A₂ and A₃ are similar. In the IR spectra (**figure 2.4.1**), a peak at 1644 cm⁻¹ indicates the presence of amide group. The presence of two peaks at 2854 cm⁻¹ and 2923 cm⁻¹ indicate the characteristic of CH₃ CH₂- group. A peak at 1697 cm⁻¹ represents the carbonyl group present in amide group. The presence of a broad peak at 3278 cm⁻¹ represents -NH group. The disappearance of two peaks for anhydride group indicate that amidation of copolymer was carried out successfully.

In the ¹H NMR spectra (**figure 2.4.2**), the methyl protons appear in the range of 0.85 to 0.89 ppm, the methylene protons appear in the range of 1.26 to 1.49 ppm for all alkyl groups. The peaks appear in the range of 2.70 to 2.75 ppm indicate the protons of -CHCO- group. A

broad peak at 3.886 ppm indicates the protons of $-\text{NCH}_2-$ group. A small peak at 8.85 ppm indicates the proton of $-\text{NH}$ group. No peaks in the range of 5-6 ppm indicate that polymerization was carried out successfully.

In the ^{13}C NMR spectra (**figure 2.4.3**), the peak at 176.96 ppm indicates the presence of amide carbonyl carbon. The peak at 41.50 ppm confirms the presence of $-\text{NCH}_2$ carbon. The peaks ranging from 14.06 – 32.27 ppm represents all sp^3 carbon atoms of alkyl groups. No peak in the range of 120-150 ppm indicates the absence of sp^2 carbons atoms and confirms the polymerization.

3.4.4.2 Analysis of molecular weight and TGA values

The experimental values of M_n and M_w of the prepared copolymers (A, A₁, A₂ and A₃) are given in **table 2.4.2**. From the values, it is found molecular weight increases with increasing the alkyl chain length of the amine used in the amidation of copolymers. From the experimental TGA values (**figure 2.4.4**), it is found that polymer A₁ has higher thermal stability than the other two copolymers. It may be due to lower molecular weight and lower PDI value.¹⁶ All the three polymers starts decomposition at 90° C. In case of A₁, a major decomposition is observed at 300° C with a 32% weight loss. The thermal stability of A₂ and A₃ are almost same. A major decomposition is observed for these two polymers at 270° C with a 41% weight loss.

3.4.4.3 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers at a concentrations range of 1% - 5% (w/w) in three types of base oils. The values are given in **table 2.4.3**. From the experimental data, it is found that VI values increase with increasing the concentration of polymer in base oil. The higher concentration of polymer increases the total volume of polymer micelles in the oil solutions and hence increases the VI.^{17, 18} The VI value of polymer A₃ is higher than polymer A₂ and A₂ is higher than A₁ in all the three base oils. The lube oil viscosity decreases with increasing temperature but expansion of polymer molecules increase with increasing temperature. As a result, the hydrodynamic volume increases and micelle size of the solvated polymer molecule also increase and resists the reduction of the viscosity of lube oil with temperature.¹⁹⁻²¹ This effect is greater in case of polymer C which may be due to its higher molecular weight.

3.4.4.4 Analysis of pour point data

The polymer doped base oils (BO1, BO2 and BO3) at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **table 2.4.4**.

From the values, it is observed that all the three polymers can be effectively used as pour point depressant and efficiency as pour point increases with increasing the concentration of polymer in base oil up to 3%. This means that at this concentration, the polymer may interact with the paraffinic wax and modify their crystals size.^{22, 23} Among the three polymers (A_1 , A_2 and A_3), the polymer A_1 is more efficient as PPD in all the three base oils. It may be due to presence of short alkyl chain in polymer A_1 . The interaction between the short alkyl chain length and paraffin in the lube oil is more effective than long alkyl chain length and wax crystal formation is prevented.²⁴ From the experimental values, it is also observed that all the three polymers are more effective as PPD in base oil, BO1. It may be due to lower viscosity of BO1.

3.4.4.5 Photo micrographic analysis

Photo micrographic analysis was used to study the pour point and its mechanism of the lube oil without and with polymeric additives. The photograph of lube oil (BO2) without and with different additives is shown in the **figure 2.4.5(a-d)**. The figure 2.4.5a is the photograph of lube oil (pour point = -6°C) without any additives where there is large number of rod shaped wax crystals. The photo micrographic images of lube oil with 3% (w/w) of A_1 , lube oil with 3% (w/w) of A_2 and lube oil with 3% (w/w) of A_3 are shown in the figures 2.4.5b, 2.4.5c, and 2.4.5d respectively. A significant wax crystal modification is observed in figure 2.4.5b (pour point = -19°C). This is in agreement with the pour point values determined by ASTM D97-09 method.

3.4.4.6 Analysis of dispersant data

The lube oil (BO1, BO2 and BO3) and lube oil with 3% (w/w) polymer of each were subjected to severe oxidation conditions using the Indiana test method as described in experimental section, in which dispersant additive increases the diameter of the black spot. This is due to the enhanced capability of the doped oil to carry the oxidation products to a longer distance from the centre of the spot. It may be due to the fact that the $-\text{NH}$ groups form hydrogen bonds with the polar end of oxidation products like alcohol, aldehyde, ketone, acids etc.^{25, 26} Moreover, the presence of amine part present in the prepared additives neutralizes some of the acidic products formed during oxidation. It is observed that efficiency as dispersant increases with increasing the molecular weight of polymers and with increasing alkyl chain length. Among the three base oils (BO1, BO2 and BO3), the polymers are more effective as dispersant in base oil BO1 (**table 2.4.5**).

3.4.5 Conclusions

From the above study it is found that the prepared copolymers are effective as viscosity index improver, pour point depressant and dispersant for lube oil. The molecular weight of the prepared polymers increases with increasing the alkyl chain length of the amines used in amidation of copolymer. The efficiencies as VII and dispersant increase with increasing the molecular weight as well as with increasing the alkyl chain length of the polymer. Whereas, the efficiency as a pour point depressant increases with decreasing molecular weight of the prepared polymers and with the decreasing the alkyl chain length. Therefore, molecular weight and alkyl chain length of the polymers have a significant role for acting as a lube oil additives.

3.4.6 References

References are given in the bibliography section of Chapter IV of Part II (Page No. 190 - 192).

3.4.7 Tables and figures

Table 2.4.1 Physical properties of the base oils

Base oil properties	<u>Base oil</u>		
	BO1	BO2	BO3
Density (g cm ⁻³) at 40 ° C	0.83	0.84	0.87
Viscosity at 40 °C in c St	7.102	23.502	107.120
Viscosity at 100 °C in c St	1.850	3.98	10.322
Viscosity index	84.56	85.15	81.5
Pour point (° C)	-3	-6	-0.5
Cloud point (° C)	-1	-4	+2

Table 2.4.2 Monomers, polymer code and M_n , M_w and PDI values of copolymers

Monomers	Polymer code	M_n	M_w	PDI
M.A + 1-D	A	16641	20559	1.24
M.A + 1-D + OAM	A ₁	16047	23118	1.44
M.A + 1-D + DAM	A ₂	11637	27190	1.93
M.A + 1-D + DDAM	A ₃	15335	30330	1.97

M.A = Maleic anhydride; 1-D = 1- Decene; OAM = Octylamine; DAM = Decylamine; DDAM = Dodecylamine; M_n = Number average molecular weight; M_w = Weight average molecular weight; PDI = Polydispersity index.

Table 2.4.3 Viscosity index values of polymers of A₁, A₂ and A₃ at different concentrations (% in w/w) in different base oils (BO1, BO2 and BO3)

Polymer	Base oil	VI of Polymer doped base oil (conc. in %, w/w)					
		0%	1%	2%	3%	4%	5%
A ₁	BO1	84.6	92	98	104	109	116
	BO2	85.2	90	98	104	108	114
	BO3	81.5	90	92	98	106	109
A ₂	BO1	84.6	93	99	108	115	119
	BO2	85.2	92	100	102	112	118
	BO3	81.5	90	95	102	112	116
A ₃	BO1	84.6	98	104	112	118	124
	BO2	85.2	98	104	110	120	126
	BO3	81.5	95	100	109	116	120

Table 2.4.4 Pour point values of polymers A₁, A₂ and A₃ at different concentrations (% in w/w) in different base oil (BO1, BO2 and BO3).

Polymer	Base oil	<u>Pour point of polymer doped base oil (conc. in %, w/w)</u>					
		0%	1%	2%	3%	4%	5%
A ₁	BO1	-3	-15	-16	-18	-18	-17
	BO2	-6	-16	-17	-19	-19	-19
	BO3	-0.5	-7	-7	-10	-10	-10
A ₂	BO1	-3	-15	-15	-16	-16	-16
	BO2	-6	-15	-15	-17	-17	-16
	BO3	-0.5	-7	-8	-9	-9	-9
A ₃	BO1	-3	-15	-15	-16	-16	-15
	BO2	-6	-14	-14	-15	-15	-15
	BO3	-0.5	-7	-8	-9	-9	-8

Table 2.4.5 Dispersancy of the lube oils (BO1, BO2, BO3) and their blends containing polymers (A₁, A₂ and A₃) after different oxidation periods

Sample	Dispersancy time, (in hour)		
	24	48	72
Lube oil (BO1) only	40	42	45
BO1 + A ₁	60	67	68
BO1 + A ₂	63.6	68	70
BO1 + A ₃	64	73	75
Lube oil (BO2) only	30	32	45
BO2 + A ₁	58	63	65.5
BO2 + A ₂	62	66	68
BO2 + A ₃	65	69.5	72
Lube oil (BO3) only	25	27	28
BO3 + A ₁	54	60	62
BO3 + A ₂	56	61	65
BO3 + A ₃	56	64	65.5

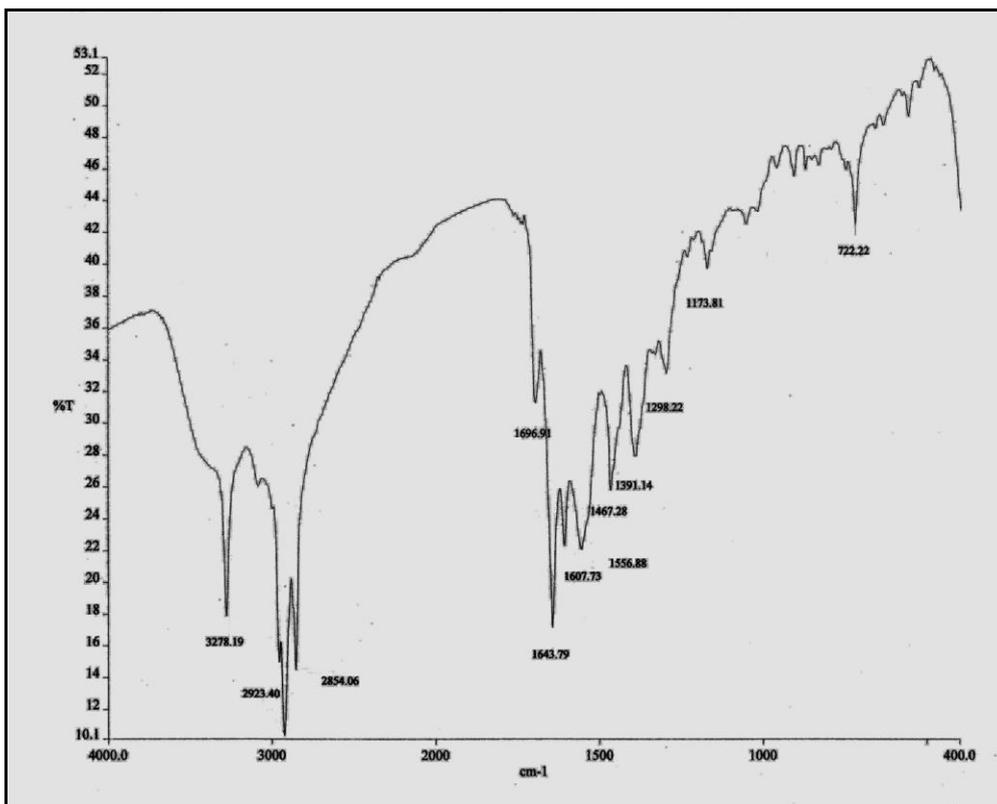


Figure 2.4.1 IR spectra of polymer A₁

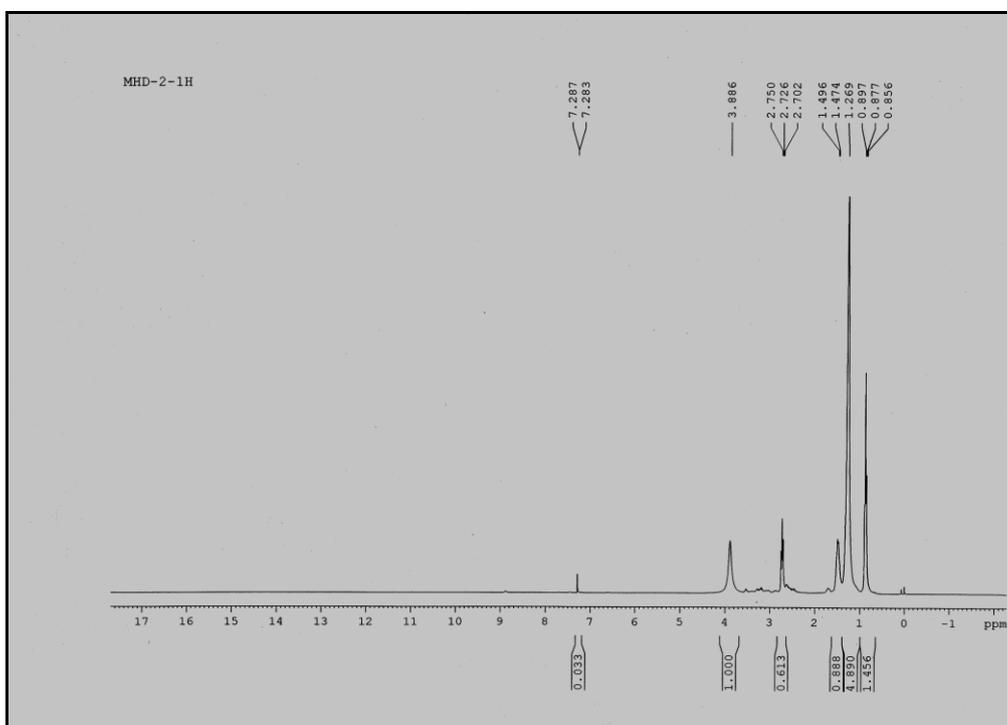


Figure 2.4.2 ¹H NMR spectra of polymer A₁

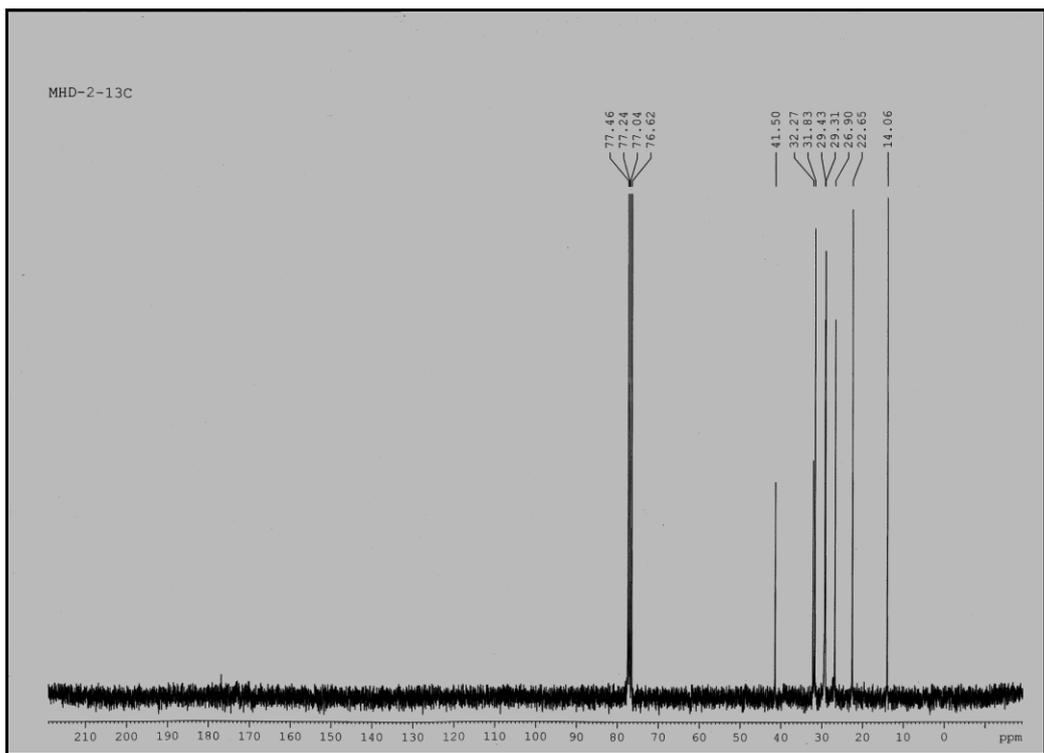


Figure 2.4.3 ^{13}C NMR spectra of polymer A₁

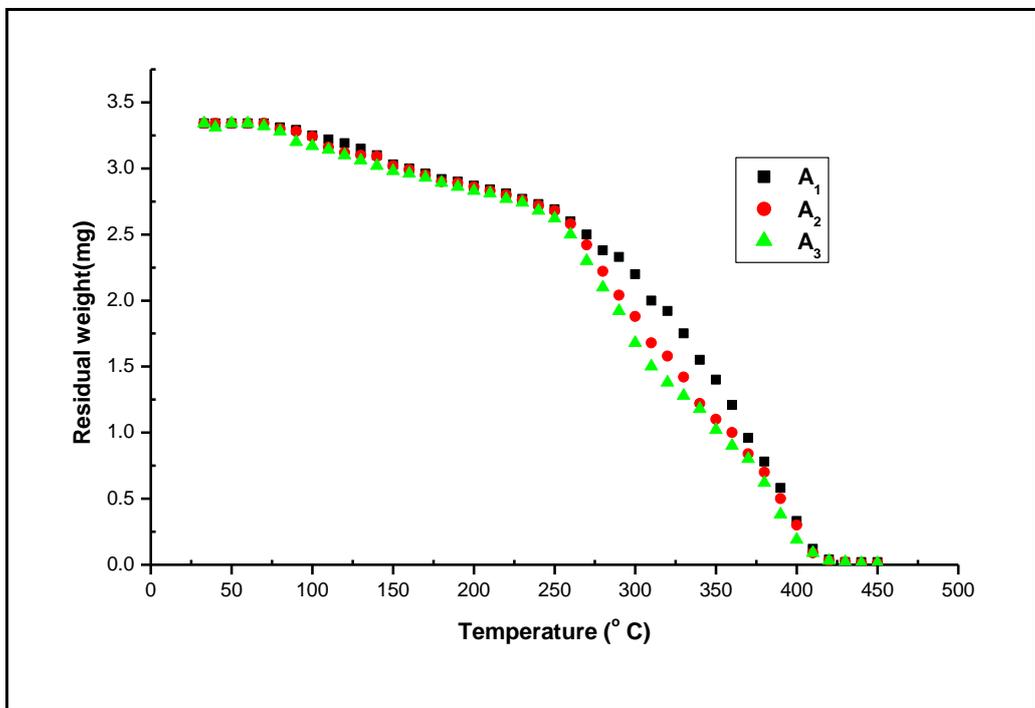
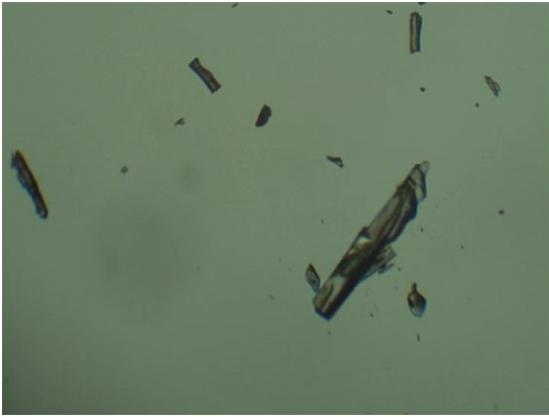
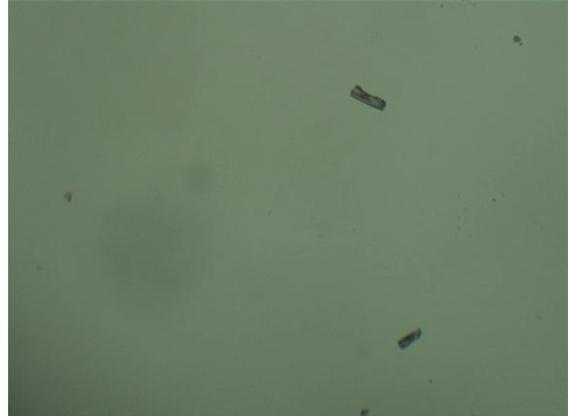


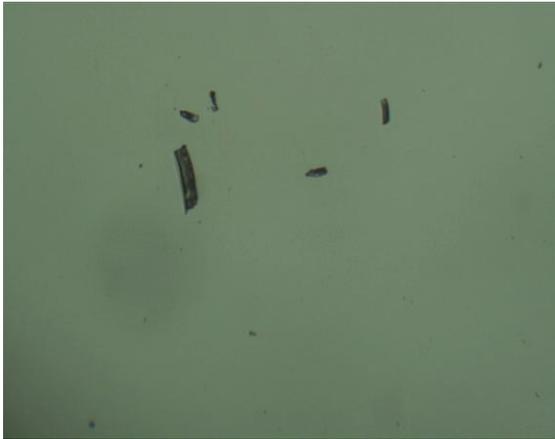
Figure 2.4.4 Thermal degradation of polymers A₁, A₂ and A₃



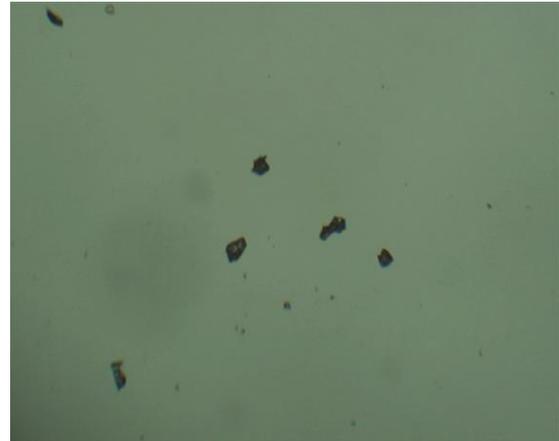
a. (pour point = -6°C)



b. (pour point = -19°C)



c. (pour point = -17°C)



d. (pour point = -15°C)

Figure 2.4.5 Photomicrograph images of a) Pure lube oil b) lube oil + 3% (w/w) of A_1
c) lube oil + 3% (w/w) of A_2 d) lube oil + 3% (w/w) of A_3

Chapter V

**Mannich bases and phosphosulphurized Mannich bases:
synthesis, characterization and performance evaluation as
potential lube oil additives**

2.5.1 Introduction

Base fluids oil generally cannot satisfy the requirements of high performance lubricants without addition of modern additives. Additives are synthetic chemical substances that can improve the different properties of lubricants. The development of modern engine and transmission technologies would have been impossible without modern lubricant additives chemistry and lubricant formulation. Modern engine oil contains a wide range of additives, which are blended with base oil to form a complete package capable of meeting demanding performance¹. The functions of lubrication additives include improvement of the viscosity index,² pour point,³ oxidative or thermal stability,⁴ anti wear performance⁵ of the base oil, to minimize rust and corrosion,⁶ to lessen the deposition of harmful chemicals on lubricated parts and so on.⁷ Dispersant additive contains a polar head group with an oil soluble hydrocarbon tail, keeps metal surfaces clean by preventing deposition of oxidation products of internal combustion engines.⁸⁻¹⁰ The mechanism of dispersancy is generally described on the basis of adsorption of the additive through its polar ends on the sludge materials.^{11, 12} Detergent additives generally neutralize acidic products which are formed during oxidation of lube oil and thereby minimize corrosion, rust and deposit formulation in the engine. Detergents additives also act to prevent the deposition of sludge in the engine. They are an integral part of any engine oil formulation and are typically metal salt of organic acid, containing a surface active polar group which can react with the metal surface to form a protective film that keeps the metal surfaces of an engine clean.¹³ The main functions of detergents in engine oils are acid neutralisation, oxidation inhibition and rust prevention. These functions provide engine cleanliness and extended trouble free operation.¹⁴ The most important mode of lubricant degradation is oxidation. Due to oxidation, there is increase of kinematic viscosity, pour point, sludge of lube oil and enhanced engine corrosion. Additives that reduce the oil oxidation are called antioxidants, which act to retard oxidation of lubricating oil, thus preventing the formation of corrosive products. Antioxidants act in two different ways, by inhibition of peroxides or as radical scavengers', which react with peroxy radicals, thus preventing further propagation of the free radical chain. Peroxide inhibitors react with hydro peroxide molecules preventing the peroxy radical oxidation resulting from high temperature. That may change the chemical structure of the base oil.¹⁵ Generally; all types of base oil should contain some antioxidants depending on the amount of unsaturation

and natural inhibition present. The refined mineral base oils contain natural inhibitors in the form of sulphur and nitrogen compounds for much application.^{16, 17}

In the present work, three Mannich bases were prepared by using P-Cresol, formaldehyde and different amines (ethylenediamine, diethylenetriamine and triethylenetetramine) and finally the Mannich bases were treated with P₂S₅ to synthesize another three phosphosulphurized Mannich bases. The efficiencies of the prepared compounds were investigated as antioxidant, detergent/dispersant, viscosity modifier and pour point depressant additive for lube oil but it was found that the prepared additives cannot improve the viscosity index and pour point depressant property of lube oil. Therefore, our study was directed for the study of antioxidant and detergent/dispersant properties of lube oil.

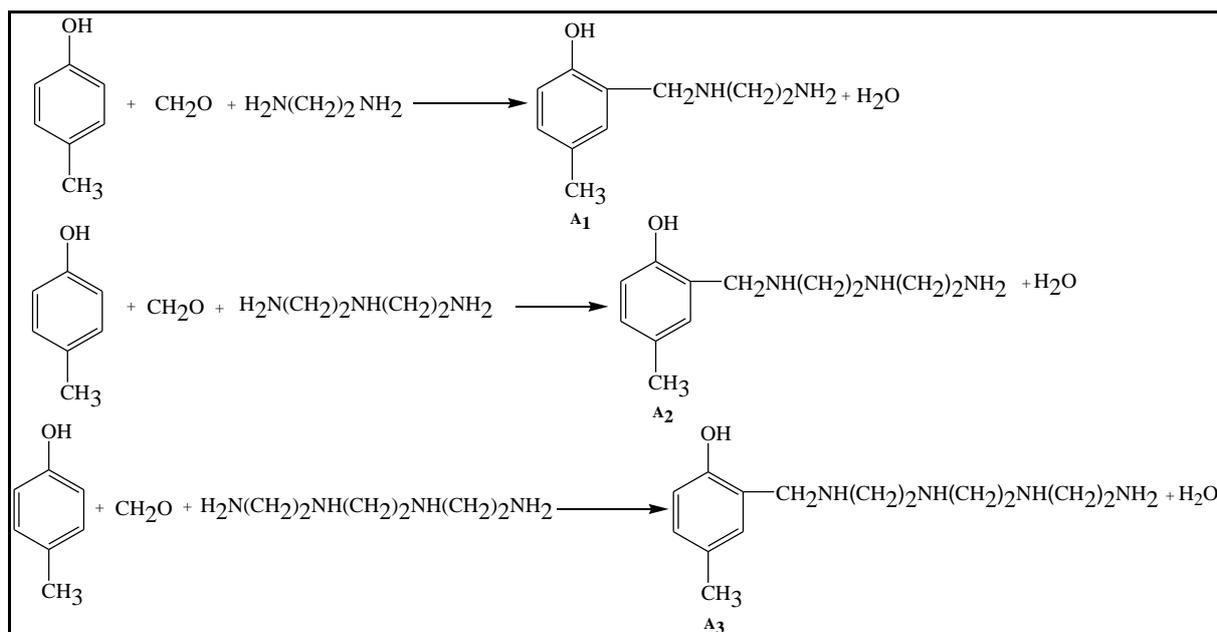
2.5.2 Experimental section

2.5.2.1 Chemicals used

P-Cresol (GC, 98%) was purchased from Thomas Baker (Chemicals) Pvt. Ltd. Formaldehyde (37% w/v) was collected from Sd. Fine Chem. Ltd. and used without any purification. Ethylenediamine (99%, SRL), diethylenetriamine (GC 97%, Sd. Fine Chem. Ltd), triethylenetetramine (GC 98%, LOBA Cheme) and Phosphorous pentasulphide (GC 98%, Sd. Fine Chem. Ltd) were used without any further purification. Benzene (Thomas Baker, 95%) and methanol (Thomas Baker, 98%) were used after purification by distillation method. Base oil was collected from IOCL, India. Properties of base oil are given in table **2.5.1**.

2.5.2.2 Preparation of Mannich bases

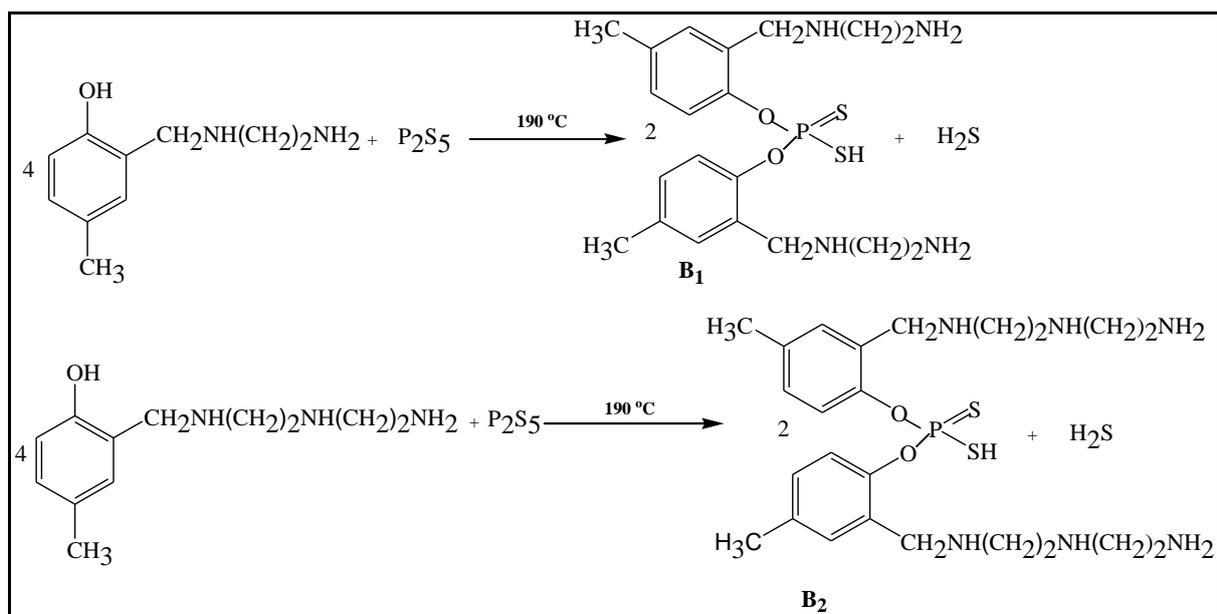
In a 5 necked round bottom flask, fitted with a mechanical stirrer, a ground joint thermometer, a condenser and a dropping funnel, the appropriate amount of p-cresol in methanol and aqueous solution of polyethylene polyamines were added. A formaldehyde (37%) solution was added drop wise during 1 hour at room temperature under nitrogen atmosphere. When the addition of formaldehyde is completed, the temperature of the mixture was raised to reflux temperature for 3 hour. The mixture was then cooled to room temperature. The upper layer was separated from the lower viscous layer (product). The product was dissolved in benzene and washed three times with distilled water to remove the excess of amine and formaldehyde. The molar ratio of p-cresol, formaldehyde and polyethylene polyamines were taken as 1:1:1 ratio. The prepared three Mannich bases with ethylenediamine, diethylenetriamine and triethylenetetramine have been designated by A₁, A₂ and A₃ respectively.

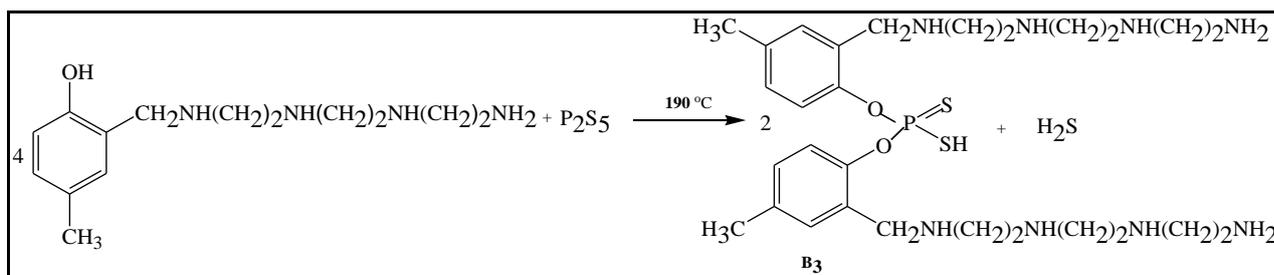


Scheme 1 Preparation of three Mannich bases A₁, A₂ and A₃

2.5.2.3 Preparation of phosphosulphurized Mannich Bases

A four necked round bottom flask, fitted with a mechanical stirrer, thermometer, condenser and inlet for passing nitrogen gas was used for the reaction. The reactions were carried out with four moles of prepared Mannich bases and one mole of P₂S₅ in methanol. The reaction mixture was maintained at 190 °C with continuous stirring for 4 hour. Three products of phosphosulphurized Mannich bases have been prepared using three Mannich bases to give B₁, B₂ and B₃ respectively.





Scheme 2 Preparation of three phosphosulphurized Mannich bases B₁, B₂ and B₃

2.5.3 Measurements

2.5.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl₃ was used as solvent and tetramethylsilane (TMS) as reference material.

2.5.3.2 Determination of the molecular weight

The mean molecular weight of the prepared six additives was determined by using Gel Permeation Chromatography (GPC, Model number-waters 2414). In this method, the samples were dissolved in HPLC grade THF (0.4%, w/v) (used as mobile phase) in the Water GPC system (polystyrene calibration) at 35 °C at a flow rate of 1ml/min.

2.5.4 Performance evaluation of the prepared compounds as lube oil additives

2.5.4.1 As antioxidant

The lube oil sample and its blends containing 3% additive by weight of each of the prepared additives were subjected to severe oxidation condition in presence of copper and iron strips at 165.5 °C for 72 hours using Indiana test method of oxidation.¹⁸ The oxidation stabilities of the lube oil blends is expressed in terms of variation of viscosity ratio and change in total acid number and it was determined by taking samples at intervals of 24 hour and up to 72 hour of oxidation and the samples were tested for:

2.5.4.1.1 Variation of viscosity ratio (V/V₀)

The variation of viscosity ratio was determined using Ostwald Viscometer (size 200, No 3205) using ASTM D-2270 method, where V= Kinematic viscosity at 40°C of sample after oxidation, V₀ = Kinematic viscosity at 40 °C of sample before oxidation.

2.5.4.1.2 Change in total acid number (Δ T.A.N)

The total acid number (TAN) is a measurement of acidity that is determined by the amount of KOH in milligrams that is needed to neutralize the acids in one gram of oxidized oil sample. The change in total acid number was calculated according to ASTM D 664-95 standard test method where Δ T.A.N = total acid number of sample after oxidation – total acid number of sample before oxidation.

2.5.4.2 As dispersant

Spot method was applied to determine dispersancy.¹⁹ A few drops of oxidized product of pure lube oil and lube oil containing 3% additive (w/w) were taken from the Indiana oxidation apparatus where samples are oxidized at 165.5 ° C in presence of Fe and Cu strips and after each 24 h intervals of oxidation and up to 72 h to make spots on filter paper (Durieux 122) and dispersancy of the sample were measured as follows:

$$\% \text{ Dispersancy} = \frac{\text{Diameter of the black spot}}{\text{Diameter of the total spot}} \times 100$$

The efficiency of dispersants has been classified as follows:

Up to 30% no dispersancy, 30-50% medium dispersancy, 50-60% good dispersancy
60-70% very good dispersancy, Above 70% excellent dispersancy.

2.5.5 Results and discussion

2.5.5.1 Determination of molecular weight

The molecular weight of the prepared Mannich bases and Phosphosulphurized Mannich bases were determined by GPC and it is observed that there is no much difference between experimental and theoretical molecular weights. The molecular weight values are depicted in **table 2.5.2**.

2.5.5.2 Spectroscopic data analysis

IR spectrum of prepared Mannich bases: The –NH and –OH group regions are overlapping in the range of 3600-3200 cm^{-1} . Peak for the presence of C-N linkage appeared at 1250 cm^{-1} and 1103 cm^{-1} . Disappearance of –CHO group range of 1720-1740 cm^{-1} and appearance of benzylic –CH₂ in the range of 2850-3000 cm^{-1} indicate that completion of the reaction. In case of ¹H-NMR, the disappearance of –CHO proton peak at δ 9.92 ppm and appearance of benzylic - CH₂ peak at δ 3.8 ppm supports the IR observation. ¹³C NMR also confirms the formation of benzylic –CH₂ proton, (appearance of peak at δ 47 ppm) (**figures 2.5.1, 2.5.2 and 2.5.3**).

The IR peaks at 2360-2372 cm^{-1} (-SH group), 1018-1040 cm^{-1} (P-O bond), 686.6 cm^{-1} , 625 cm^{-1} and at 455-463 cm^{-1} (P=S bond) and in the range 1100 – 1040 cm^{-1} (Ar-O bonds) indicate the formation of phosphosulphurized Mannich bases B₁, B₂ and B₃ (**figures 2.5.4, 2.5.5 and 2.5.6**).

2.5.6 Performance analysis of Mannich bases

The prepared compounds A₁, A₂ and A₃ were added to the lube oil samples and the oxidation stability as well as detergency/ dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

2.5.6.1 As antioxidant

The prepared Mannich bases A₁, A₂ and A₃ were added to the lube oil samples in 3% concentration by weight and the blends were subjected to severe oxidation condition as described in experimental section. The oxidation stability is expressed in terms of increase in kinematic viscosity ratio (v/v_0), and change in total acid number ($\Delta\text{T.A.N}$), compared with lube oil samples free from additives. Results are given in **figures 2.5.7 and 2.5.8**, which indicate the followings:

The additives A₁, A₂ and A₃ exert better oxidation resistance properties to the additive doped lube oil than the additive free oil. It may be due to the presence of phenolic or amino groups in their structures, which act as chain breaking inhibitors (antioxidants) by donation of labile hydrogen from groups (-OH or -NH) to stabilize the chain radicals; i.e., these inhibitors destroy the peroxide radicals and thus, the oxidation chain is broken.^{20, 21} The presence of amine part present in the prepared Mannich bases neutralizes some of the acidic products formed during oxidation. The kinematic viscosity ratio (V/V_0) and total acid number change ($\Delta\text{T.A.N}$) decrease with increasing the number of -NH groups present in the amines used. The performances of the additives follow the order $A_3 > A_2 > A_1$.

2.5.6.2 As dispersant/ detergent

The base oil with 3% (w/w) additives were subjected to severe oxidation conditions using the Indiana test method as described in experimental section, in which the efficiency of the dispersant additive increases the diameter of the black spot. This is due to the enhanced capability of the doped oil to carry the oxidation products to a longer distance from the centre of the spot. It may be due to the fact that the -NH groups form hydrogen bonds with the polar end of alcohol, aldehyde, ketone, acids etc which are formed during oxidation.^{22, 23} The values of dispersants are given in **table 2.5.3**. From the data, it is clear that dispersancy increases with increasing the number of -NH groups present in the prepared additive. The

highest dispersancy was found in case of A₃ due to presence of higher number of –NH groups.

2.5.7 Performance analysis of phosphosulphurized Mannich bases

The prepared compounds B₁, B₂ and B₃ were added to the lube oil samples and the oxidation stability as well as detergency/ dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

2.5.7.1 As antioxidant

Mannich bases were treated with P₂S₅ to produce the additives B₁, B₂ and B₃. The prepared additives were added to the base oil and subjected to severe oxidation conditions using the Indiana test method discussed in experimental section. The oxidation stability is expressed in terms of change in total acid number (Δ T.A.N) and increase in kinematic viscosity ratio (v/v_0) and compared with the additive free lube oil. Results are given in **figures 2.5.9** and **2.5.10** which indicate the followings:

With increasing the number of –NH groups, the oxidation stability increases and therefore B₃ gave better results than others. In comparison to Mannich bases, phosphosulphurized Mannich bases gave somewhat better results. It is due to presence of phosphorous and sulphur. The sulphur and phosphorous compounds combine with metal to form sulphide and phosphide films that prevents the contact between metal surfaces and lube oil, and hence interfere with the catalytic action of metal on lube oil oxidation process.^{24, 25}

2.5.7.2 As dispersant/detergent

The dispersancy values of phosphosulphurized Mannich bases are not very much different from those of dispersancy of Mannich bases. The values are given in **table 2.5.4**. The dispersancy capability mainly depends on the number of –NH groups present on the prepared additives. That is why B₃ has highest dispersancy capacity than B₂ and B₁.

2.5.8 Conclusions

This comparative study indicated that, addition of very small amount of prepared additives to lube oil enhances the efficiency as antioxidant and dispersant. It is also found that phosphosulphurized Mannich bases are more efficient as antioxidant than Mannich bases only. The performance of the additives increases with increasing number of –NH groups present in the additive. The prepared Mannich bases and phosphosulphurized Mannich bases additives have no any action on viscosity index and pour point of lube oil.

2.5.9 References

References are given in the bibliography section of chapter V of part II (Page No 192 - 194).

2.5.10 Tables and figures

Table 2.5.1 Physical properties of base oil

Density (g cm ⁻³) at 40 ° C	0.84
Viscosity at 40 ° C in c St	23.502
Viscosity at 100 ° C in c St	3.98
Viscosity Index	85.12
Pour point (° C)	- 6

Table 2.5.2 Theoretical and determined mean molecular weights of compounds A₁, A₂, A₃, B₁, B₂ and B₃

Prepared compounds	Theoretical	Determined
A ₁	180	189
A ₂	223	228
A ₃	266	276
B ₁	454	462
B ₂	540	546
B ₃	626	635

Table 2.5.3 Dispersancy of the base oil and its blends containing additives (A₁, A₂ and A₃) after different oxidation periods

Sample code	<u>Dispersancy time (in hour)</u>		
	24	48	72
Base oil only	42	40	35
Base oil +additive A ₁	45	53	55.5
Base oil +additive A ₂	63.6	66	68
Base oil +additive A ₃	66.6	71	75.75

Table 2.5.4 Dispersancy of the base oil and its blends containing additives (B₁, B₂ and B₃) after different oxidation periods

Sample code	<u>Dispersancy time (in hour)</u>		
	24	48	72
Base oil only	42	40	35
Base oil +additive B ₁	60	62	66
Base oil +additive B ₂	63	71	74
Base oil +additive B ₃	64	71	77

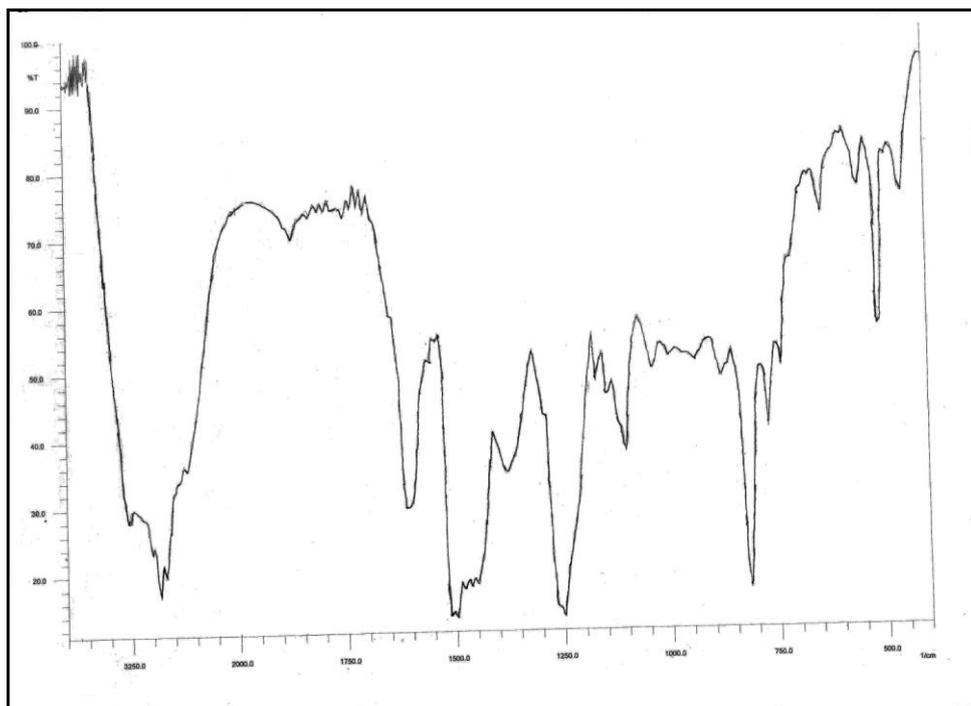


Figure 2.5.1 IR spectra of Mannich base A₃

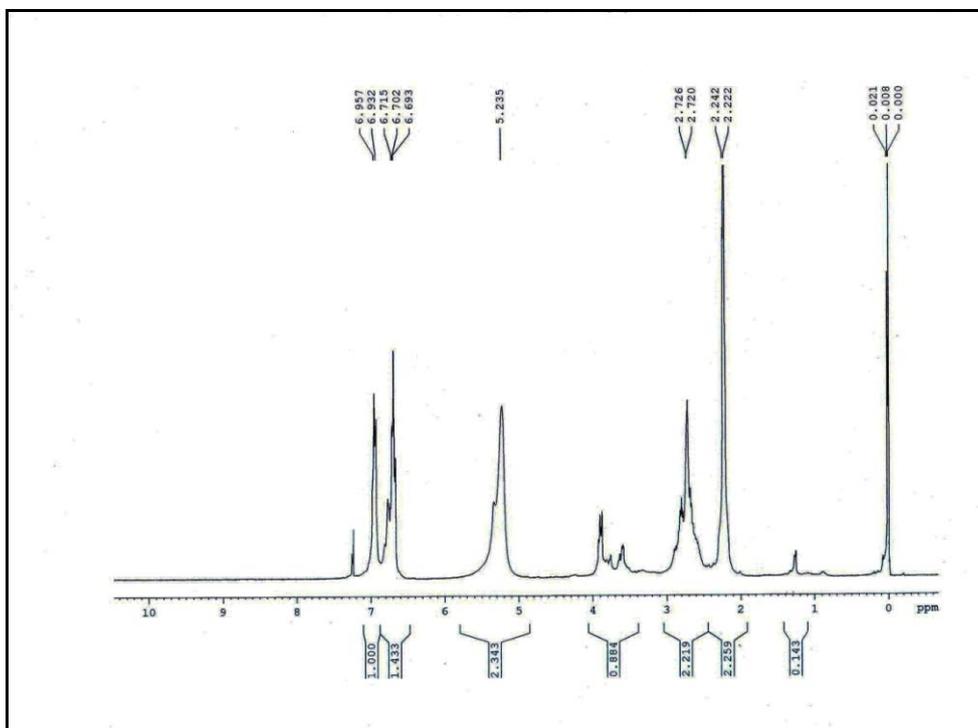


Figure 2.5.2 ¹H NMR spectra of Mannich base A₃

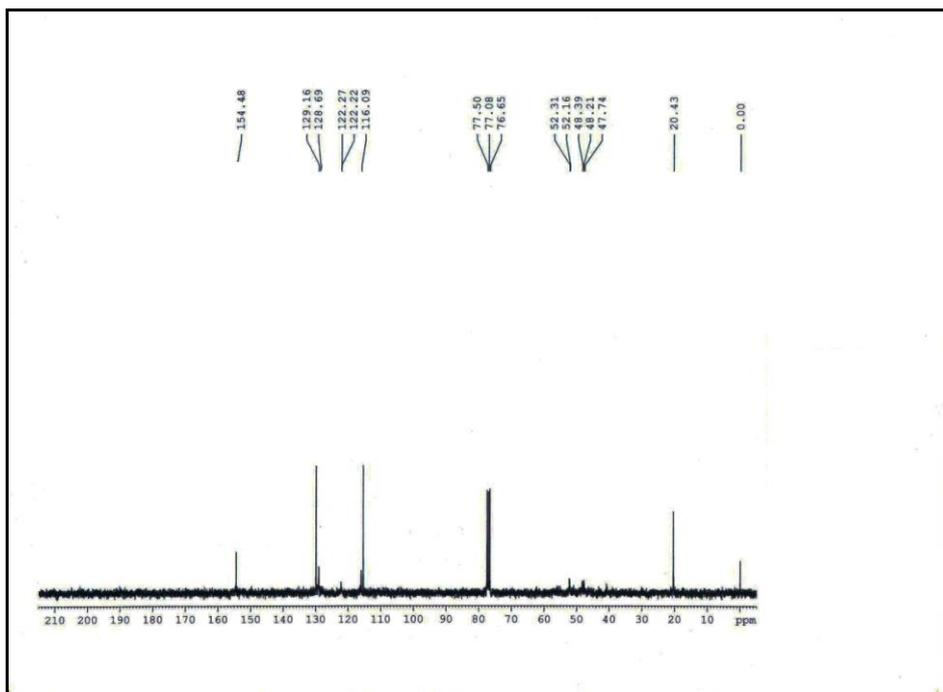


Figure 2.5.3 ^{13}C NMR spectra of Mannich base A_3

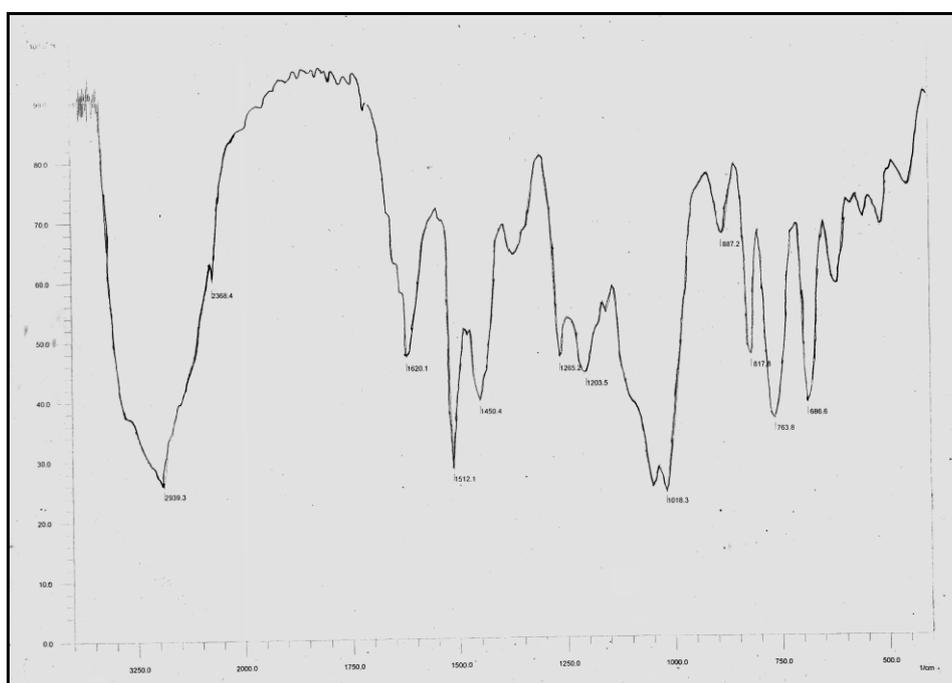


Figure 2.5.4 IR spectra of phosphosulphurized Mannich base B_1

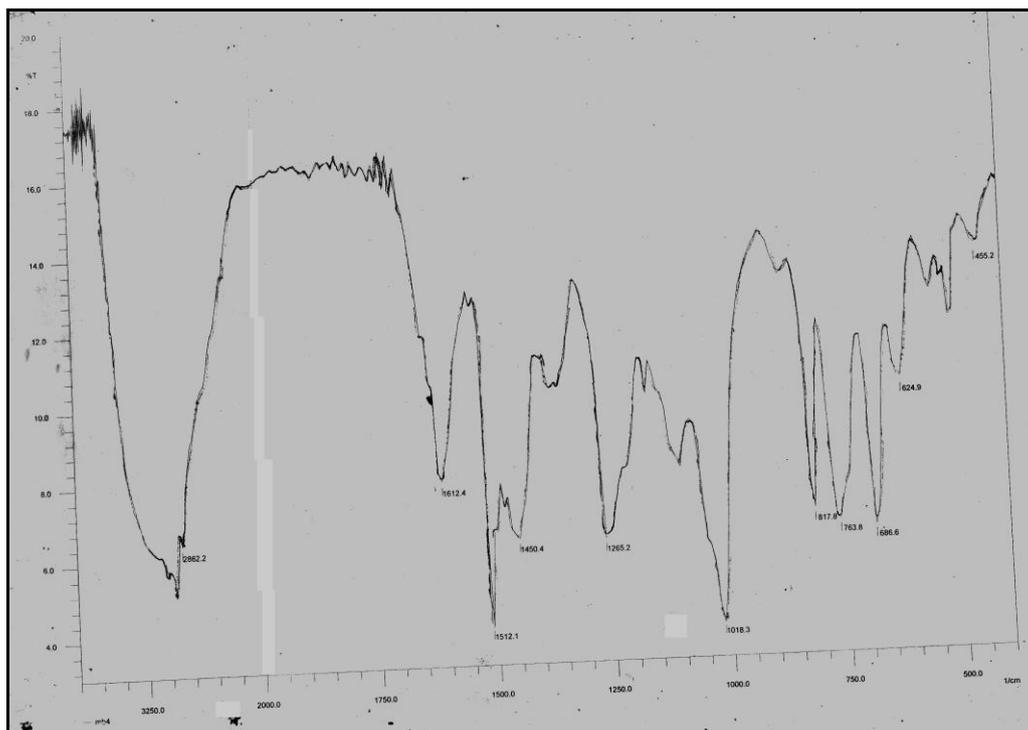


Figure 2.5.5 IR spectra of phosphosulphurized Mannich base B₂

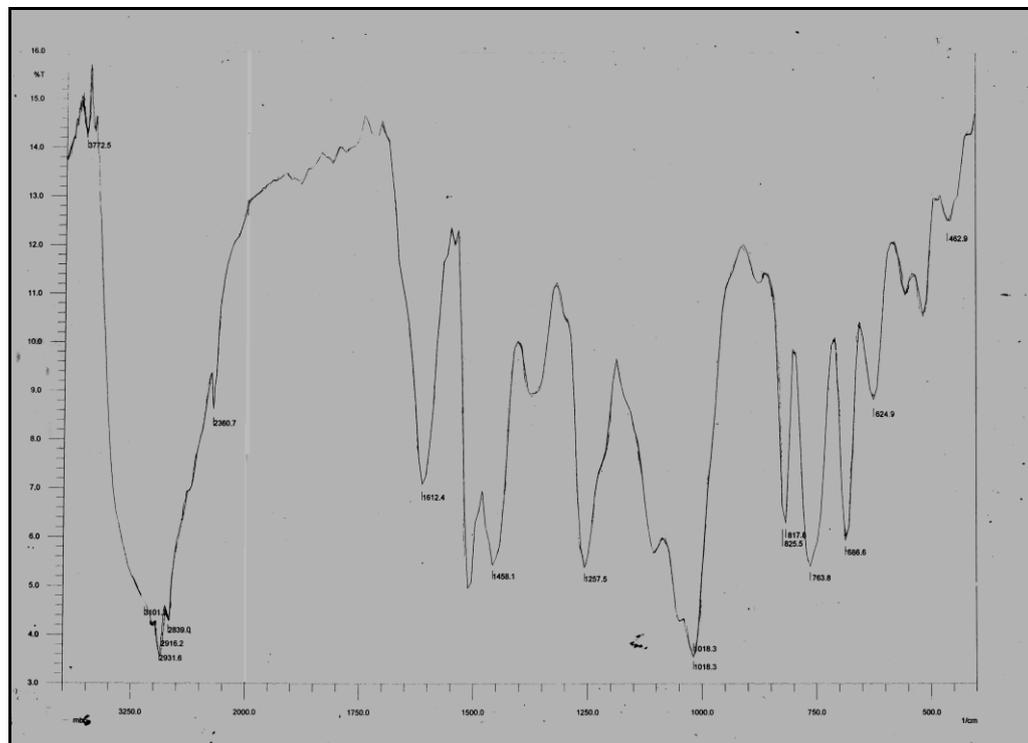


Figure 2.5.6 IR spectra of phosphosulphurized Mannich base B₃

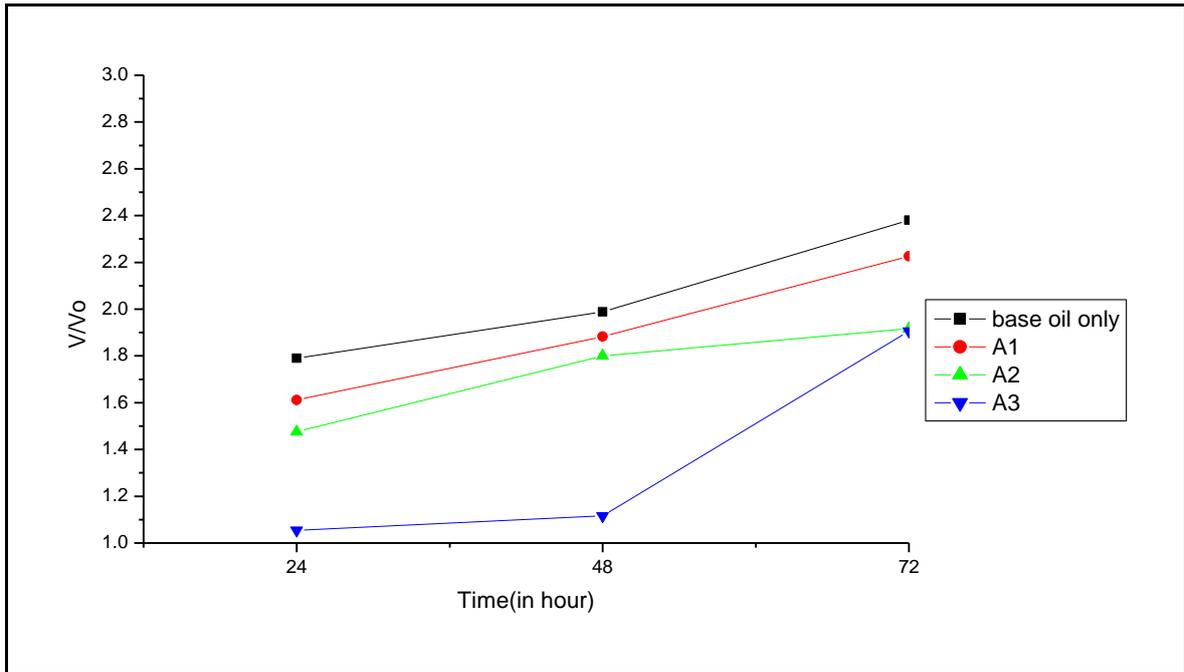


Figure 2.5.7 Variation of V/V_0 with oxidation time of lube oil without and with Mannich bases additives A_1 , A_2 and A_3

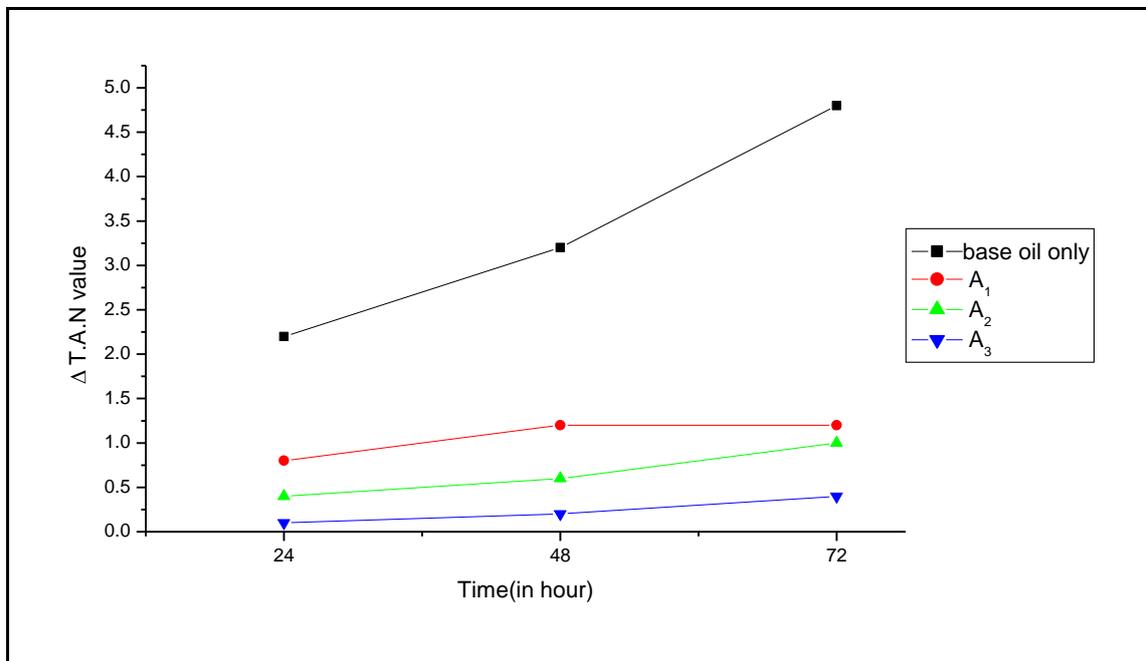


Figure 2.5.8 Variation of $\Delta T.A.N$ with oxidation time of lube oil without and with Mannich bases additives A_1 , A_2 and A_3

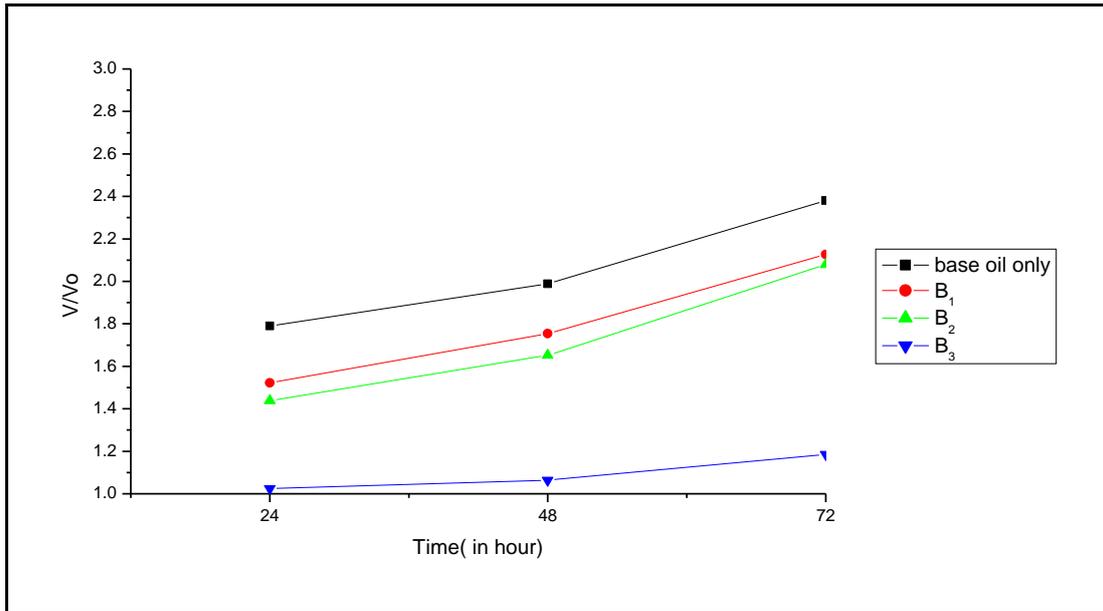


Figure 2.5.9 Variation of V/V_o with oxidation time of lube oil without and with Phosphosulphurized Mannich bases additives B_1 , B_2 and B_3

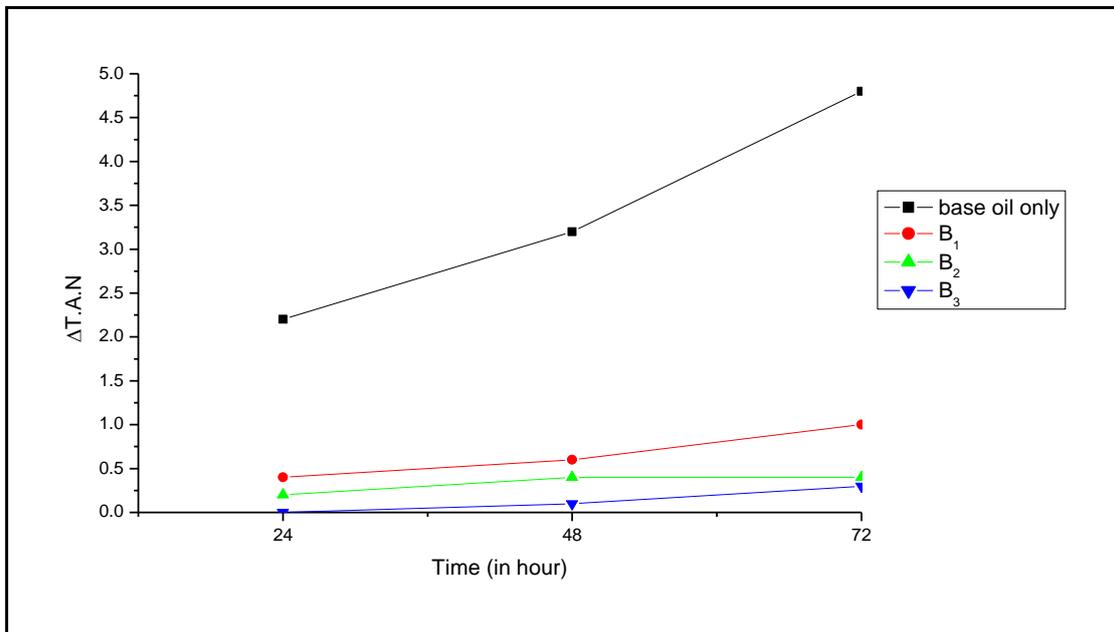


Figure 2.5.10 Variation of $\Delta T.A.N$ with oxidation time of lube oil without and with phosphosulphurized Mannich bases additives B_1 , B_2 and B_3

Part III

Biodegradable multifunctional lube oil additives

Chapter I

Background of the present investigation

It is well known that mineral lubricants are environmentally unacceptable due to their non biodegradability and toxicity.^{1,2} They do contaminate with soil, drinking water, sea water and affect human health, plant life, and aquatic animals to a great extent. Therefore, strict specifications on various environmental issues such as biodegradability, toxicity, health and safety, and emissions are required in certain specific areas.³ Therefore, demands being placed to the lubricating oil company to produce biodegradable and environmentally benign lubricants and the lubricant industries have been trying to formulate biodegradable lubricants with quality superior to those based on petroleum oil.⁴

Generally most of the additives used in lubricating oil are synthetic ester and are harmful to the environment. The additives prepared from vegetable oils, i.e., triglycerides of long chain carboxylic acids (**figure 3.1**) for lube oils are highly accepted from the view point of increasing global environmental pollution.⁵ The most common vegetable oils are soya bean oil, sunflower oil, castor oil, karanja oil, neem oil, rice bran oil, rapeseed oil, mahua oil⁶ etc. All of them contain triglycerides of long chain carboxylic acids. They are biodegradable and nontoxic.

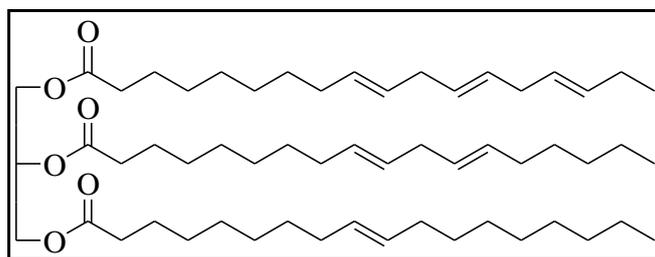


Figure 3.1 General structure of vegetable oil (triglyceride)

Compared to mineral oils vegetable oils have high viscosity index,⁷ excellent tribological properties,⁸ low volatility and high flash point. Therefore, vegetable oil can be used in a series of application such as lubricants or lubricant additives, additives in polymer, coating, resins etc. Vegetable oils don't have satisfactory pour point values but pour point values can be improved by chemical modification.⁹ Polar ester groups of vegetable oil are able to stick fast to metal surfaces and hence exhibit good boundary lubrication properties. In addition, vegetable oils have high solubilising capacity for polar contaminants and additive molecules.¹⁰

Vegetable oil as lubricant or as additive has some drawbacks. Poor oxidation and thermal stability, high temperature-sensitive tribological behaviour, poor cold flow improvers and gumming effect are considered as limitations for their application in industrial lubricants.^{11, 12} But the limitations can be mitigated by means of chemical modification¹³ of the olefin groups or carboxyl group or fatty acid chain which maintain the better performance as well as enhanced thermal and oxidative stability.¹⁴ There are many references from where it is evident that chemically modified vegetable oils have eminent scope for use as base fluids. Vinci et al. have proposed a thermo – oxidative stable lubricant based on methyl 12-hydroxy stearate, a derivative of castor oil with 70% renewable carbon content.¹⁵ Regueira et al. studied the compressibility and viscosities of vegetable oils for their use as hydrolytic fluid and lubricant.¹⁶ Joseph et al. found that a mixture of amine and phenolic antioxidant can be applied to enhance the thermo – oxidative stability of vegetable oils when used as lubricant base oils at temperature around 120° C.¹⁷ Mendoza et al. proposed a formulated sunflower base oil for hydraulic system of agricultural tractors with biodegradability of 89%, an improved pour point of -27° C and enhanced oxidation stability.¹⁸ Suhane et al. found that a mixture of castor oil and mahua oil in a fixed ratios can act as a lubricant for automotive application and found better performances than servo gear oil.¹⁹ There are lots of references where vegetable oils are used as mineral lubricating oil additives or as lubricants.^{20- 22}

U. S. Patent No. 4970010 described the use of vegetable oil derivatives as lubricating oil additives. U. S. Patent No. 5229023 discussed the synthesis and evaluation of vegetable oil based lubricant additive which can be used as thermal oxidative stability enhancers and viscosity modifiers. The synthesis of jojoba oil based lube oil additive was discussed in the U. S Patent No. 4873008. U. S. Patent No. 5282989 disclosed the vegetable oil derivatives as lubricant additives. U. S. Patent No. 5888947 disclosed vegetable oil as lubricants for internal combustion engines.

In 2009, Franco et al. reported the blending of high-oleic sunflower oil (HOSO) with polymeric additives, such as ethylene - vinyl acetate (EVA) and styrene-butadiene-styrene (SBS) copolymers at different concentrations in lubricant formulation and studied the improved kinematic viscosity and viscosity index.²³

In 2015, Nasser et al. reported homo and copolymers of jojoba oil as lubricating oil additives and performance of the additives was evaluated as VII and PPD.²⁴ In 1993, Bisht et al. reported the application of jojoba oil as a compound and as an additive in lubricating oil base stocks. Their results showed that jojoba oil or compound of it can enhance properties such as

viscosity index improvement, antirust, antifoam, antiwear, and friction reduction properties to the blend with lubricating oil.²⁵

In 2011, Ghosh et al. reported the copolymer of sunflower oil with methyl acrylate and decyl acrylate and performance of the copolymers were evaluated as VII for lube oil.²⁶ In 2014, again Ghosh et al. studied the homopolymer of sunflower oil as lubricating oil additive. The research group prepared the polymer by two different methods: microwave and thermal method and performance of the polymer was evaluated as VII, PPD and AW for lube oil.²⁷

In 2013, Karmakar et al. studied the homopolymer of sunflower oil and soya bean oil as lube oil additives. The performance of the additives in lube oil was studied as VII and PPD.²⁸ In 2015, Karmakar et al. again reported the homopolymer of soya bean oil and its copolymers with methyl acrylate, 1-decene and styrene. The performance of these additives in different lube oils was evaluated as PPD, VII and AW.⁵

In 1954, Gast et al. reported additive obtained by ring opening of epoxidized fatty acid esters followed by esterification of hydroxyl groups. The product showed excellent performance for lower temperature lubricant applications.²⁹ In 2000, Wu et al. reported the epoxidized rapeseed oil as a biodegradable lubricant which has higher oxidative stability and better friction reducing as well as extreme pressure abilities.³⁰

Recently, the application of triglycerides obtained from plant oils in polymer chemistry was appraised with a centre of interest on cross – linked system for coating and resin application with a conclusion that triglycerides are expected to play a key role during 21st century to synthesize polymers from renewable sources.^{31, 32} In 2012, at Singapore the International Conferences on Chemical Processes and Environmental Issues (ICCEI'2012) had discussed the synthesis of pour point depressants from sunflower oil. Thus, there is ample scope to work on this field to develop environmental benign lube oil additives with better performances than chemically synthetic lube oil additives. With this view in mind the author has undertaken a systematic study on biodegradable lube oil additives using vegetable oils (sunflower oil and castor oil). The performance of the additives in lubricating oil was mainly evaluated as PPD, VII and antiwear.

References

References are given in bibliography section of Chapter I of Part III (Page No. 194 - 197).

Chapter II

Sunflower oil based terpolymer as sustainable lubricant additive

3.2.1 Introduction

Modern engines must be lubricated to prolong its lifetime. A lubricant performs a number of works in the engine including lubrication, cooling, cleaning and protecting metal surfaces against corrosion. Lubricant comprises base fluid called lubricating oil and a package of additives. The primary function of a lubricating oil is to lubricate and additives carrier.¹

A terpolymer is a copolymer consisting of three different monomers. A terpolymer has a greater interest (in comparison to copolymers having two monomers) due to the presence of different morphology that has been observed so far in the bulk. Moreover, due to the presence of a third block, it may introduce some new set of functions and render some additional parameters to control the copolymer properties.^{2,3}

The commercial synthetic acrylate based additives for lube oil are non-biodegradable and due to the increasing environmental pollution research on environmentally benign polymeric additives in the lubricant chemistry is increasing day by day. There are many works where biodegradable vegetable oils are used for the synthesis of lube oil additives.^{4,5} Due to excellent tribological properties, higher viscosity index, less evaporation, enhanced lubricity which are important properties of lubricant⁶ and mostly polyunsaturated fatty acid composition, sunflower oil was chosen for the present work. Composition of sunflower oil is given in **table 3.2.1**.

Viscosity index (VI) is an arbitrary numbering scale that measures the resistance power of changes of oil viscosity with changes in temperature. A higher viscosity index indicates small changes of viscosity of lube oil with temperature. A low viscosity index indicates higher changes of viscosity with temperature. Therefore, the oil that has high viscosity index can be expected to undergo very small changes in viscosity with rise in temperature. The additive that increases the viscosity index is called viscosity index improver (VII) or viscosity modifier (VM). The viscosity modifier in solution exists as a random coil, which is swollen by lube oil solvent at high temperature and polymer molecules changes from tight coils to an open configuration which has a greater volume. This increase in volume causes increases of viscosity of the oil which offsets the normal reduction in viscosity with increasing temperature.⁷ Antiwear agent is an important additive in lube oil. For the prevention of metal to metal contact in the engine parts, the antiwear additives are to be added with the lubricating oil and acts by forming a layer between the metal surfaces.⁸

Most of the base oil contains some dissolved paraffinic wax. At low temperature, the wax crystallizes to form a rigid structure that trap the oil in small packets in the structure. With sufficient formation of these crystal structures, the oil loses its flow capability. The lowest temperature at which the lube oil just stops its flowing is called pour point .To overcome this problem some high molecular weight polymers are used as pour point depressant (PPD). Pour point depressants, otherwise known as lube oil flow improvers (LOFI), are those additives that improve the low temperature fluidity of the fluid. The pour point depressants act by preventing the formation of a wax crystal structure that would resist the oil flow at low temperatures.⁹

In the present work, the author prepared three terpolymers of octyl acrylate, sunflower oil and styrene at different ratio by weight (1:1:1, 2:1:1 and 3:1:1). The best performance as well as higher molecular weight is observed when the ratio is 2:1:1 (w/w). That is why at this ratio, another two polymers were prepared with different long chain alkyl acrylate (decyl acrylate and dodecyl acrylate). The biodegradable test of the prepared polymers was carried out by disc diffusion method. The author had investigated the efficiency of the prepared polymers as viscosity index improvers, pour point depressant and antiwear additives in two types of base oils. Moreover, powder XRD and photo micrographic image were carried out to study the pour point mechanism of lube oil without and with polymeric additives.

3.2.2 Experimental section

3.2.2.1 Chemicals used

Refined sunflower oil was collected from local market and its fatty acid composition is given **table 3.2.1**. Acrylic acid (99%, Merck Specialities Pvt. Ltd.), styrene (99%, Sigma-Aldrich), 1-octanol (99%, LOBA chemie, India), 1- decanol (99%, Sd. fine chemicals, India) and 1-dodecanol (98%, Sd. fine chemicals, India) were used in esterification without further purification. Toluene (99.5%, Merck Specialities Pvt. Ltd.) and methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. Hydroquinone (99%, Merck Specialities Pvt. Ltd.), and azobisisobutyronitrile (AIBN, 98%, Spectrochem Pvt. Ltd.) were purified by recrystallization before use. Conc. H₂SO₄ (98%, Merck Specialities Pvt. Ltd.) was used as received. Base oils were collected from IOCL and BPCL, India. Physical properties of the base oils are given in **table 3.2.2**.

3.2.2.2 Preparation of the esters and their purification

Three esters were prepared by reacting acrylic acid with different alcohols (1-octanol, 1-decanol and 1-dodecanol) in the molar ratio of 1.1:1 in the presence of conc. H₂SO₄ as a

catalyst, 0.25% (w/w) hydroquinone with respect to the total reactants as polymerization inhibitor, and toluene as solvent by using Dean Stark apparatus. The process of esterification and its purification were carried out by the procedure as reported in the chapter II of part I (1.2.2.2 & 1.2.2.3).

3.2.2.3 Preparation of terpolymers

Three terpolymers consisting of octyl acrylate, sunflower oil and styrene were prepared in the ratio of 1:1:1(w/w), 3:1:1(w/w) and 2:1:1(w/w) separately to get three polymers designated by A, B and C respectively. Another two polymers consisting of different alkyl acrylates (decyl acrylate and dodecyl acrylate), sunflower oil and styrene at the ratio of 2:1:1(w/w) were prepared to get the polymers designated by D and E respectively. The polymerization was carried out in three necked round bottom flask fitted with a magnetic stirrer, thermometer, condenser and an inlet for the introduction of nitrogen. The monomers were mixed in toluene solvent and temperature was kept constant at 90° C and then AIBN (1% w/w, with respect to the total monomer) was added and heated for 8 hours. After the reaction is over, the product was poured into methanol with continuous stirring, filtered off and dried.

3.2.3 Measurements

3.2.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

3.2.3.2 Determination of the molecular weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (polystyrene calibration) equipped with a 2414 detector, waters 515 HPLC pump and 717 plus auto sampler. Sample solutions (0.4% w/v in HPLC grade THF) are prepared by dissolving ~4 mg of polymer per ml THF and filtering (0.45- μm Millipore PTFE) to remove suspended particulates. The pump flow rate is 1.0 mL/min with THF as the carrier solvent, and injection volumes are set to 20 μL . The polydispersity index which indicates the nature of the distribution of the molecular weights in the polymers was also calculated.

3.2.3.3 Thermo gravimetric analysis (TGA) data

TGA data was measured on Shimadzu TGA-50 system in air using an alumina crucible at a heating rate of 10° C/ min.

3.2.3.4 Biodegradability test (Disc diffusion method)

The biodegradability test was carried out against *Fussarium equisetae*, *Alternaria alternata* and *Colletrichum gleosporoides* fungals. All the experiments were performed in petridishes and were kept incubator at 37° C for 30 days after addition of approximately 2g of the polymer samples. The fungal growth was confirmed by a change of yellow to blackish colour. Culture media strains were prepared by mixing suitable amount of potato extract, dextrose and agar powder. After 30 days, the polymer samples were recovered from the fungal media by dissolving in chloroform, purified and dried. The dried samples were weighed.¹⁰

3.2.3.5 Performance evaluation as viscosity index improver (VII)

In general the VII property is expressed in terms of an experimental parameter called viscosity index (VI). Greater the values of VI better is the additive performance as VII. Viscosity index was calculated by dissolving prepared polymer in two types of base oils (BO1 and BO2) through the viscosity index test according to ASTM D 2270-10. The kinematic viscosity of the polymer doped base oil was determined at 40° C and 100° C. Different concentrations of additives [ranging from 1% - 5% (w/w)] were used to study the effect of additive concentration on VI.

3.2.3.6 Performance evaluation as pour point depressant (PPD)

Pour point depressants were determined in polymer doped different base oils (BO1 and BO2) through the pour point test according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging from 1% - 5% (w/w).

3.2.3.7 Evaluation of tribological performance

The antiwear performance in terms of wear scar diameter (WSD) of the lubricant compositions was evaluated by four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method. In this experiment 392 N (40 Kg) load at 75 ° C for 60 min was applied to measure the wear scar diameter (WSD). The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm respectively.

3.2.3.8 Photographic and powder XRD study

The photomicrograph showing wax behaviour of lube oil (BO2) without and with polymers at 2% (w/w) concentration has been recorded at 0° C temperature. A Banbros polarizing microscope model BPL-400B was used for photographic analysis. The adopted magnification was 200X. For powder XRD (Rigaku, smart lab, 9Kw) analysis, the lube oil without polymer

and with 2% (w/w) polymer were mixed with suitable amount of alumina and PXRD was carried out.

3.2.3.9 Rheological study

Rheological study was carried out with lube oil (BO2) without and with 5% (w/w) copolymer using Brookfield Rheometer (Model DV-III ultra). Dynamic viscosity (cp) and shear rate (sec^{-1}) were measured at two temperatures (40°C and 100°C).

3.2.4 Results and discussion

3.2.4.1 Spectroscopic data analysis

The spectroscopic data of all the prepared five polymers are similar. The IR absorption band at 1744 cm^{-1} was for the ester carbonyl group. The peaks at 2857 cm^{-1} and 2931.5 cm^{-1} were the characteristic of $\text{CH}_3\text{-CH}_2\text{-}$ group. The peaks at 1458.6 cm^{-1} , 1270 cm^{-1} and 1175 cm^{-1} were due to CO stretching vibration and absorption bands at 1051.3 cm^{-1} and 982.5 cm^{-1} were due to bending of C-H bond. Peaks at 810 cm^{-1} , 756 cm^{-1} , 723.6 cm^{-1} and 695 cm^{-1} were attributed to the C-H bending of the phenyl group of styrene. A peak at 3000 cm^{-1} was due to C-H stretching of aromatic ring (**figure 3.2.1**). In the ^1H NMR, the methyl protons appear in the range of 0.87 - 0.89 ppm, the methylene protons appear in the range of 1.28 - 1.62 ppm for all alkyl groups. The peaks in the range of 2.03 - 2.29 ppm appear for the protons of -COCH- group of alkyl acrylate. A peak at 4.08 ppm indicates the protons of $-\text{OCH}_2$ of alkyl acrylate. The peaks in the range of 4.10 - 4.14 ppm indicate the protons of $-\text{COOCH}_2$ group of sunflower oil. A broad peak in the range of 6.80 - 7.64 ppm indicates the protons of aromatic ring (**figure 3.2.2**). In the ^{13}C NMR, the peaks in the range of 14.14 - 41.03 ppm appear due to carbons of all CH_3 and CH_2 groups. The peaks at 58.13 ppm indicate the carbons of $-\text{CH}-$ of $-\text{COCH}-$ group of alkyl acrylate. The peaks in the range of 60 - 62.08 ppm represent the carbons of $-\text{OCH}_2$ groups of alkyl acrylate. The CH_2 carbons of $-\text{OCOCH}_2\text{-}$ group of sunflower oil showed peaks in the range of 64.61– 68.99 ppm. The aromatic carbons appear in the range of 127.93 -130.88 ppm. The peaks in the range of 165.65 -173.00 ppm confirms the carbons of ester groups (**figure 3.2.3**).

3.2.4.2 Molecular weight data analysis

The experimental values of number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of polymer A, B, C, D and E are given in **table 3.2.3**. The higher molecular weight is observed when the ratio of acrylate, sunflower oil and styrene is 2:1:1(w/w). Moreover at this ratio, molecular weight increases with increasing the alkyl chain length of alkyl acrylate.

3.2.4.3 TGA data analysis

The TGA values of the five polymers are given in **figure 3.2.5**. From the figure, it is clear that the thermal degradation of polymer E is less than the other polymers which signifies that E is thermally more stable. The polymers A, B, C and D are almost equally stable. In case of polymer E, initial decomposition starts at 250 ° C with a 12% weight loss and another major decomposition is observed at 420° C with a 63% weight loss. For other polymers, initial decomposition is observed approximately at 210° C with a 10% weight loss and another major decomposition is found at 400 ° C with a 60% weight loss.

3.2.4.4 Analysis of biodegradability test results

The biodegradability test were carried out against three different fungals like *Fussarium equisetae*, *Alterneria alternata* and *Colletrichum gleosproides* but it is found that only *Alterneria alternata* is effective against the prepared terpolymers. The loss of mass after biodegradation of the prepared terpolymers is given in **table 3.2.4**; it was further confirmed by the shifting of IR frequency of the ester carbonyl group from 1744 cm⁻¹ to 1730 cm⁻¹ along with other shifted peaks (**figure 3.2.4**). Moreover, molecular weight of the recovered samples after biodegradation was determined by GPC method and the results were compared with the respective samples before biodegradation and given in **table 3.2.5**. Among the five polymers, polymer E is highly biodegradable whereas polymer B is the least.

3.2.4.5 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers in two types of base oils (BO1 and BO2) in the concentration range 1% - 5% (w/w). The experimental values of VI are given in **figure 3.2.6 & 3.2.7**. From the experimental data, it is found that VI values increase with increase in concentration of polymer in lube oil. The viscosity of lube oil decreases with the increase in temperature, but simultaneous expansion of polymer chains take place at high temperature leading to an increase in their hydrodynamic volume. This fact is actually responsible for the reduction of the viscosity of the polymer doped lube oil. Therefore, a higher treat level of the polymer may lead to exert higher thickening effect and consequently a much better VI property.¹¹ Among the five polymers, polymer E has highest effect on VI for both the base oils. It may be due to highest molecular weight of polymer E. Among the polymers C, D and E, it is found that there is a gradual increase in the VI property with an increase in their alkyl chain length. Among the copolymers (A, B and C), prepared by using different weight ratios of the respective monomers, copolymer C showed highest VI property.

Further analysis indicates that when the ratio of alkyl acrylate, sunflower and styrene is 2:1:1(w/w), much better VI improver property is predicted.

3.2.4.6 Analysis of pour point data

The polymer doped base oils (BO1 and BO2) at different concentration ranging from 1% - 5% (w/w) were tested for pour point and experimental values are given in **figures 3.2.8** and **3.2.9**. From the values, it is observed that efficiency as pour point depressant decreases with increasing the concentration of polymer in base oil. It may be due to the decrease in solvation power.¹² Consideration of the alkyl chain lengths of the polymer (C, D and E), it is observed that the polymer having shorter alkyl chain length (polymer C) has greater efficiency as pour point depressant. This may be because of the more effective interaction between the short alkyl chain length and paraffinic structure present in the lube oil than the long alkyl, causing the inhibition of wax crystal network formation; similar observation is already reported elsewhere.¹³ Among the three polymers A, B and C, prepared by using different monomer to monomer ratio (w/w), it is found that when the ratio of alkyl acrylate, sunflower and styrene is 2:1:1(w/w), the depression of pour point is maximum.

3.2.4.7 Analysis of tribological properties

The tribological properties of the lubricant compositions were determined by measuring WSD values through FBWT apparatus applying 392 N load and shown in **table 3.2.6**. The anti wear performance of the base oil is significantly improved when the additives are blended with it and is reflected in lower WSD values of the lubricant compositions. The WSD values gradually decreases from A to E. This means that the lube oil blended with the terpolymer E (formed by DDA, SFO and styrene in 2:1:1 ratio) showed lowest value in WSD ($18.33 \pm 1.5\%$, $16.18 \pm 1.5\%$ in BO1 and BO2 oil respectively) followed by D (formed by DA, SFO and styrene in 2:1:1 ratio), $16.9 \pm 1.5\%$ and $14.03 \pm 1.5\%$ in BO1 and BO2 oil respectively. Lubricants form a film on the rubbing zone of engine through chemical and physical bonding by the base oil and functional groups of the additive molecules with the metal atoms on the surface. Stronger the film lower will be the friction. The terpolymers, due to higher number of polar side chains, form stronger films. So, they show excellent antiwear properties. Best antiwear performance (lower WSD) for E and D are due to the longer hydrocarbon chains of DDA and DA counterpart of the respective terpolymer molecules that provide an excellent molecular barrier along with the polar functional groups which coordinate with iron to form stronger protective films on the metal surface.^{14, 15}

3.2.4.8 Powder XRD and photo micrographic images analysis

Powder XRD and photo micrographic analysis were used to study the action mechanism of the pour point depressant (PPD) with the lube oil. The influence of the PPD on the thermodynamics of wax crystallization may be due to the change of wax lattice structure to a different form caused by the long chain polymeric structure of the PPD.¹⁶ It was confirmed by means of X-ray diffraction experiments. The wax present in lube oil is orthorhombic phase.¹⁷ After adding PPD to the lube oil the diffraction line intensities of the orthorhombic phase decrease without any significant variation of Bragg angle values. This may be due to the transformation of wax crystal lattice from orthorhombic (an ordered phase) to hexagonal phase (a disordered phase) in presence of PPD.^{18, 19} It is evident from the **figure 3.2.10** that lube oil without any PPD showed highest intensity. The intensity of lube oil with 2% (w/w) PPD decreases and lowest intensities are found in case of polymer C and D. This is in agreement with the observed pour point values determined by ASTM D 97-09 method.

The photo micro graphs images of lube oil (BO2) without and with different additives are shown in **figure 3.2.11(a-f)**. The figure 3.2.11a, the photograph of the fresh lube oil (pour point = - 6°C) showed large number of cyclic crystalline and some needle shaped wax crystals. When it is treated with the additive (2%, w/w solution), either polymer A (pour point = -10°C) or polymer E (pour point = -12°C), there occurs a small change in the size of wax crystal (figure 3.2.11b and 3.2.11f). But when the same lube oil is treated with (same treatment level) polymer C (pour point = -16°C) or polymer D (pour point= -15°C), a significant reduction of the wax crystal size takes place which appears as a very small dispersed crystals of waxes²⁰ (figure 3.2.11d and 3.2.11e) and is responsible for reducing the pour point to greater extent. Therefore, a correlation between the depression of pour point and degree of wax structure modification has been verified.

3.2.4.9 Analysis of rheological study

Rheological study was carried out at 40° C and 100° C with lube oil (BO2) without and with 5% (w/w) polymer. For fresh lube oil, there is no significant change in viscosity with the increase in shear rate. This indicates that pure lube oil behaves like a Newtonian fluid.²¹ For polymer blended lube oil, it is observed that there is a gradual drop in the viscosity up to a shear rate of 32 S⁻¹, and hence the sample behaves like a non- Newtonian fluid.²² But at high shear rate viscosity of the lubricants approximately remains constant and behaves like Newtonian fluids.²³ At low temperature, viscosity modifiers in lube oil exist as spherical coil form having random orientation and exert high viscosity in absence of shear.²⁴ When shear is applied, the polymeric VM starts rearranging itself in the direction of flow and thereby

decrease the viscosity.²⁵ At high shear rate all the polymers are arranged in the direction of flow and there is a negligible change in viscosity. Viscosity modifiers at high temperature (100° C) exist in the expanded form and hence are easily arranged in the direction of flow under shear and viscosity approximately remains constant under any shear rate for all lubricants. This indicates that the prepared copolymers can compensate the drop of lube oil viscosity. The decrease of viscosity may be due to the applied shear and also due to the rise of temperature from 40° C to 100° C (**figures 3.2.12** and **3.2.13**).

3.2.5 Conclusions

From the above study, it is found that all the prepared terpolymers based on different alkyl acrylates, sunflower oil and styrene are effective as VM, PPD and antiwear additives. The terpolymer prepared by taking monomers in 2:1:1 (w/w) ratio was found to be the most efficient compared to the others. Therefore, it can be said that monomer to monomer ratio by weight has a significant role for the preparation of effective terpolymers. The tribological and VI performance of the prepared terpolymers increases with increasing the alkyl chain length whereas PPD performance decreases. Due to biodegradability the additives are eco-friendly also. Therefore, the above study is definitely a potential approach to formulate multifunctional, better performing and sustainable lubricant composition.

3.2.6 References

References are given in bibliography section of chapter II of Part III (Page No. 197 - 199).

3.2.7 Tables and figures

Table 3.2.1 Composition of sunflower oil

<u>Fatty acid</u>	<u>% Composition</u>
(Carbon atoms: Double bonds)	
C 14:0 (Myristic acid)	0.56
C 16:0 (Palmitic acid)	6.8
C 18:0 (Stearic acid)	4.2
C 20:0 (arachidic acid)	0.41
C 18:1 (Oleic acid)	23.3
C 18:2 (Linoleic acid)	60.8
C 18:3 (Linolenic acid)	2.9

Table 3.2.2 Physical properties of the base oils

Base oil properties	Base oil	
	BO1	BO2
Density (g cm ⁻³) at 40 ° C	0.83	0.84
Viscosity at 40 °C in c St	7.102	23.502
Viscosity at 100 °C in c St	1.850	3.98
Viscosity index	84.56	85.15
Pour point (° C)	-3	-6
Cloud point (° C)	-1	-4

Table 3.2.3 Polymers designation, monomers, monomers ratio, molecular weight values of the polymers A, B, C, D and E

Polymer code no.	Monomers	Monomer ratio(w/w)	Molecular weight		
			M _n	M _w	PDI
A	OA, sunflower oil, styrene	1:1:1	10418	14461	1.39
B	OA, sunflower oil, styrene	3:1:1	12240	15275	1.25
C	OA, sunflower oil, styrene	2:1:1	13611	17003	1.25
D	DA, sunflower oil, styrene	2:1:1	13623	20522	1.51
E	DDA, sunflower oil, styrene	2:1:1	21643	30042	1.39

OA= octyl acrylate; DA= decyl acrylate; DDA= dodecyl acrylate;

M_n = number average molecular weight; M_w = Weight average molecular weight; PDI = polydispersity index

Table 3.2.4 Results of biodegradability test

Fungal pathogens	Polymer samples	Incubation periods(days)	Initial weight (gm)	Final weight (gm)	Weight loss (%)
<i>Alternaria alternata</i>	A	30	2.01	1.48	26.4
	B	30	2.03	1.66	18.2
	C	30	2.05	1.57	23.4
	D	30	2.00	1.52	24
	E	30	2.011	1.41	29.8

Table 3.2.5 Comparative molecular weight (determined by GPC method)

Polymer code	<u>Before biodegradation</u>		<u>After biodegradation</u>	
	M _n	M _w	M _n	M _w
A	10418	14461	9175	12588
B	12240	15725	12082	14880
C	13611	17003	13012	15835
D	13623	20522	12908	18416
E	21643	30042	20073	26872

Table 3.2.6 Antiwear property in terms of wear scar diameter (WSD in mm) values of different lubricant compositions

Polymer code	Base fluids	WSD of lubricant in mm at different additive concentrations (ppm x 10 ⁴)					
		0	1	2	3	4	5
A	BO1	0.982	0.965	0.955	0.93	0.891	0.846
	BO2	1.119	1.079	1.062	1.048	1.016	0.992
B	BO1	0.982	0.964	0.952	0.928	0.89	0.842
	BO2	1.119	1.078	1.061	1.046	1.012	0.984
C	BO1	0.982	0.951	0.944	0.919	0.875	0.833
	BO2	1.119	1.072	1.053	1.038	1.006	0.974
D	BO1	0.982	0.938	0.927	0.906	0.861	0.816
	BO2	1.119	1.061	1.048	1.03	0.991	0.962
E	BO1	0.982	0.919	0.908	0.885	0.844	0.802
	BO2	1.119	1.046	1.031	0.985	0.958	0.938

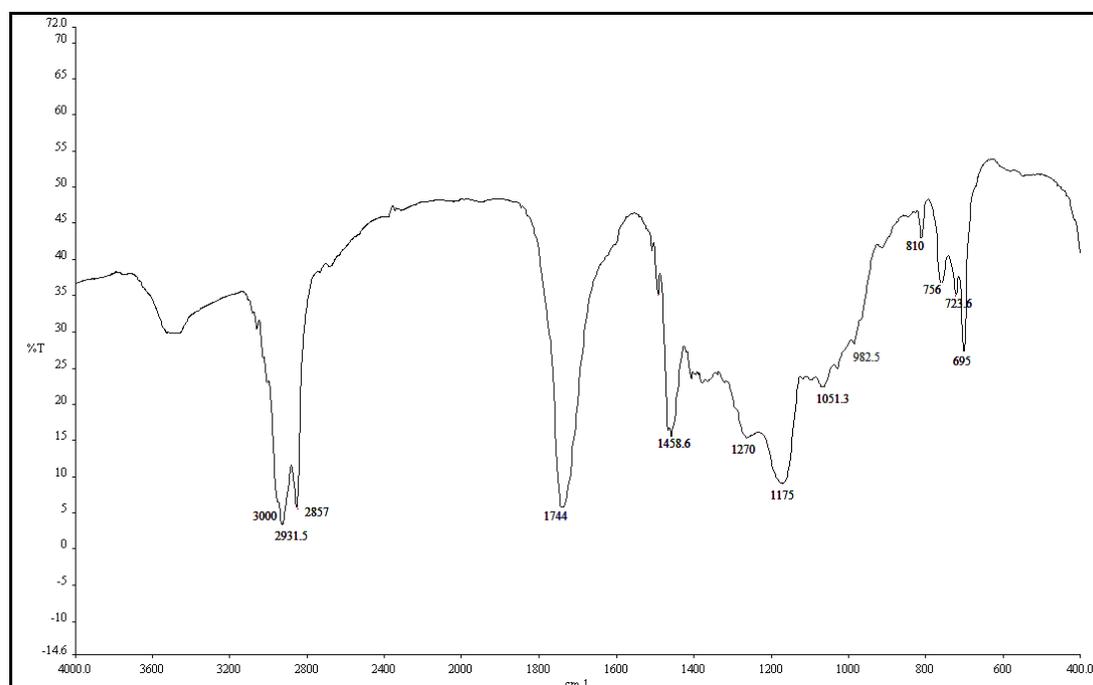


Figure 3.2.1 IR spectra of terpolymer E

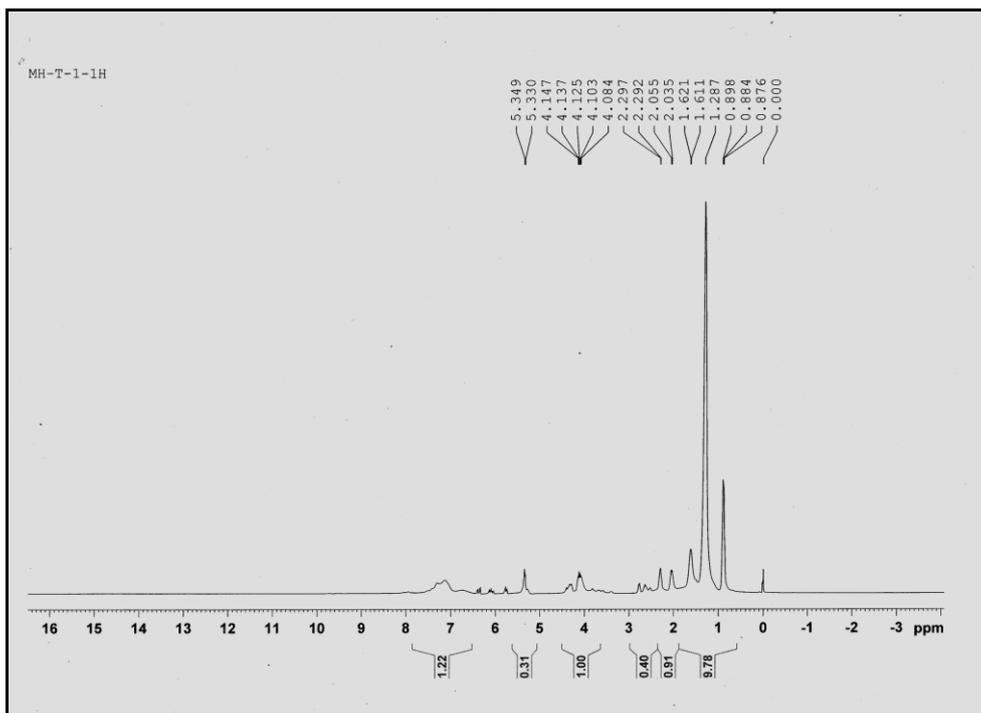


Figure 3.2.2 ^1H NMR spectra of terpolymer E

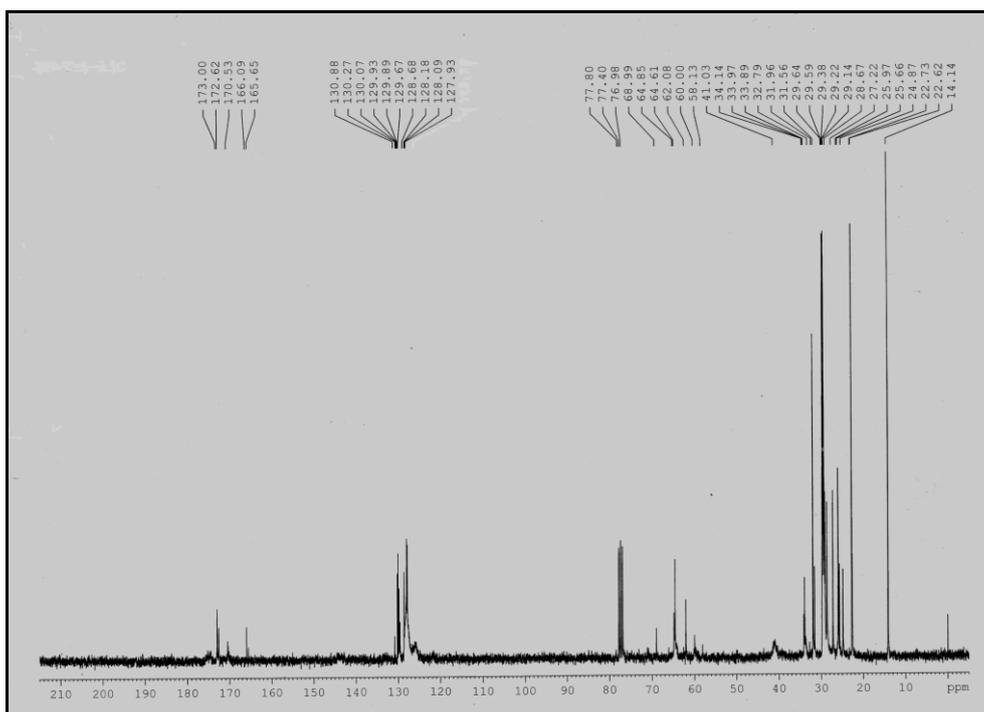


Figure 3.2.3 ^{13}C NMR spectra of terpolymer E

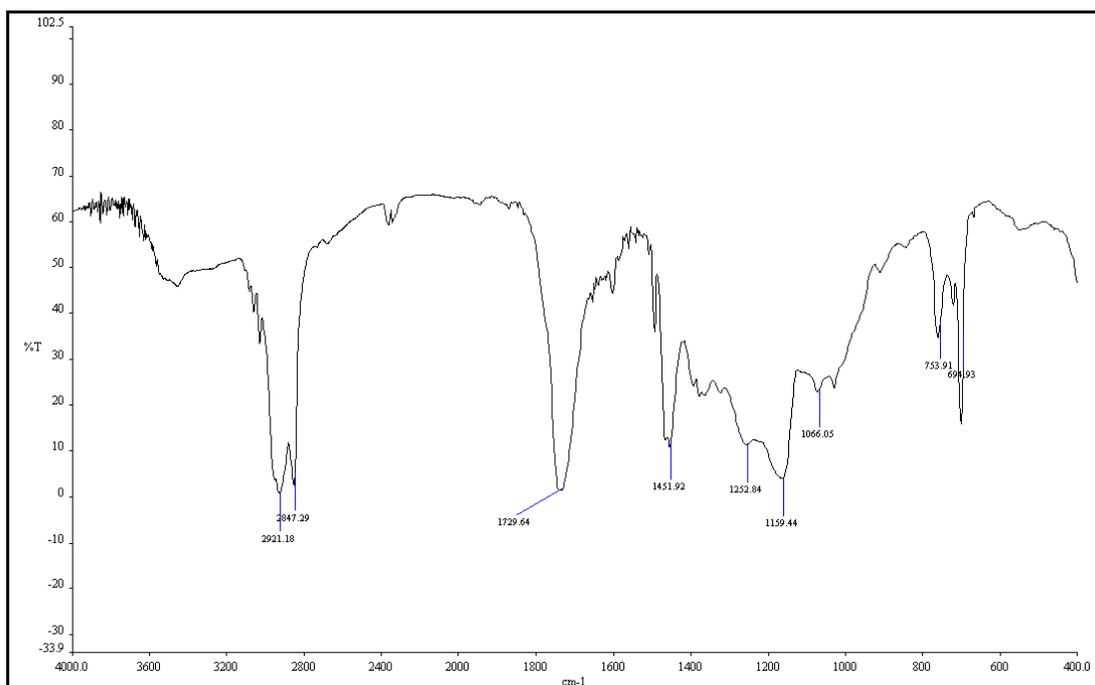


Figure 3.2.4 IR spectra of terpolymer E after biodegradable

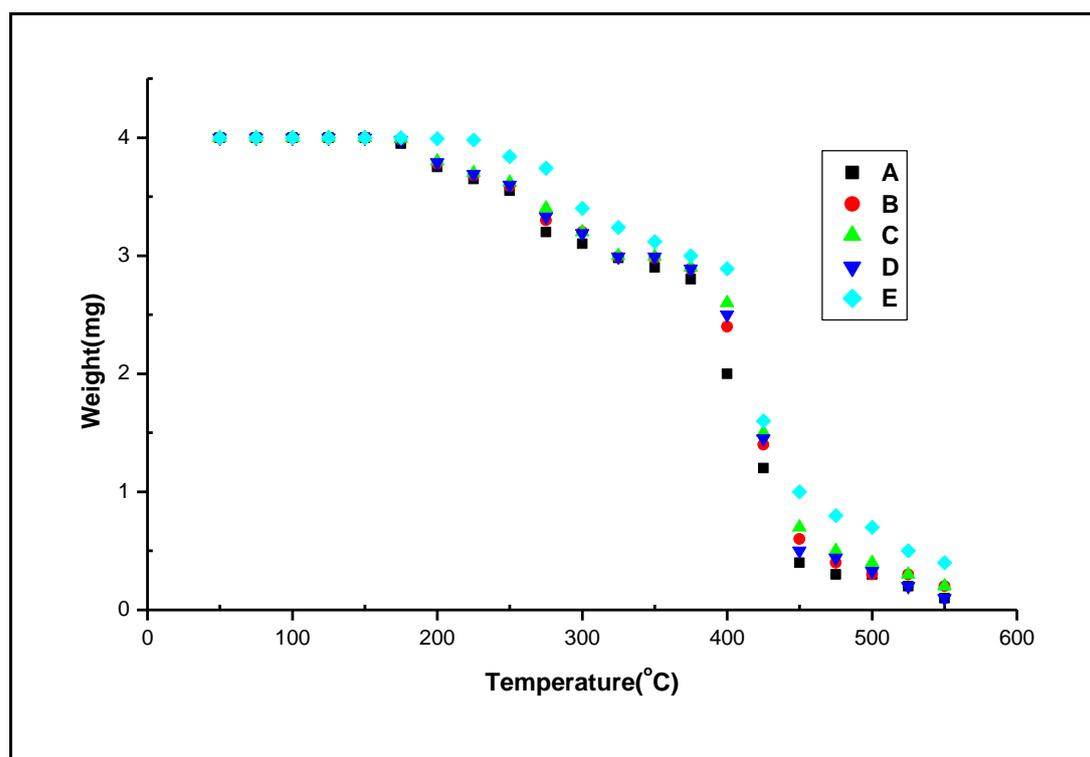


Figure 3.2.5 Thermal degradation of the polymers A, B, C, D and E

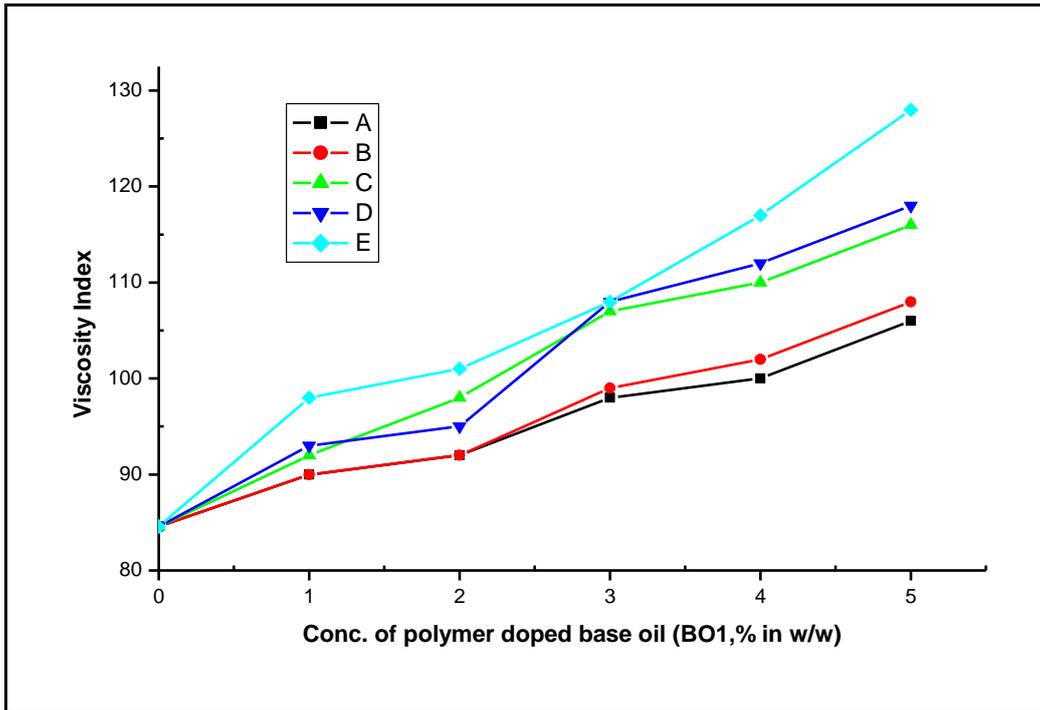


Figure 3.2.6 Variation of viscosity index of polymer doped base oil (BO1) at different concentrations

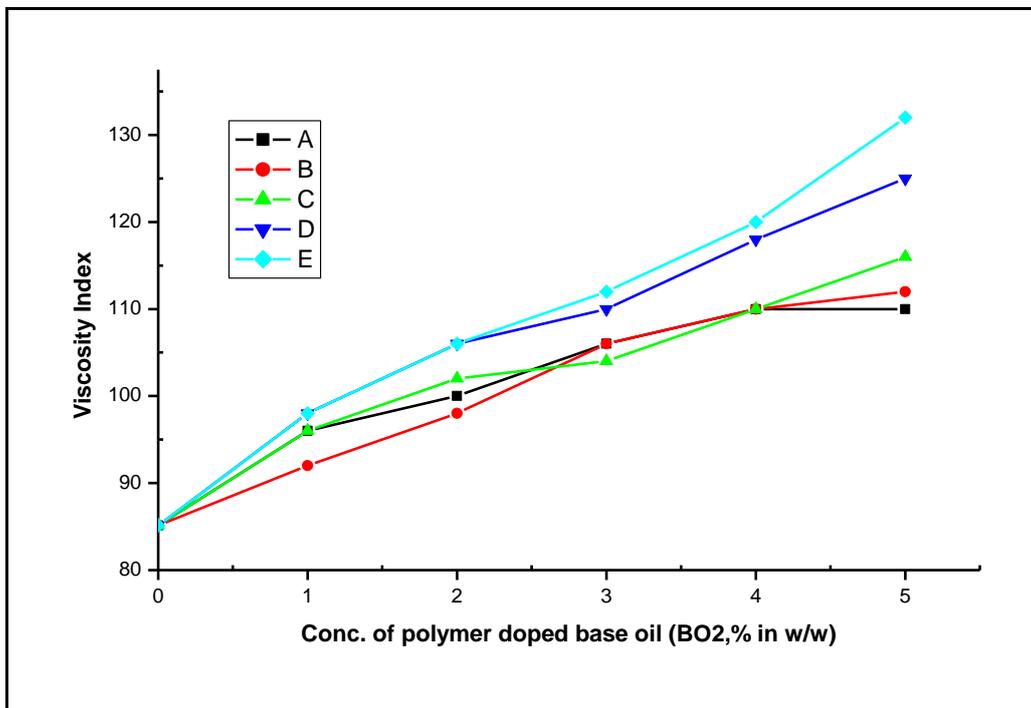


Figure 3.2.7 Variation of viscosity index of polymer doped base oil (BO2) at different concentrations

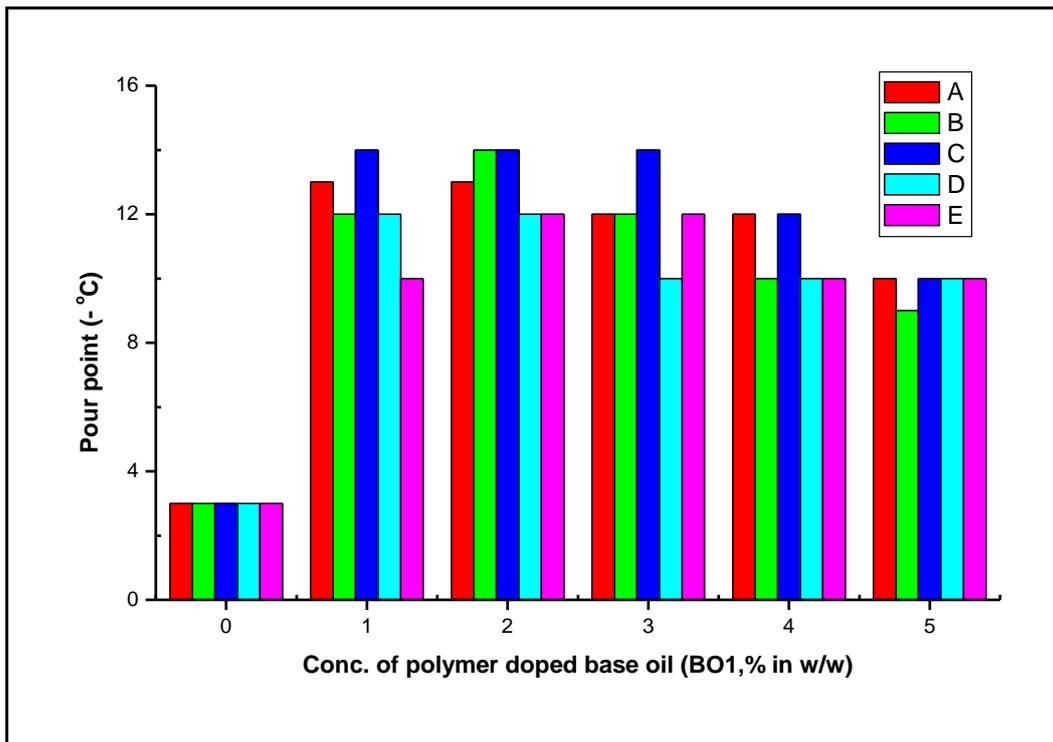


Figure 3.2.8 Variation of pour point of polymer doped base oil (BO1) at different concentrations

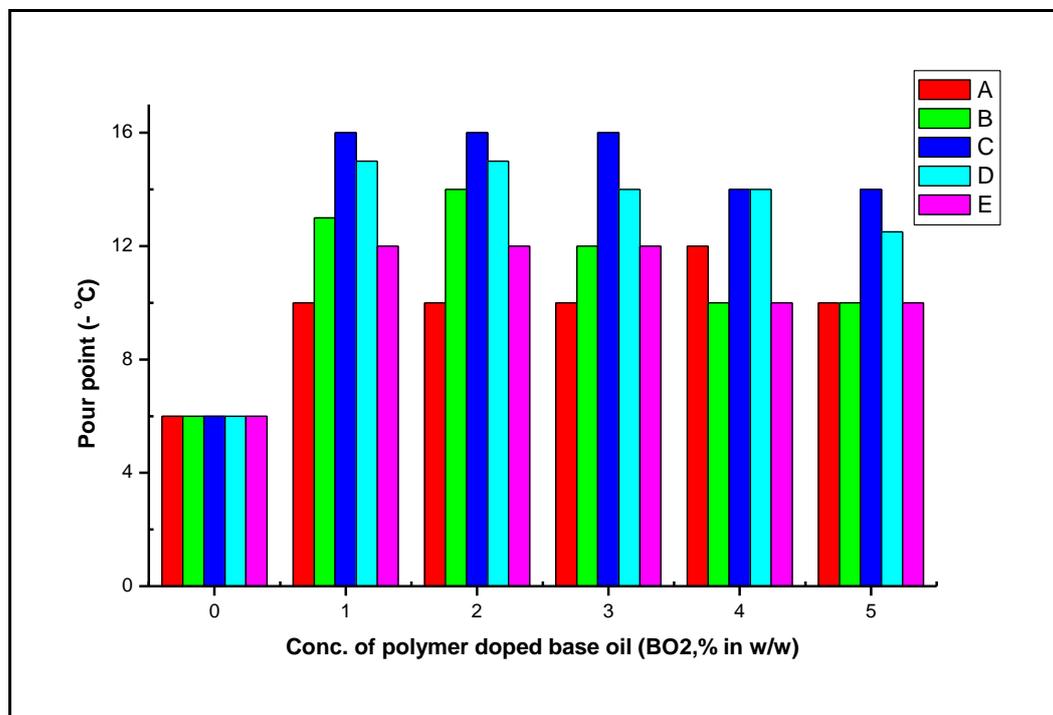


Figure 3.2.9 Variation of pour point of polymer doped base oil (BO2) at different concentrations

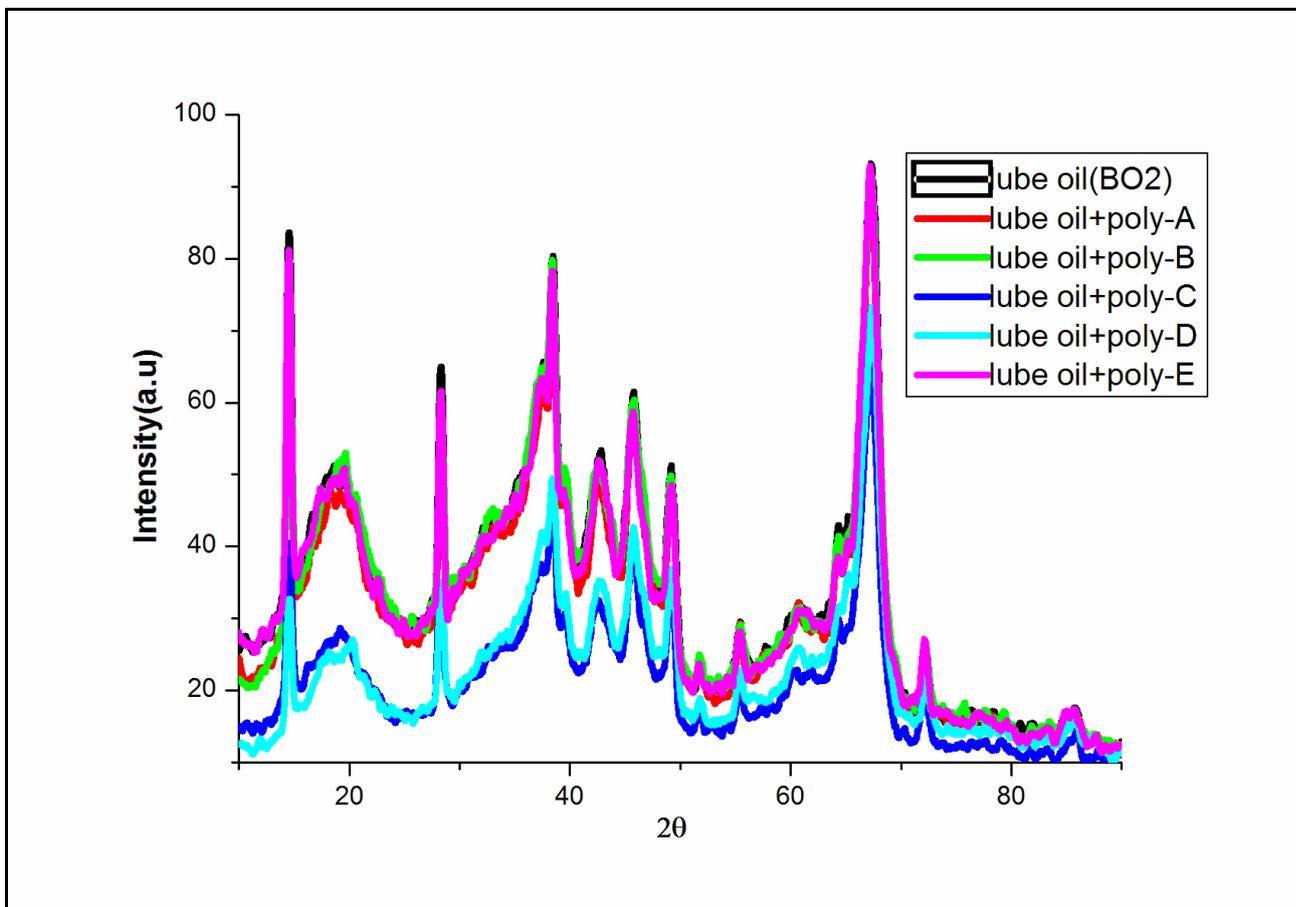
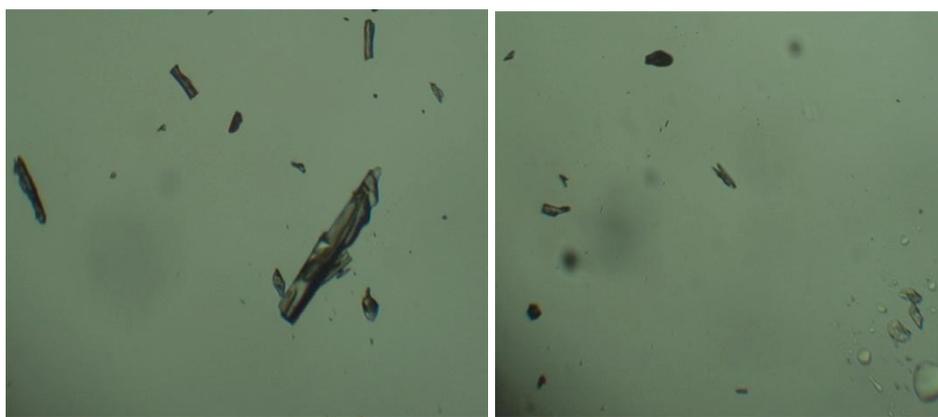
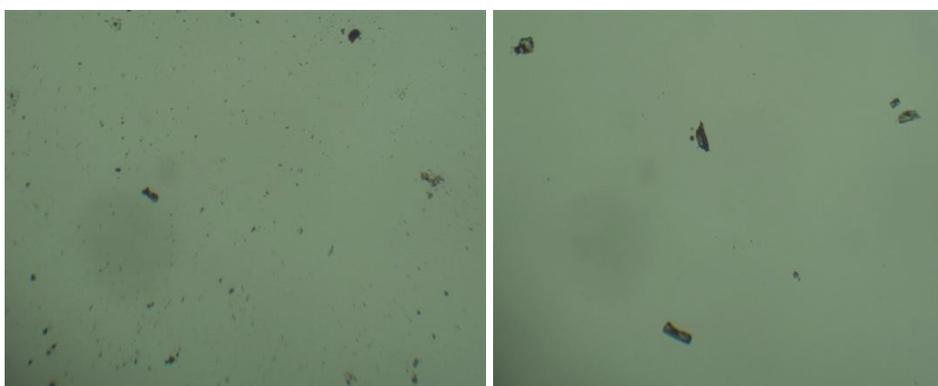


Figure 3.2.10 XRD (powder) patterns of lube oil without and with polymeric additives



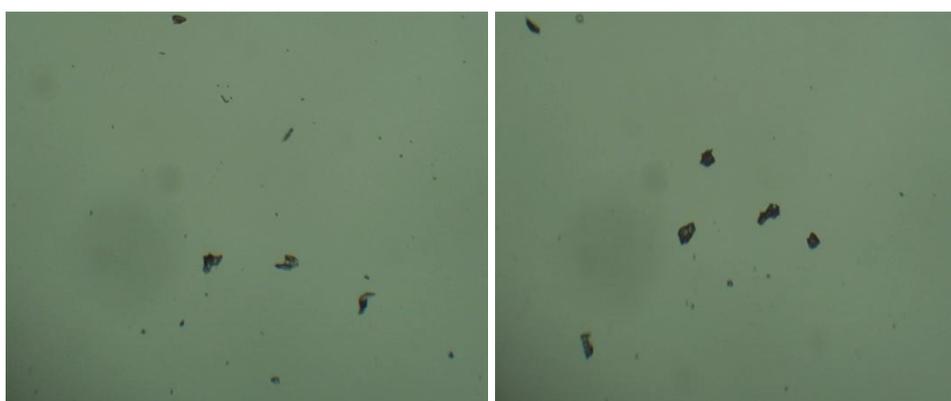
11a (pour point = -6°C)

11b (pour point = -10°C)



11c (pour point = -14°C)

11d (pour point = -16°C)



11e (pour point = -15°C)

11f (pour point = -12°C)

Figure 3.2.11 Photomicrograph of (a) Untreated base oil (BO2); (b) BO2 + polymer A (2%, w/w); (c) BO2+ polymer B (2%, w/w); (d) BO2 + polymer C (2%, w/w); (e) BO2 + polymer D (2%, w/w); (f) BO2 + polymer E (2%, w/w)

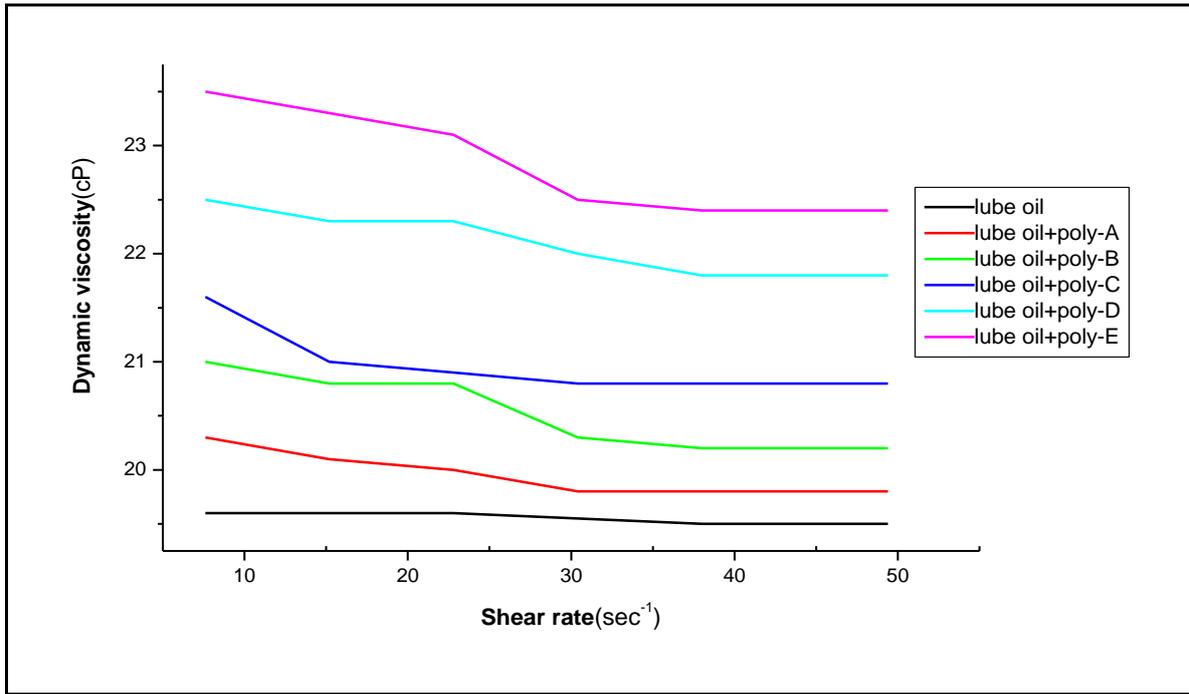


Figure 3.2.12 Variation of dynamic viscosity with shear rate at 40° C

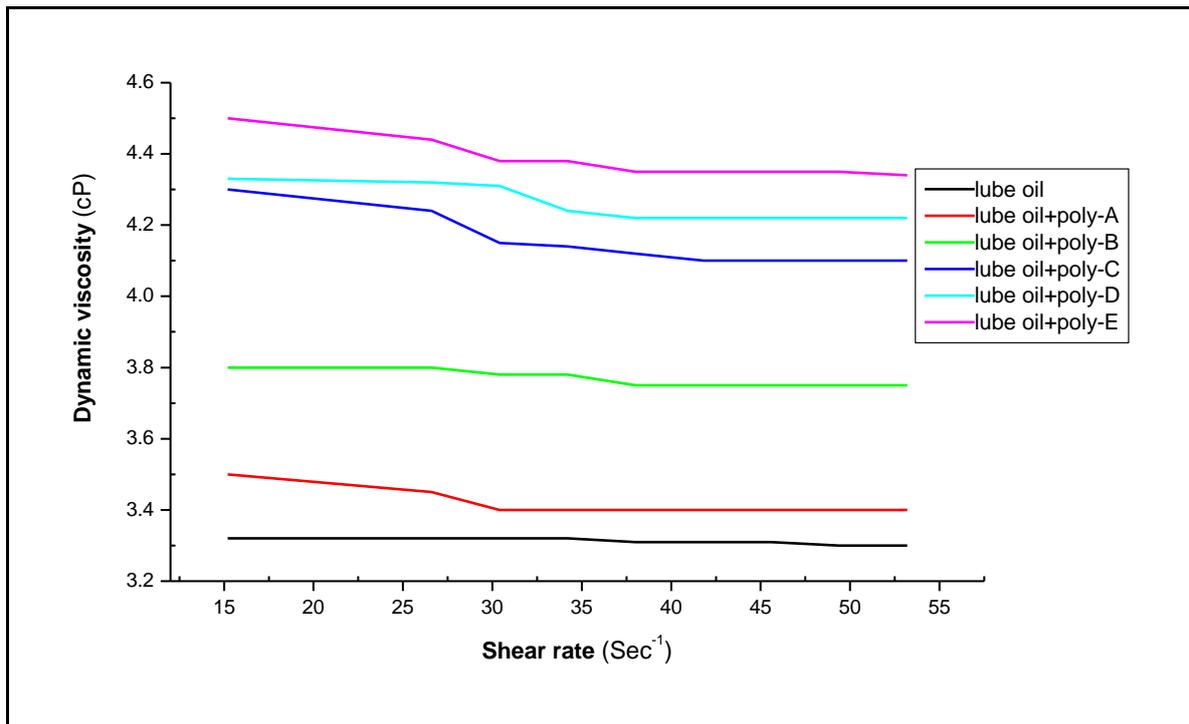


Figure 3.2.13 Variation of dynamic viscosity with shear rate at 100 ° C

Chapter III

Castor oil as potential multifunctional additive in the formulation of eco-friendly lubricant

3.3.1 Introduction

The lubricants derived from petroleum based materials although exhibit satisfactory performance but create many environmental hazards due to their eco-toxicity and non-biodegradability. Moreover, the non-renewable sources of the commonly used lubricants are depleting and therefore their costs are increasing gradually. The use of bio-based resources for the preparation lubricant has solved this problem and simultaneously reduces environmental impacts significantly. Vegetable oils have potential advantages compared with synthetic petroleum resources owing to their biodegradable properties, low-toxicity and in many cases lower cost. They have excellent antiwear properties,¹⁻⁴ high viscosity index (VI),⁵ low volatility,^{5, 6} and enhanced extreme pressure (EP) additives performance.^{7, 8} So, the use of vegetable oils or their derivatives as additives as well as base stocks to formulate environmental sustainable lubricant composition has attracted much attention recently. But, due to few drawbacks like poor fluidity at low temperature (pour point), poor oxidative stability, poor bio resistance and poor hydrolytic stability⁹⁻¹² the direct use of vegetable oils as lubricant base stock does not give satisfactory performance. However, these limitations can be mitigated by means of chemical derivatization e.g. epoxidation, metathesis, polymerization etc. of the oleo chemicals of the vegetable oils.¹³⁻¹⁶ There are lots of examples where chemically modified vegetable oils have been used as additive or base stocks in the formulation of bio-lubricant.¹⁷⁻²²

Castor oil from castor seeds contains high percentage of triacylglycerols of ricinoleic acid (85-95%) which is a C-18 fatty acid. It contains a double bond at C-9 and a hydroxyl group at C-12 (**figure 3.3.1**). The trifunctional nature of castor oil provides rigidity to the structure and the long fatty acid chain lends flexibility. Due to the unique oleo chemical properties castor oil can be used as a potential feedstock for a variety of end applications. It is widely used in diverse fields such as paints, adhesives, lubricants, pharmaceuticals, cosmetics, paper, rubber, agriculture etc.²³⁻²⁸ The high flash point and polar functional groups of castor oil make it efficient in the application of automotive engine and gear box as lubricant.²⁸⁻³⁰ Quinchia et al. studied tribological properties of sunflower, soybean and castor oil based lubricants and have found that castor oil showed the best tribological properties.³¹ Chinchkar et al. have explained the application of castor oil as green lubricant.³² The potential use of castor oil methyl esters

as bio lubricants due to its high viscosity, low pour point, and good lubricity was explained by Madankar et al.³³ Copolymerization of castor oil with acrylates increase the polarity of the unit as well as enhance thermal and mechanical stability significantly.³⁴ However reports regarding the application of acrylate copolymers of castor oil as multifunctional additive for lubricant are very few.

Therefore, in this work the author have synthesized few polymeric materials by copolymerizing castor oil with dodecyl acrylate in different percentage ratios to get thermally stable, cost effective, better performing as well as eco-friendly lubricant additives. Dodecyl acrylate was chosen due to its long hydrocarbon chain which imparts better additive performance. The present work comprises preparation of copolymers of dodecyl acrylate with castor oil (CO) at different percentage compositions viz. 5%, 10%, 15%, 20% and 25% using AIBN initiator. Evaluation of the efficiency of the polymers as viscosity index improver (VII), pour point depressant (PPD) and antiwear additives in mineral base oil (paraffinic) were carried out according to respective standard ASTM methods. Similar experimental analysis with homopolymer of castor oil and dodecyl acrylate were also carried out to make a comparison with the co polymeric additives. Photo micrographic images were taken to study the action mechanism of the additives as pour point depressant.

3.3.2 Experimental section

3.3.2.1 Chemicals used

Refined castor oil (~85% unsaturation) was collected from local market and its fatty acid composition and properties are given in **table 3.3.1**. Toluene (GC 99.5%) was collected from Merck (Mumbai, India). AIBN (GC 98%), obtained from Spectrochem Pvt. Ltd. Mumbai (India) was recrystallized from CHCl₃-MeOH before use. Dodecyl acrylate (GC 90%, Aldrich, India) was used as received. Methanol (98%, Thomas Baker Pvt. Ltd.) was used after distillation. The mineral base oil (SN150) was collected from IOCL, Dhakuria, West Bengal, India and the properties are given in **table 3.3.2**.

3.3.2.2 Synthesis of the polymers

The copolymers were prepared through free radical polymerization method taking the monomers of castor oil and dodecyl acrylate (DDA) at different ratios (**table 3.3.3**) in presence of AIBN initiator. The polymerization was carried out in a three necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen. In the flask, mixture of desired mass of castor oil and acrylate was heated to 90 ° C and maintained for half an hour in minimum amount of toluene solvent.

Initiator AIBN (1% w/w, with respect to the total monomer) was then added and heated for 6 hour keeping the temperature constant at 90°C. After the reaction is over, the product was poured into methanol with continuous stirring, filtered off and dried. The homopolymer of castor oil and DDA were also prepared in the similar procedure.

3.3.3 Measurements

3.3.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

3.3.3.2 Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (polystyrene calibration) equipped with a 2414 detector, waters 515 HPLC pump and 717 plus auto sampler. Sample solutions (0.4% w/v in HPLC grade THF) are prepared by dissolving ~4 mg of polymer per ml THF and filtering (0.45- μm Millipore PTFE) to remove suspended particulates. The pump flow rate is 1.0 mL/min with THF as the carrier solvent, and injection volumes are set to 20 μL . The polydispersity index³⁵ which indicates the nature of the distribution of the molecular weights in the polymers was also calculated.

3.3.3.3 Thermo gravimetric analysis (TGA)

TGA data was measured on Shimadzu TGA-50 system, at a heating rate of 10° C / min.

3.3.4 Performance evaluation

3.3.4.1 Evaluation of viscosity index (VI)

Viscosity index, an important parameter to determine the resistance of change of viscosity of the lubricant with temperature variation, was calculated according to ASTM D 2270-10. The kinematic viscosities which are essential to calculate the VI values of the lubricant composition were determined at 40° C and 100° C. Additives at different concentrations ranging from 1% - 5% (w/w) were blended with the lube oil to study the effect of concentration of additives on VI.

3.3.4.2 Evaluation of pour point

Pour points of the additive furnished base oils were determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India).

3.3.4.3 Photographic images analysis

The photomicrograph showing wax behaviour of base oil (pour point = -6°C) without and with polymers has been recorded. A Banbros polarizing microscope model BPL-400B was used for photographic analysis. The adopted magnification was 200X.

3.3.4.4 Evaluation of tribological performance

The antiwear performance in terms of wear scar diameter (WSD) and coefficient of friction (COF) of the lubricant compositions were evaluated by Four-ball wear test apparatus (FBWT) following the ASTM D 4172-94 method.³ In this experiment 392 N (40 Kg) load at 75°C for 60 min was applied to measure the wear scar diameter (WSD). The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm respectively. The coefficient of friction (COF) was also calculated by multiplication of the mean friction torque and spring constant.³⁵ The frictional torque on the lower balls may be expressed as;

$$\mu = T\sqrt{6}/3w \times r \quad (1)$$

Where, μ = coefficient of friction, T = frictional torque in kg/mm, w = applied load in kg, r = distance from the centre of the contact surfaces on the lower balls to the axis of rotation, which is 3.67mm.

3.3.4.5 Biodegradability test

Biodegradability of the additives is tested through soil burial test (SBT) method as per ISO 846:1997 standard.³⁶ The soil sample was collected from North Bengal University campus having 25% moisture and pH 7.2. Percentage weight loss (PWL) of the polymer samples after a definite interval of times was calculated to determine the extent of degradation which was also confirmed by observing the shift in IR frequency of the ester carbonyl groups after the test. In the SBT method, a film was prepared by taking 1.5 g of each of the polymer samples separately and then buried in soil. Then the soils with the samples are incubated in a bacteriological incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) at 30°C with relative humidity of 60% for 3 months and thus subjected to the action of microorganisms present in the soil. After each regular interval of 15 days, the soil sample is taken out and washed with CHCl_3 , purified and dried in an oven at 50°C . The dried samples weighed and decomposition was calculated in terms of percentage weight loss of the polymeric samples.³⁵

3.3.5 Results and discussion

3.3.5.1 Spectroscopic data analysis

The homopolymer of DDA exhibited IR absorption band at 1722.5 cm^{-1} for the ester carbonyl group. The peaks at 2853.5 cm^{-1} and 2924 cm^{-1} are the characteristic of $\text{CH}_3\text{-CH}_2\text{-}$ group. The

peaks at 1456 cm^{-1} and 1164 cm^{-1} due to CO stretching vibration and absorption band at 720 cm^{-1} is due to bending of C-H bond (**figure 3.3.2**). The homopolymer of castor oil (CO) exhibited IR absorption band at 1735 cm^{-1} for the ester carbonyl group. The peaks at 2854 cm^{-1} and 2922 cm^{-1} are the stretching vibration of $\text{CH}_3\text{-CH}_2\text{-}$ group. A broad peak at 3443 cm^{-1} is due to free -OH group present in castor oil (**figure 3.3.3**). The IR spectra of five copolymers (P-2 to P-6) are similar. The absorption band at 1732 cm^{-1} is due to ester carbonyl group. The peaks at 2853 cm^{-1} and 2924 cm^{-1} are the characteristic of $\text{CH}_3\text{-CH}_2\text{-}$ group and a broad peak at 3445 cm^{-1} is due to -OH group (**figure 3.3.4**).

In the ^1H NMR spectra of homopolymer of DDA, the peaks at 3.63 ppm and 3.93 ppm indicate the protons of -OCH_2 group. The protons of CH_3 and CH_2 groups appear in the range of 0.88 - 1.81 ppm (**figure 3.3.5**). In the ^1H NMR spectra of homopolymer of castor oil, the peaks in the range of 4.11- 4.32 ppm indicate the protons of -COOCH_2 group of castor oil. The peaks in the range of 3.60 – 3.71 ppm are for the -OH group of castor oil. The peaks ranging from 0.86 – 2.34 ppm are for the protons of sp^3 carbons. No peaks in the range of 5-6 ppm indicate the polymerization was carried out successfully (**figure 3.3.6**). In the ^1H NMR spectra of copolymers, the methyl protons appear in the range of 0.868 – 1.291 ppm, the methylene protons in the range of 1.466 – 1.596 ppm for all alkyl groups. The peaks in the range of 1.616 – 2.038 ppm appear for the protons of -COCH- group of alkyl acrylate. The peaks in the range of 2.215 – 2.318 ppm are for the -OH groups of ricinoleic acid present in castor oil. Peaks at 3.607 – 3.656 ppm indicate the protons of -OCH_2 of alkyl acrylate. The peaks in the range of 3.988 – 4.156 ppm indicate the protons of -COOCH_2 group of castor oil. No peaks in the range of 5-6 ppm indicate that polymerization was carried out successfully (**figure 3.3.7**).

In the ^{13}C NMR spectra of homopolymer of DDA, the ester carbonyl group appears in the range of 176.73-177.84 ppm and homopolymer of castor oil, the ester carbonyl group appears in the range of 172.93-177.41 ppm. In the ^{13}C NMR spectra of copolymers (P-2 to P-6), the peaks in the range of 14.05 – 41.30 ppm appear due to carbons of all CH_3 and CH_2 groups. The peak at 58.11 ppm represents the carbons of -OCH_2 groups of alkyl acrylate. The carbons of -OOCH_2 group of castor oil appear at 62.78-64.87 ppm. The peak at 71.50 ppm is the carbon which is joined to -OH group of castor oil. The peaks ranging from 166.31- 174.63 ppm confirm the carbons of ester groups. No peaks in the range of 120 – 150 ppm indicate that polymerization was carried out successfully (**figures 3.3.8, 3.3.9 and 3.3.10**).

3.3.5.2 Molecular weight data analysis

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity indices (PDI) of the prepared polymers (P-1 to P-7) are given in **table 3.3.3**. From the experimental values, it is found that among the seven polymers, P-3 has highest molecular weight followed by P-4. This signifies that when the percentage of castor oil is 10, then degree of polymerization is highest and we get a long chain copolymer with narrow molecular weight distribution. Beyond this, with increasing CO in the backbone of DDA, the molecular weight values of the copolymers gradually decrease and the homopolymer of castor oil showed lowest molecular weight. Therefore, percentage of castor oil has a significant role during polymerization.

3.3.5.3 TGA data analysis

The TGA values of the seven polymers are given in **figure 3.3.11**. It is found that thermal stability of homopolymer of DDA (i.e. P-1) is higher among all the polymers and the stability decreases with increasing the percentage of castor oil in the copolymer composition. At 320° C temperature the percentage of decomposition of the polymers from P-1 to P-7 are 20.48, 25.38, 29.11, 30.42, 35.48, 39.18 and 57.52 respectively. Whereas at 400 ° C, the percentage weight loss of the polymers were 42.13, 47.19, 53.84, 55.47, 59.35, 66.72 and 98.79 respectively. The homopolymer of castor oil (P-7) showed highest degradation i.e. lowest thermal stability. Due to copolymerization of castor oil with DDA, the thermal stability increases. Therefore, copolymerization with DDA has a significant importance to improve thermal stability of castor oil.

3.3.5.4 Analysis of viscosity index (VI) data

VI was calculated by dissolving the prepared polymers (P-1 to P-7) at different concentrations from 1% to 5% (w/w) to the base oils. The experimental values of VI are given in **figure 3.3.12**. It is found that VI values increase with increasing the concentration of polymers in lube oil. The viscosity of lube oil decreases with increasing temperature but expansion of polymer molecules take place with increasing temperature. Because of this, the size of micelle increases. This increased in micelle size counterbalance the reduction of the viscosity of the polymer doped lube oil.³⁷ Therefore, with increasing the concentration of polymer in lube oil leads to an increase in the total volume of polymer micelle in lube oil, thus exerting higher thickening effect and improves the VI property.³⁸ It is also observed that the VI value increases by incorporation of castor oil in the backbone of homopolymer of DDA. This may be due to higher crosslink density of the copolymers.³⁹ The copolymer P-3

(DDA+10% CO) has highest effect on VI increment ($76.5\% \pm 2$ at 5% additive concentration) followed by P-4, P-5 and P-6 among the polymers. The higher VI values of the base oils blended with P-3 are due to greater volume of the solvated additive molecule i.e. micelle compared to others. This may be due to higher degree of polymerization of P-3 with a narrow molecular weight distribution compared to others which is reflected in its higher average molecular weights and lower PDI value.

3.3.5.5 Analysis of pour point data

The pour points of the lubricant compositions prepared by blending the additives at different concentration levels ranging from 1%–5% (w/w) are given in **figure 3.3.13**. All the polymers showed excellent results as PPD and the efficiency increases with increasing the concentration of polymers up to certain limit (4% concentration). This indicates that at this concentrations the polymer molecules interact with the paraffinic wax and decrease their crystals size.⁴⁰ The polymer P-2 has greater efficiency as PPD among the seven polymers followed by P-1 i.e. homopolymer of DDA. It may be due to smaller polymer molecules with polar alkyl side chains. The interaction between the short alkyl chain length and paraffin in the lube oil is more effective than long alkyl chain length and wax crystal formation is effectively inhibited.⁴¹ Moreover, it is also found that with increasing the percentage of castor oil in copolymers, the efficiency as PPD decreases. It was further observed that when diluents like n-decane solvent (10% (w/w)) is added to the lubricant compositions, the pour point decreases to a certain extent. The decrease in pour point is due to dissolution of asphaltenes present in lube oil.^{42, 43} Of course, due to addition of solvent (n-decane), the viscosity decreases to a certain extent, may be due to effect of dilution. The effect of solvent towards increment in pour points of the additive furnished lubricants is shown in **figure 3.3.14**.

3.3.5.6 Photo micrographic images analysis

Photo micrographic analysis was used to study the pour point and its mechanism of the lube oil without and with polymeric additives and is shown in **figure 3.3.15 (a-h)**. The figure 3.3.15a is the photograph of lube oil (pour point = -6°C) without any additives where there is large number of rod shaped wax crystals. The photo micrographic images of lube oil blended with different additives like P-1, P-2, P-3, P-4, P-5, P-6 and P-7 at 4% (w/w) concentration are shown in the figures 3.3.15 (b, c, d, e, f, g and h) along with the image of pure base oil. The results are in agreement with the pour point values determined by ASTM D97-09 method. A significant wax crystal modification is observed due to the addition of P-2, P-1 and P-3 in the base stock which are shown in figures 3.3.15c (pour point = -19°C),

3.3.15b (pour point = - 17° C) and 3.3.15d ((pour point = - 17° C) respectively. The copolymers of DDA with 5% and 10% CO have greater pour point improvement capacities.

3.3.5.7 Analysis of tribological properties

The tribological properties of the lubricant compositions were determined by measuring WSD and COF values through FBWT apparatus applying 392 N load and shown in **figures 3.3.16** and **3.3.17** respectively. The anti wear performance of the base oil is significantly improved when the additives are blended with it and is reflected in the lower WSD and COF values of the lubricant compositions. The copolymers showed better result compared to the homopolymers of DDA and CO. The base oil blended with the copolymer of DDA with 10% CO i.e. P-3 at 5% concentration showed highest reduction in WSD ($55.9\pm 1.5\%$) and COF ($60\pm 1.5\%$) values compared to the other copolymers whereas the homopolymer of DDA showed minimal ($43.8\pm 1.4\%$). The film formed by the lubricant between the metal surfaces undergoing friction (through chemical and physical bonding between the functional groups of the additive molecules and metal atoms on the surface area of the rubbing zone) protect against wear during terbochemical process. The copolymers due to more polar ends which are definitely due to polar hydroxyl groups of CO counterpart formed stronger layer with metal atoms and perform better tribological performance compared to the homopolymer of DDA. The better antiwear performance of the copolymer P-3 in base oil indicated that the film formed by the lubricant is strengthened mostly. The higher degree of polymerization with narrow molecular weight distribution and higher number of polar side chains of the ester carbonyl groups and hydroxyl groups of P-3 are probably the reasons for exhibition of its better antiwear performance.⁴⁴⁻⁴⁶

3.3.5.8 Analysis of biodegradability test results

The results of SBT test are mentioned in **figure 3.3.18**. The degradation of homopolymer of DDA by the microbes in soil is very low and even after 90 days only 1.05 percent was decomposed. Significant biodegradation was observed due to copolymerization of DDA with castor oil and the percentage of decomposition increases with increasing castor oil in the copolymer composition. It was also found that the degradation of the recovered samples taken every 15 days increases with increasing time. The homopolymer of castor oil showed highest degradation and after 90 days' span the recovered sample showed $32.2\pm 2\%$ weight loss. P-6 showed $20.21\pm 2\%$ weight loss after three months which is higher among the copolymers. Therefore, castor oil has a significant importance for inducing biodegradability of the additives. Moreover, molecular weight of the recovered samples after 90 days

biodegradation was determined by GPC method and the results were compared with the respective samples before biodegradation and given in **table 3.3.4**. The IR spectra of the recovered samples after biodegradation are depicted in **figures 3.3.19** and **3.3.20**.

3.3.6 Conclusions

From the above study it was found that the copolymers of dodecyl acrylate and castor showed better performance as viscosity modifier, pour point depressant and antiwear additive for lube oil. Castor oil has a significant role in enhancing performances of the additives. The oxy-rich property of castor oil molecules along with long hydrocarbon chains with polar ends of DDA molecules are the key reasons for exhibiting better PPD and antiwear performance of the co polymeric additives. On the other hand, higher cross link density and molecular weight of the copolymers are responsible for showing higher viscosity index values. Moreover, due to biodegradability the additives are eco-friendly also. Therefore, the above study is definitely a potential approach to formulate a cost effective and sustainable lubricant composition.

3.3.7 References

References are given in bibliography section of chapter III of Part III (Page No. 199 - 202).

3.3.8 Tables and figures

Table 3.3.1 Properties of castor oil

Physical properties	
Density (g.cm ⁻³) at 40 °C	0.95
Kinematic Viscosity (c St) at 40 °C	225.7
Kinematic Viscosity (c St) at 100 °C	18.5
Viscosity index	91
Flash point	210° C
Pour point	-6° C
Cloud point	-4° C
Chemical composition	
Fatty acids	Average percentage range
Ricinoleic acid	83–85
Oleic acid	4–5
Linoleic acid	2–3
α – Linoleic acid	0.5–1
Stearic acid	0.5–1
Palmitic acid	0.5–1
Dihydroxystearic acid	0.3 – 0.5

Table 3.3.2 Physical properties of the mineral base oil

Properties	SN150
Density (g.cm ⁻³) at 40 ⁰ C	0.84
Viscosity at 40 ⁰ C in c St	23.502
Viscosity at 100 ⁰ C in c St	3.980
Viscosity Index	85.15
Cloud Point, °C	-4
Pour Point, °C	-6

Table 3.3.3 Percentage composition and molecular weight of the prepared polymers

Polymers	% of monomers		Average molecular weights		
	DDA	CO	M _n	M _w	PDI
P-1	100	0	17824	24588	1.38
P-2	95	5	8848	13515	1.53
P-3	90	10	35170	44644	1.27
P-4	85	15	15671	31312	1.99
P-5	80	20	16535	24538	1.48
P-6	75	25	8972	14700	1.64
P-7	0	100	7928	10022	1.26

M_n is number average molecular weight; M_w is weight average molecular weight; PDI is polydispersity index; DDA = Dodecyl acrylate; CO = Castor oil

Table 3.3.4 Comparative molecular weight (determined by GPC)

Polymer code	<u>Before biodegradation</u>		<u>After biodegradation</u>	
	M_n	M_w	M_n	M_w
P-1	17824	24588	17824	24588
P-2	8848	13515	8642	12898
P-3	35170	44644	34178	42975
P-4	15671	31312	15020	30526
P-5	16535	24538	15622	23534
P-6	8972	14700	7838	13170
P-7	7928	10022	5865	7225

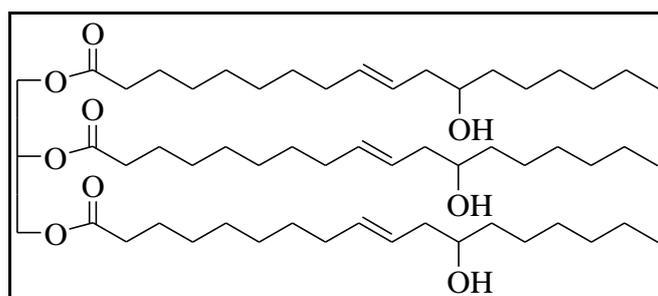


Figure 3.3.1 Triricinolein, the major component of castor oil

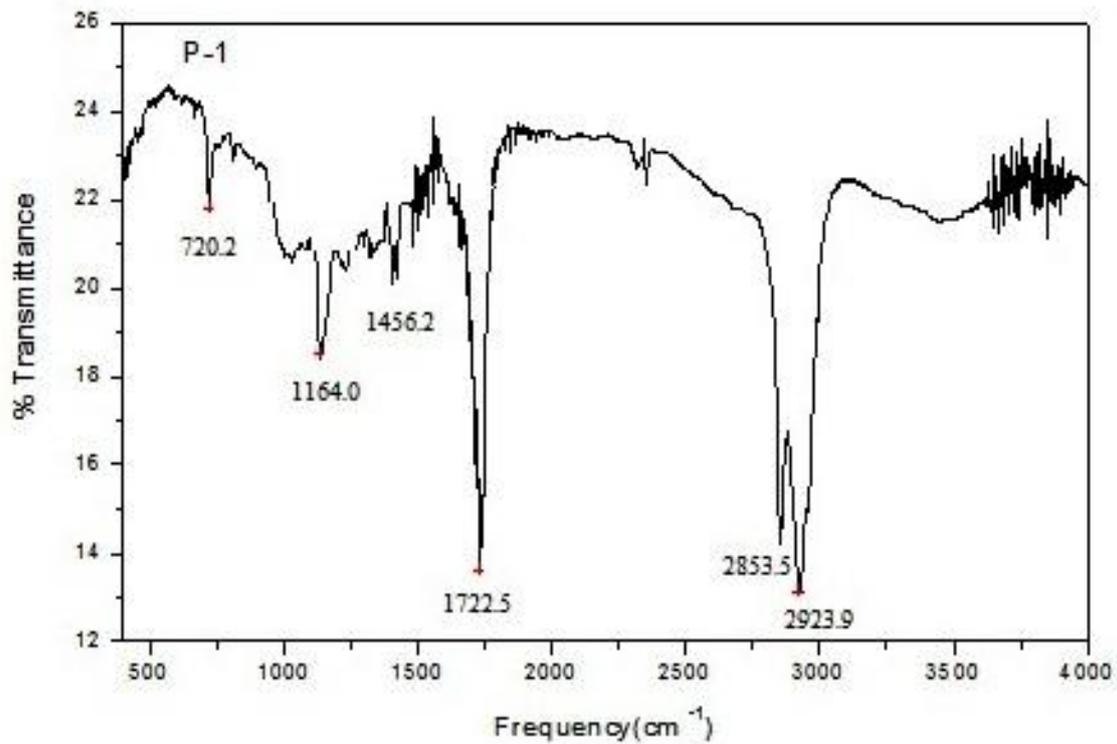


Figure 3.3.2 IR spectra of homopolymer of DDA (P-1)

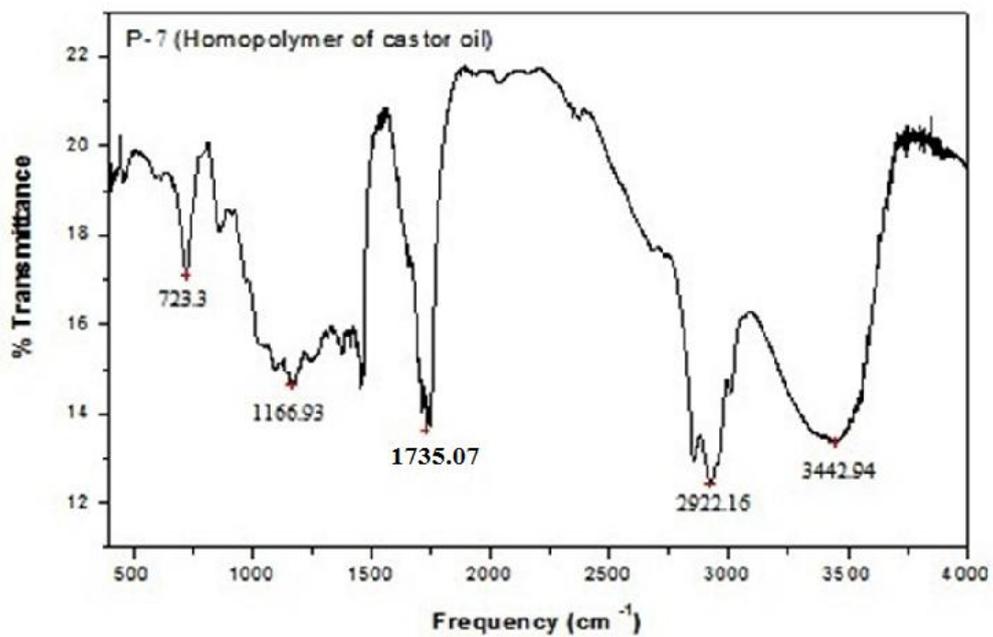


Figure 3.3.3 IR spectra of homopolymer of castor oil

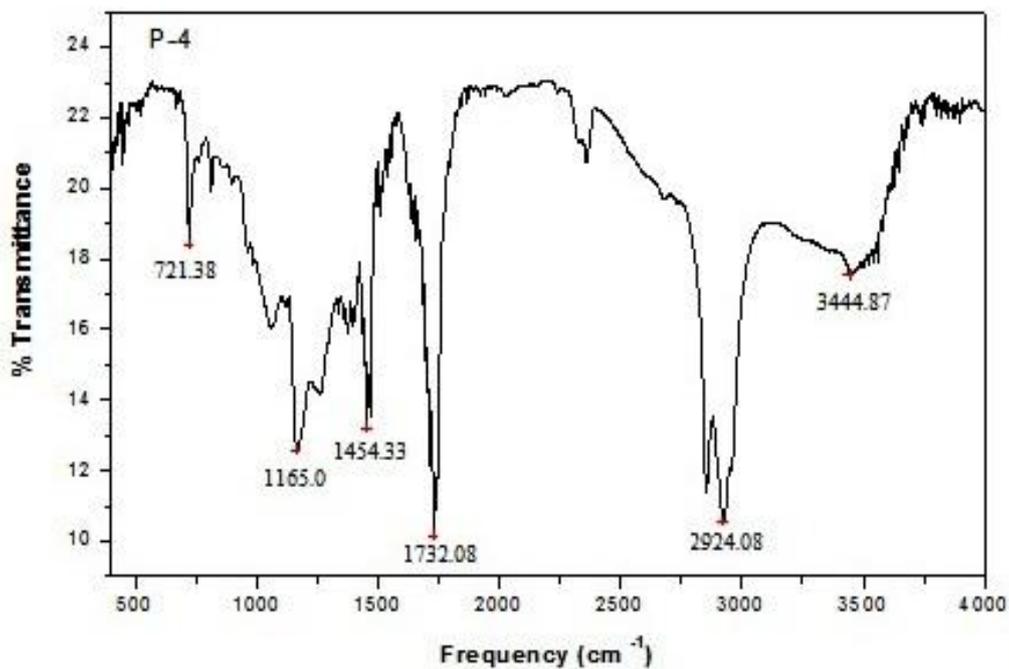


Figure 3.3.4 IR spectra of copolymer of DDA with 15% (w/w) of CO (P-4)

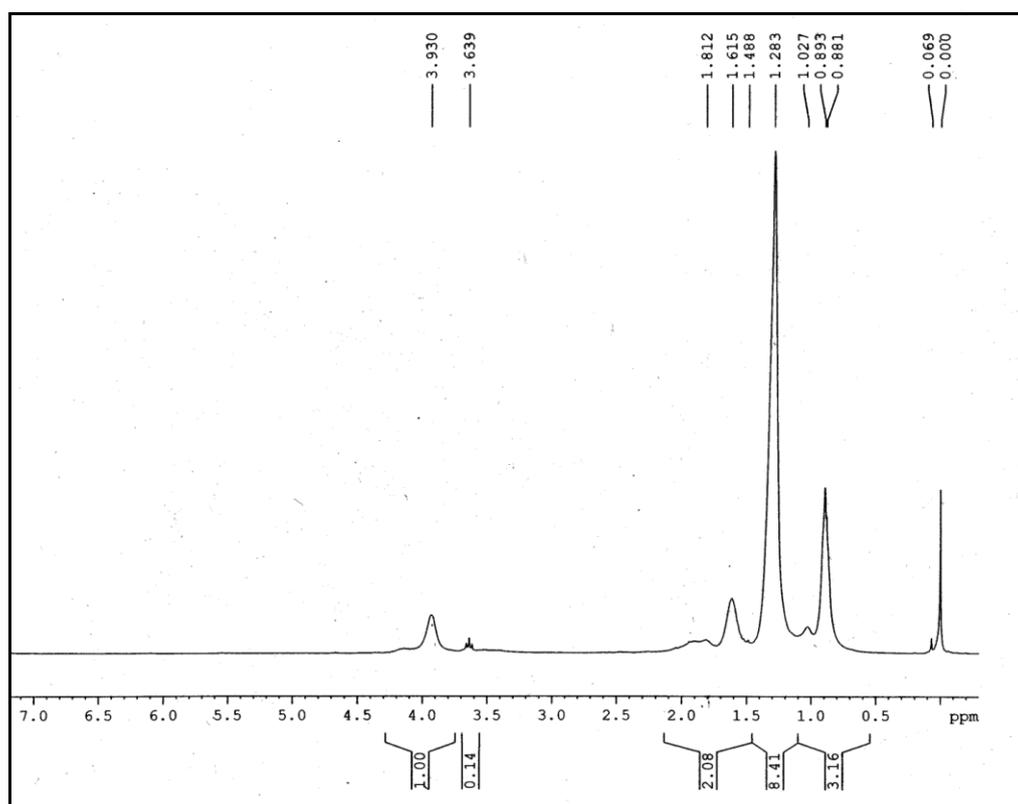


Figure 3.3.5 ¹H NMR spectra of homopolymer of DDA (P-1)

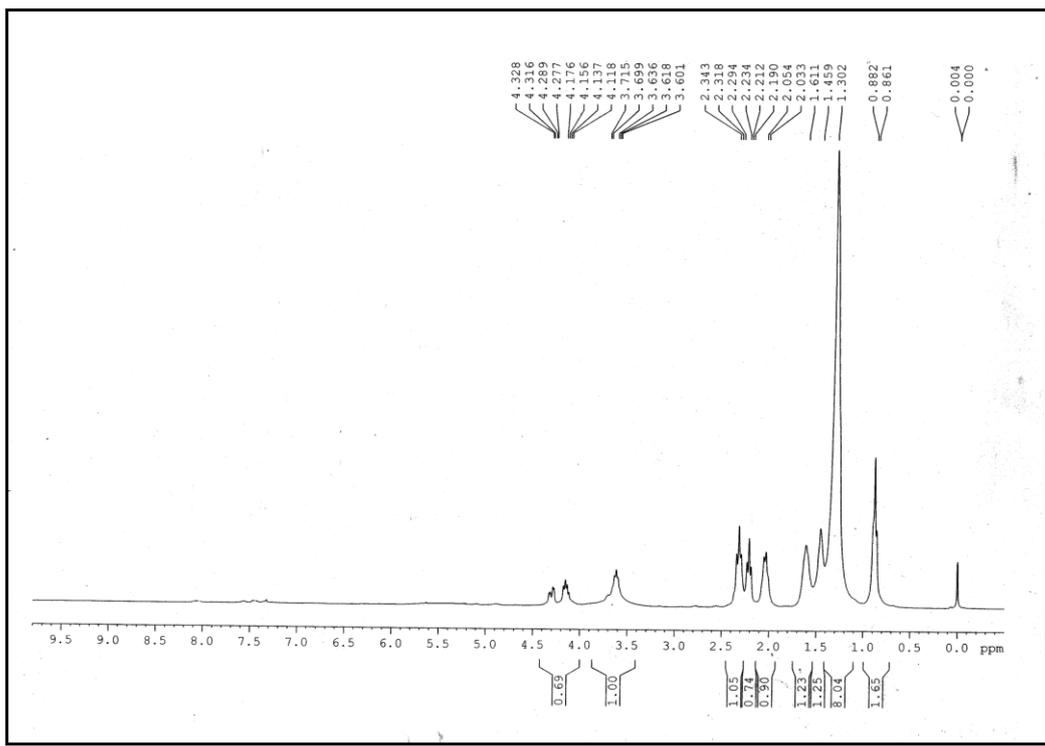


Figure 3.3.6 ^1H NMR spectra of homopolymer of castor oil

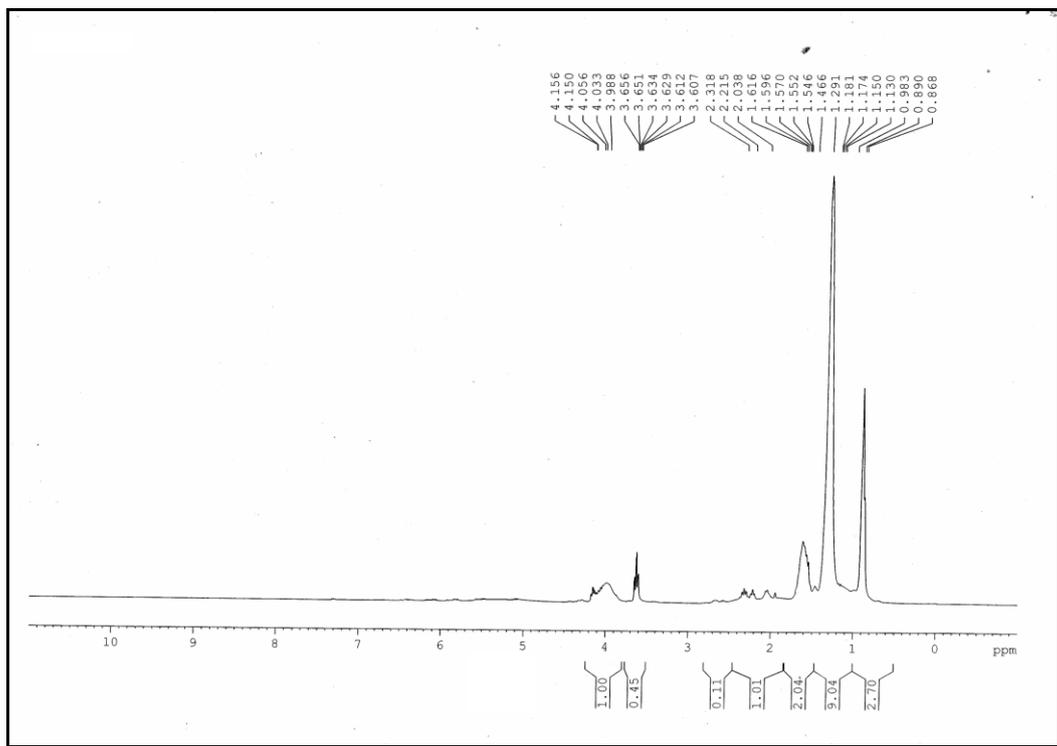


Figure 3.3.7 ^1H NMR spectra of copolymer of DDA with 15% (w/w) of CO (P-4)

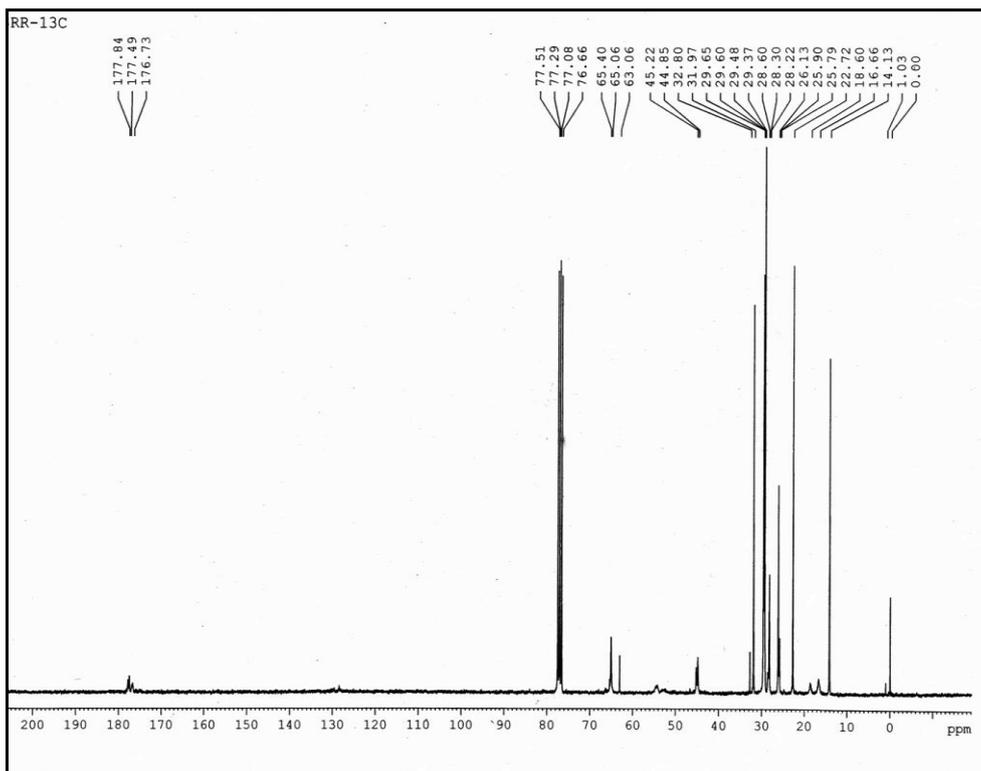


Figure 3.3.8 ^{13}C NMR spectra of homopolymer of DDA

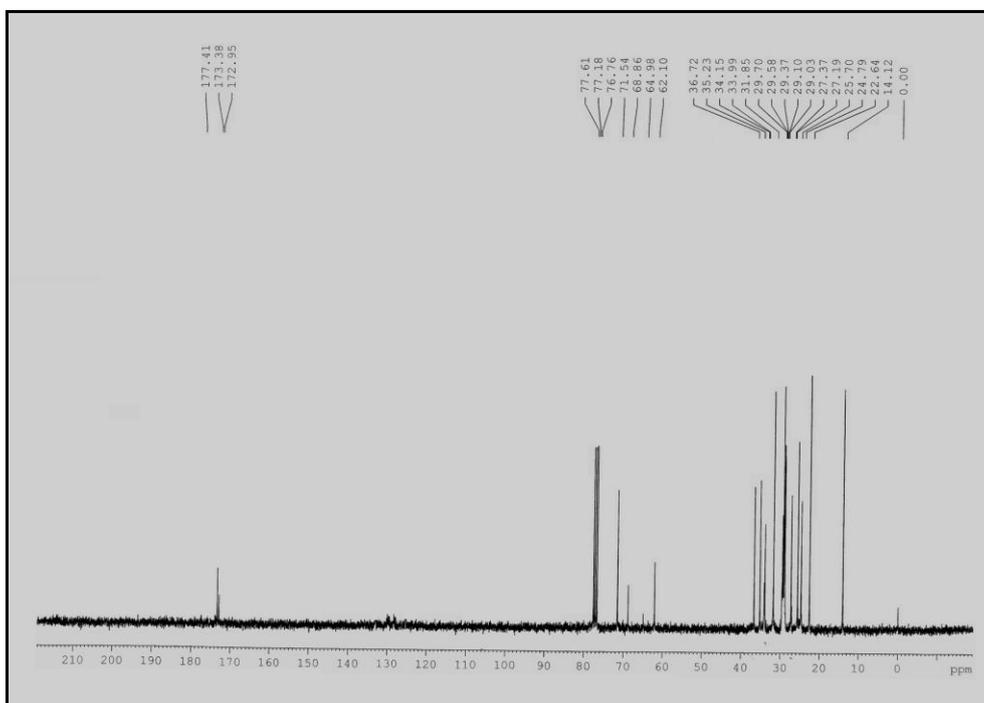


Figure 3.3.9 ^{13}C NMR spectra of homopolymer of castor oil

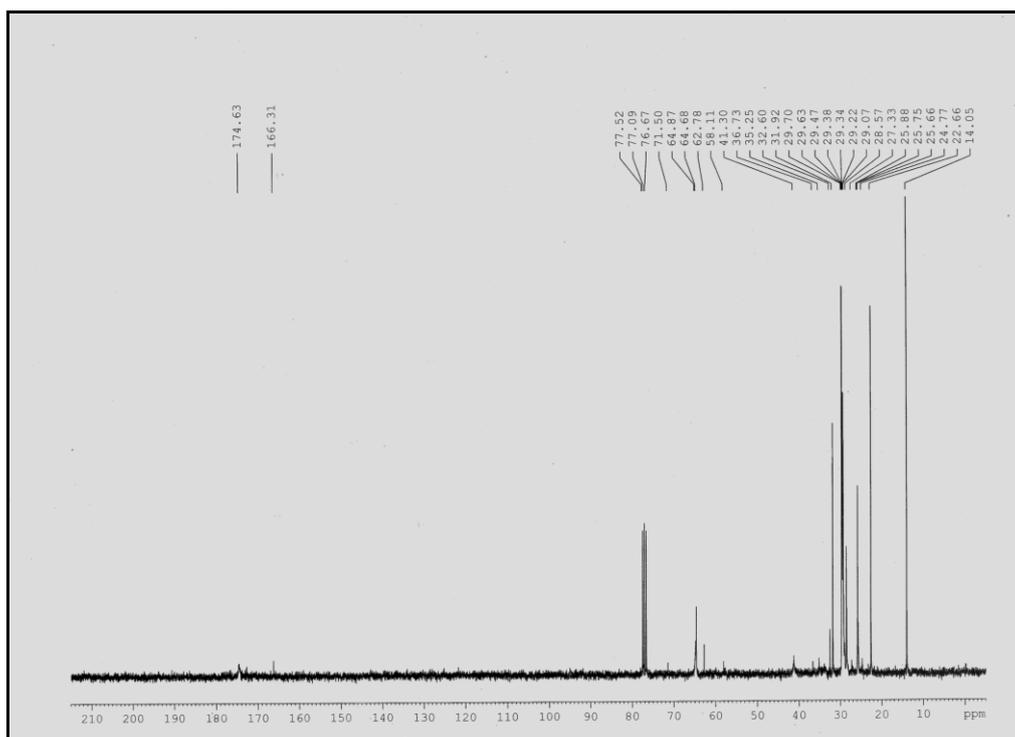


Figure 3.3.10 ^{13}C NMR spectra of copolymer of DDA with 15% (w/w) of CO

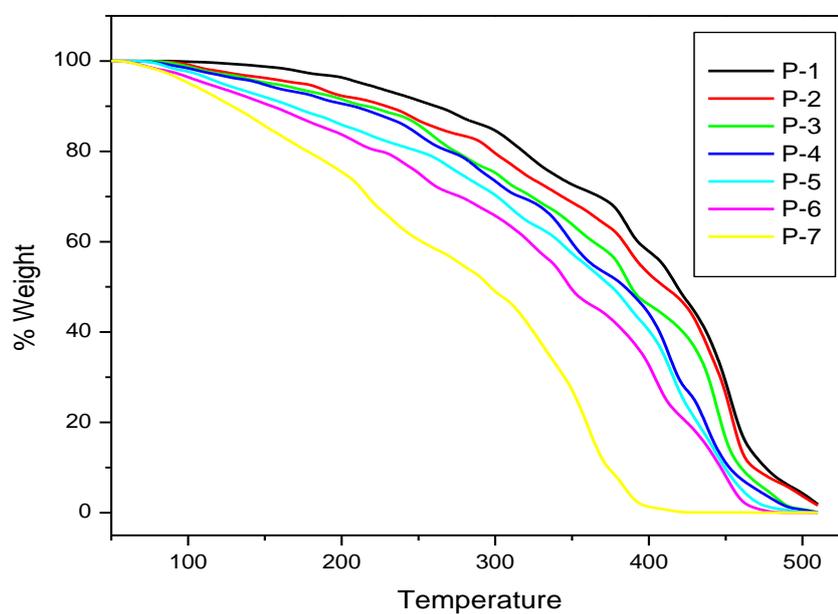


Figure 3.3.11 TGA of the additive furnished lubricant

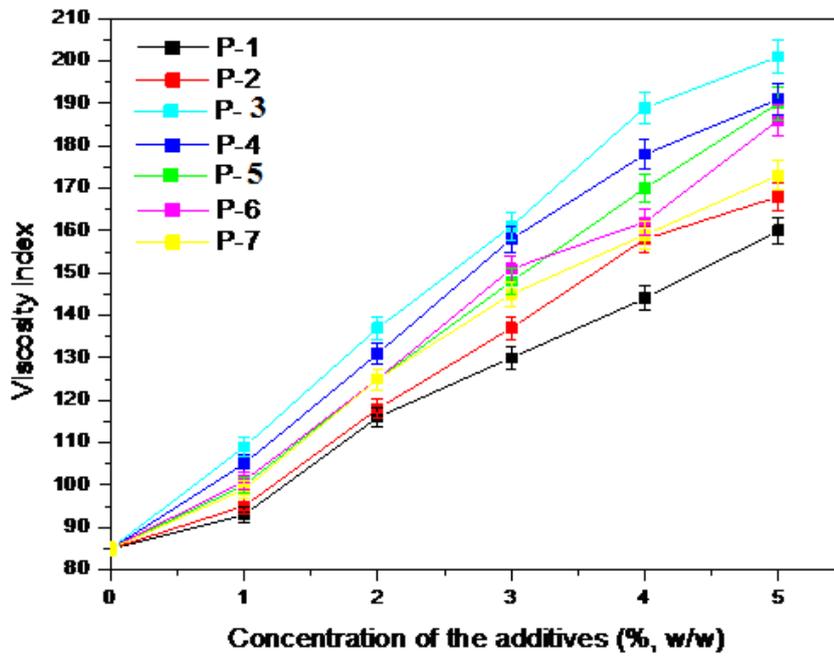


Figure 2.3.12 Variation of viscosity index of base oil blended with additives at different concentrations

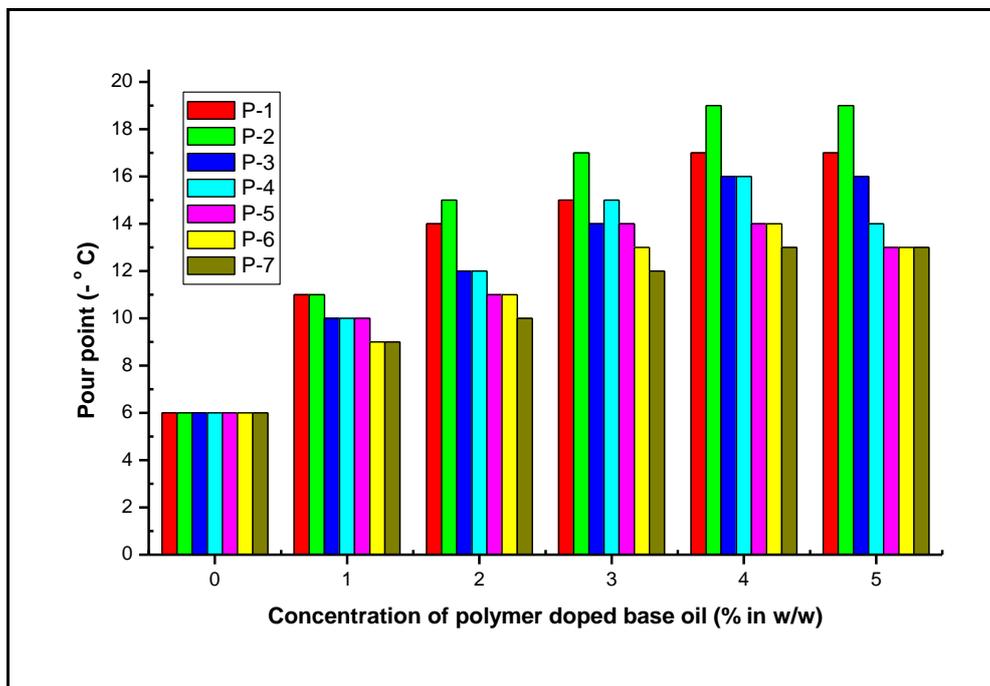


Figure 3.3.13 Pour points of the lubricant at different additive concentration levels

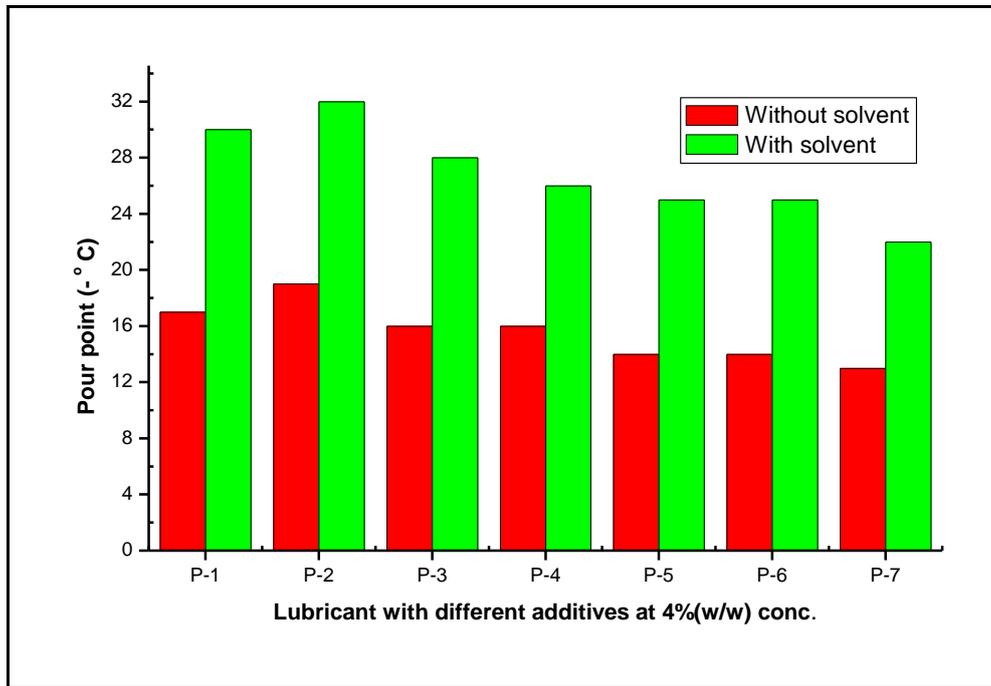


Figure 3.3.14 Pour point of lubricant at 4% (w/w) additive concentration before and after addition of 10% (w/w) n- decane solvent

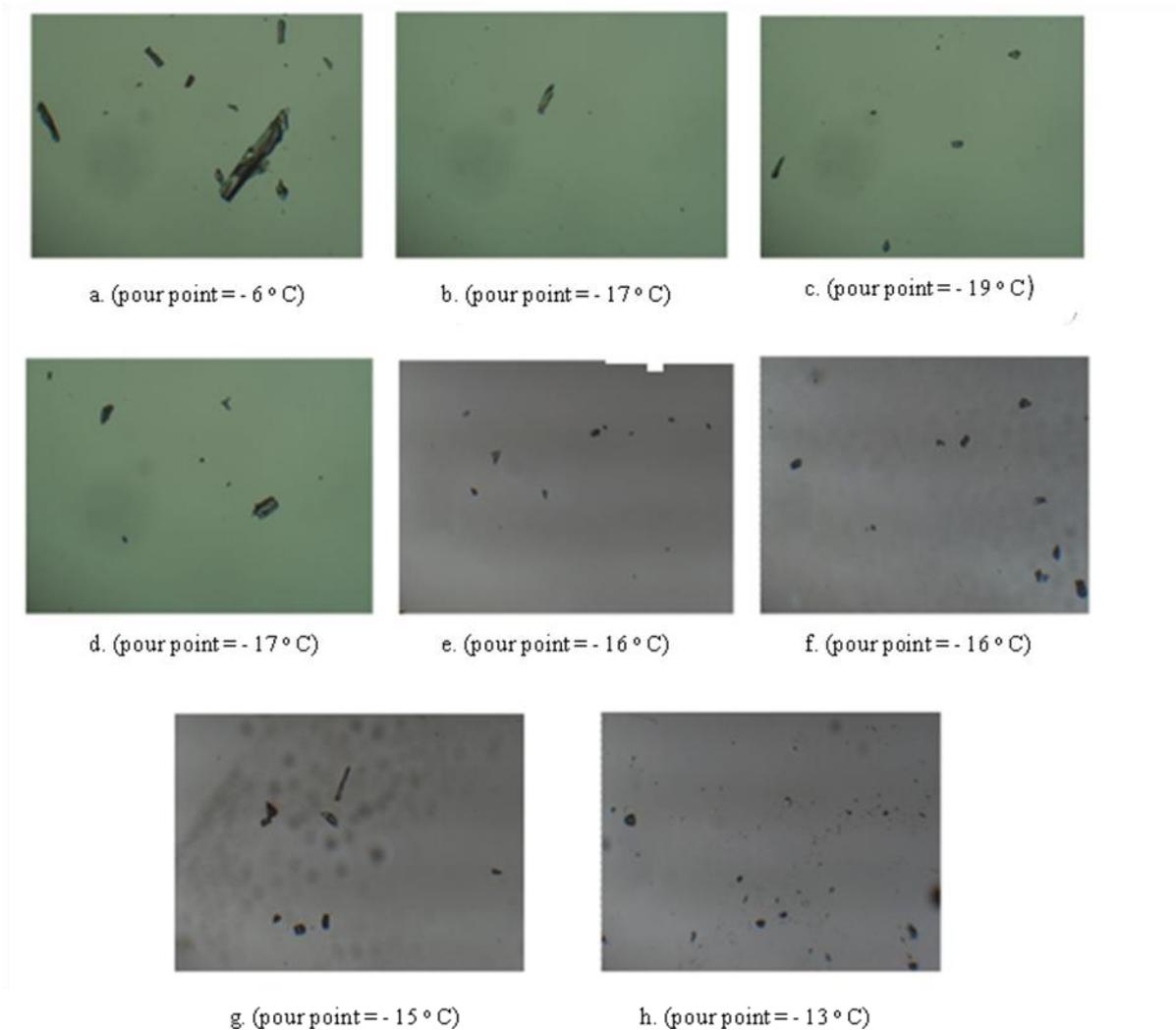


Figure 3.3.15 Photomicrograph images of a) Pure lube oil b) Lube oil + 4% (w/w) of P-1 c) Lube oil + 4% (w/w) of P-2 d) Lube oil + 4% (w/w) of P-3 e) Lube oil + 4% (w/w) of P-4 f) Lube oil + 4% (w/w) of P-5 g) Lube oil + 4% (w/w) of P-6 h) Lube oil + 4% (w/w) of P-7

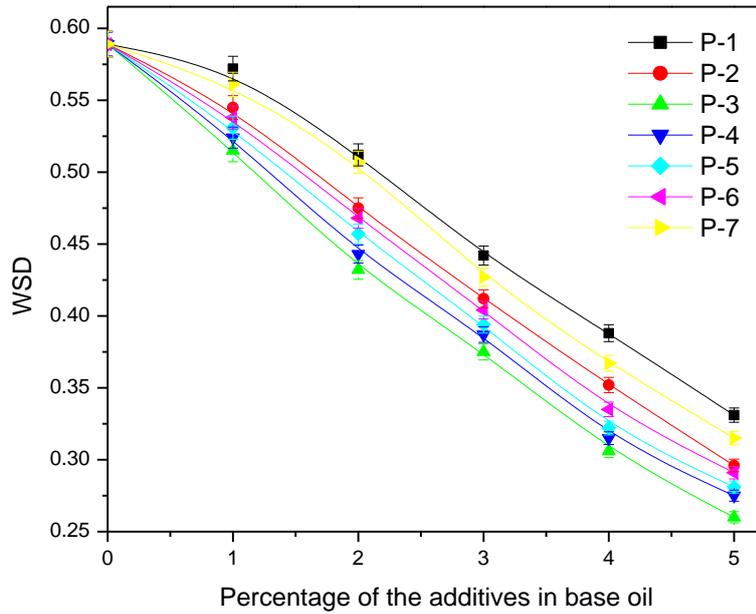


Figure 3.3.16 Wear scar diameter (WSD) of the lube oil blended with additives at different percentages (w/w)

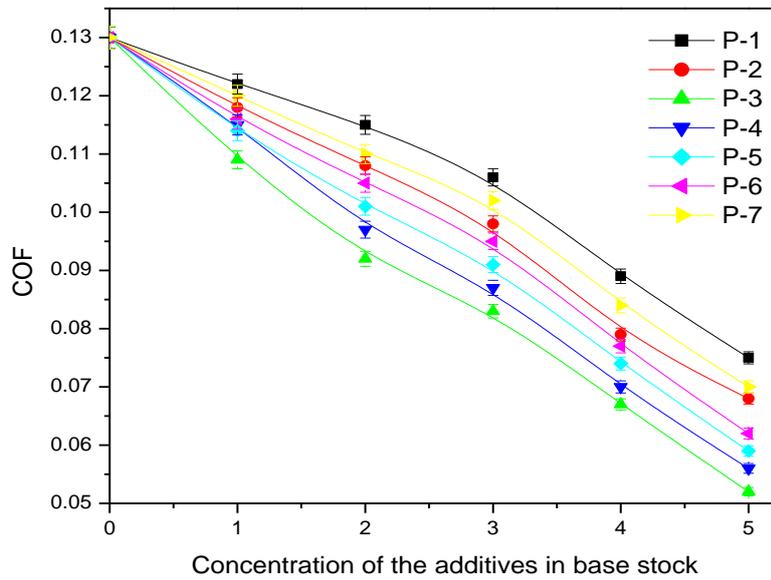


Figure 3.3.17 Coefficient of friction (COF) of the lube oil blended with additives at different percentages (w/w)

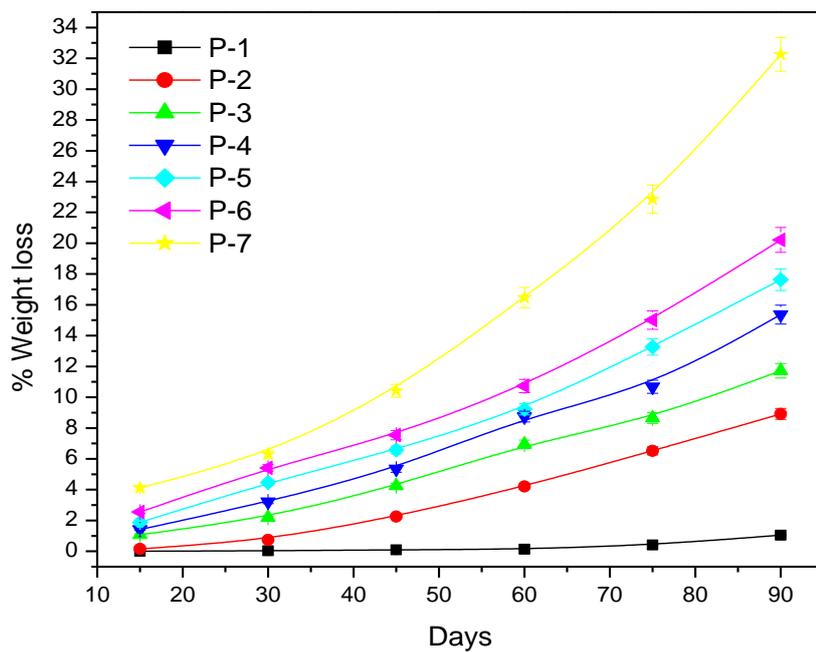


Figure 3.3.18 Biodegradability test (SBT) of the lubricant compositions

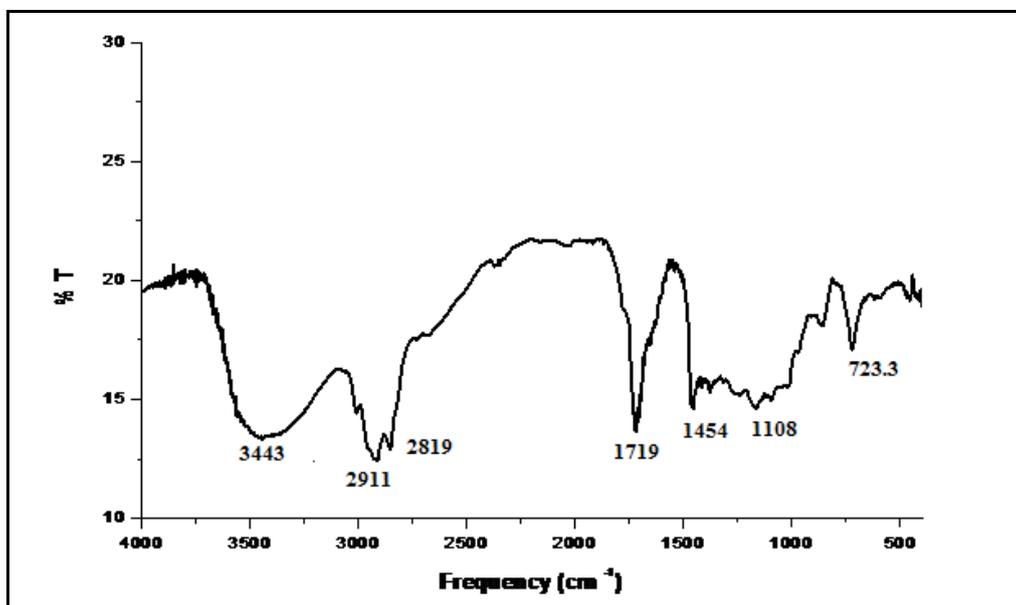


Figure 3.3.19 IR spectra of homopolymer of CO (P-7) after biodegradable

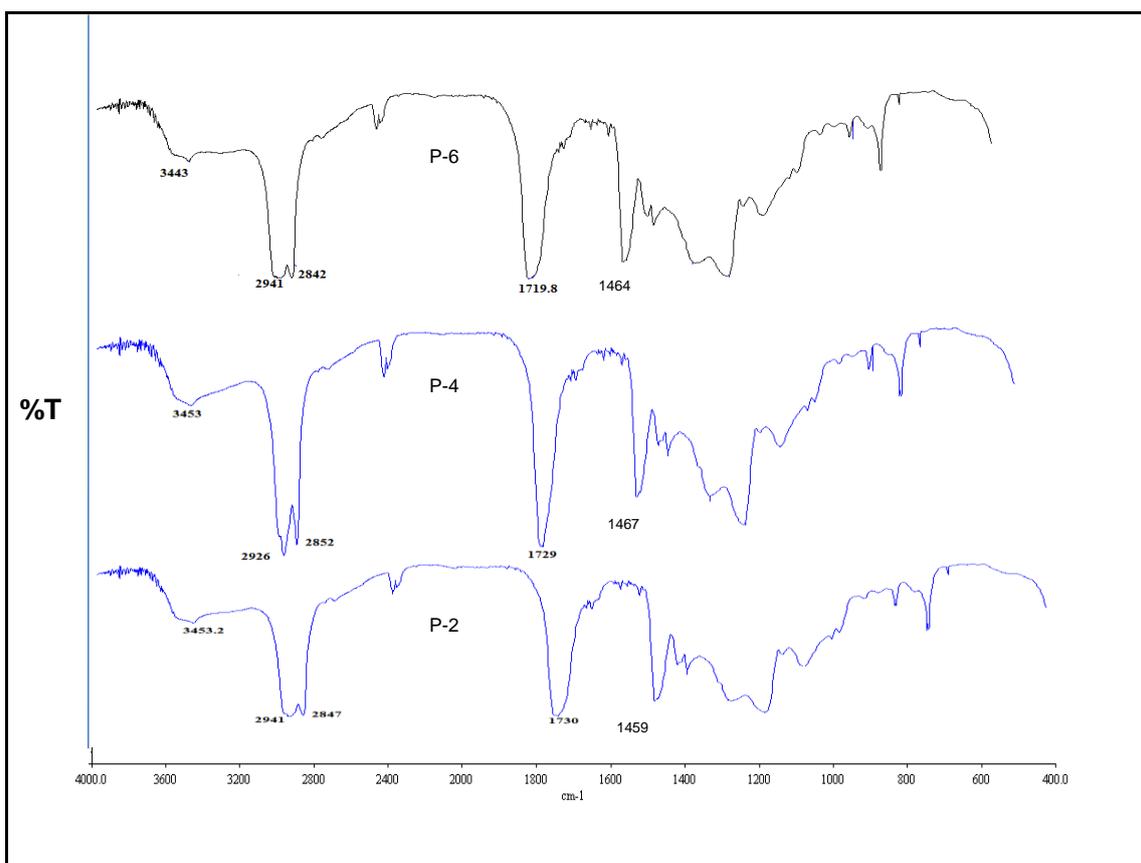


Figure 3.3.20 IR spectra of P-2, P-4 and P-6 after biodegradable

Chapter IV

Castor oil based multifunctional greener additives for lubricating oil

3.4.1 Introduction

Modern lubricants are composed of mineral lubricating oil and a package of additives. The mineral lubricating oil and chemically synthesized additives is toxic and non biodegradable to the environment. The throwing of used mineral oil is threats for animals, plants and aquatic animals.¹ The physiochemical properties of lands and waters are drastically changed due to contamination with finished mineral lubricating oil.² The vegetable oils are biodegradable, poor toxicity, renewable,³ high viscosity index, better thermal stability and tribological properties.^{4, 5} Hence, application of vegetable oils as a base stock or derivatives of vegetables oils as additives for base stocks to formulate environmental sustainable lubricant composition has given much interest in research recently. But due to some limitations like poor oxidative stability, low flow property at low temperature (pour point), high coefficient of friction at elevated temperature and poor hydrolytic stability,⁶⁻⁸ the direct use of vegetable oils as lubricant base stock does not give satisfactory performance. However, they can be effectively used as additives^{9, 10} and low oxidative stability which is due to presence of unsaturation,¹¹ low flow properties of vegetable oils can be improved by means of chemical modification.¹²⁻¹⁴ There are many research papers where chemically modified vegetable oils were used as an additive for lube oil or as a bio-lubricant.¹⁵⁻¹⁸

The main constituents of vegetable oils are triglyceride. The triglyceride contains several reactive sites, such as double bonds and ester groups. Castor oil is a well known vegetable oil which contains high percentage of triacylglycerols of ricinoleic acid (85-95%) which is a C-18 fatty acid. It contains a double bond at C-9 and a nonconjugated hydroxyl group at C-12 (**figure 3.3.1**). The trifunctional nature of castor oil contributes rigidity to the structure and the long fatty acid chain imparts flexibility. Due to the unique oleo chemical properties, castor oil is very versatile in its end applications. It is widely used in making paints, adhesives, lubricants, pharmaceuticals, cosmetics, paper, rubber, agriculture etc.¹⁹⁻²² Due to presence of free hydroxyl group on ricinoleic acid, it can interact with metal surfaces of engine parts, thereby giving excellent lubricity. The high flash point and polar functional groups of castor oil make it efficient in the application of automotive engine and gear box as lubricant.^{23, 24} Quinchia et al. studied tribological properties of sunflower, soybean and castor oil blended with ethylene – vinyl acetate copolymer and ethyl cellulose based lubricants and have found that castor oil showed the best tribological properties and may be due presence of hydroxyl group that increases both viscosity and polarity.²⁵ Chinchkar et al. have explained

that due to environmental concerns and need for bio – based products, castor oil and its derivatives have the potential to be used in many industries.²⁶ Madankar et al. explained the potential use of castor oil methyl esters as bio lubricants due to its high viscosity, low pour point, and good lubricity.²⁷ Many researchers explained that castor oil and its derivatives are most suitable as additive for diesel fuel.²⁸⁻³⁰ However reports regarding the application of copolymers of castor oil as multifunctional additive for lubricant are very scanty.

Therefore, in this work author have synthesized homopolymer of castor oil and four copolymers of castor oil with 10% (w/w) of methyl methacrylate (MMA), 10% (w/w) of dodecyl acrylate (DDA), 10% (w/w) of 1- decene and 10% (w/w) of styrene to get thermally stable, cost effective, better performing as well as eco-friendly lubricant additives. The performance of the prepared additives were evaluated as viscosity index improver (VII), pour point depressant (PPD) and antiwear additives in mineral base oil according to respective standard ASTM methods.

3.4.2 Experimental section

3.4.2.1 Chemicals used

Refined castor oil (~85% unsaturation) was collected from local market and its fatty acid composition and properties are given in **table 3.3.1**. Toluene (GC 99.5%) was collected from Merck (Mumbai, India). AIBN (GC 98%), obtained from Spectrochem Pvt. Ltd. Mumbai (India) was recrystallized from CHCl₃-MeOH before use. Dodecyl acrylate (GC 90%, Aldrich, India), styrene (99%, Sigma-Aldrich), 1-decene (95%, Acros organics) and methyl methacrylate (99%, Sigma-Aldrich) were used as received. Hexane (99.5%, S. d Fine Cheme Ltd.) and methanol (98%, Thomas Baker Pvt. Ltd.) were used after distillation. The mineral base oils BO1 and BO2 was collected from IOCL, Dhakuria, West Bengal, India and their properties were tested before experiment and given in the **table 3.4.1**.

3.4.2.2 Synthesis of the polymers

Preparation of homopolymer of castor oil (CO) and its copolymers with methyl methacrylate (MMA), dodecyl acrylate (DDA), 1- decene and styrene at a fixed concentration of 10% (w/w) of each was carried out in a four necked round bottom flask fitted with a magnetic stirrer, condenser, thermometer and an inlet for the introduction of nitrogen at 90 ° C for 6 hour by free radical pathway in the presence of toluene as solvent and AIBN (1%, w/w) as initiator. At the end of the reaction time, the reaction mixture was poured into methanol while the reaction mixture stirred to terminate the polymerization process and precipitate the

polymer. The polymers were further purified by repeated precipitation of their hexane solution by methanol followed by drying under vacuum at 40°C.

3.4.3 Measurements

3.4.3.1 Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range of 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

3.4.3.2 Molecular weight determination

The number average molecular weight (M_n) and weight average molecular weight (M_w) were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 35° C at a flow rate of 1mL/min.

3.4.3.3 Thermo gravimetric analysis (TGA)

TGA data was measured on Shimadzu TGA-50 system, at a heating rate of 10° C / min.

3.4.4 Performance evaluation

3.4.4.1 Evaluation of viscosity index (VI)

Viscosity index is an important parameter to determine the resistance of viscosity change of the lubricant with temperature variation. A higher VI value indicates smaller change in viscosity with temperature change. VI was calculated according to ASTM D 2270-10 in two types of base oils (BO1 and BO2). The kinematic viscosities which are used to calculate the VI values of the lubricant composition were determined at 40 ° C and 100 ° C. Additives at different concentrations ranging from 1% - 5% (w/w) were blended with the lube oil to study the effect of concentration of additives on VI.

3.4.4.2 Evaluation of pour point

The pour point of a liquid is the temperature at which it loses its flow characteristics. When a PPD is added to base oil, it decreases the pour point. Pour points of the additive doped base oils were determined according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India) in two types of base oil (BO1 and BO2). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging 1% - 5% (w/w).

3.4.4.3 Evaluation of tribological performance

The antiwear performance in terms of wear scar diameter (WSD) of the lube oil without and with additives at a concentration range of 1% - 5% (w/w) was evaluated by Four-ball wear

test apparatus (FBWT) following the ASTM D 4172-94 method. In this experiment 392 N (40 Kg) load at 75 ° C for 60 min was applied to measure the wear scar diameter (WSD). The diameter and rotating speed of the ball were 12.7 mm and 1200 rpm respectively.³¹

3.4.4.4 Biodegradability test

Biodegradability of the prepared polymers is carried out through soil burial test (SBT) method as per ISO 846:1997 standard.³² The soil sample was collected from North Bengal University campus having pH 7.2 and 25% moisture. Percentage weight loss (PWL) of the polymer samples after a definite interval of times was calculated to determine the extent of degradation which was also confirmed by observing the shift in IR frequency of the ester carbonyl groups after the test as well as change in molecular weight determined by GPC method. A film was prepared by taking about 2.0 g of each of the samples separately and then buried in soil. Then the soils with the samples are incubated in a Bacteriological Incubator apparatus (Sigma Scientific Instruments Pvt. Ltd., Chennai, India) at 30° C with relative humidity of 60% for 3 months and thus subjected to the action of microorganisms present in the soil. After each regular interval of 15 days, the soil sample is taken out and the polymer sample was recovered from it by dissolving in chloroform, filtered, dried and percentage of decomposition was measured.³¹

3.4.5 Results and discussion

3.4.5.1 Analysis of spectroscopic data

The absorptions at 1732, 1744.4, 1742, 1742 and 1739.5 cm⁻¹ for the homopolymer of CO (P-1), copolymer with MMA (P-2), DDA (P-3), 1- decene (P-4) and styrene (P-5) respectively, showed the presence of ester carbonyl group. The peaks ranging from 1452 to 1169 cm⁻¹ were due to C-O stretching vibration and the peaks from 2847 to 2931 cm⁻¹ were the stretching vibration of the paraffinic C-H bonds of -CH₃ and -CH₂- groups. Peaks at 724.4 cm⁻¹ and 699.8 cm⁻¹ were attributed to the C-H bond of the phenyl group of styrene (P-5). Peaks ranging from 3433.5 to 3443.4 cm⁻¹ were due to -OH group present in castor oil (**figure 3.4.1**). The ¹H NMR of homo and copolymer of castor oil showed broad peak in the range of 3.01 to 4.328 ppm due to -OCH₂ groups. The peaks appeared in the range of 2.31 to 2.98 represent the -OH groups of castor oil. Peaks appeared in the range of 0.51 to 1.30 ppm and 1.40 to 2.43 ppm indicates the methyl and methylene protons respectively. The peaks appeared in the range of 7.12 to 7.33 ppm indicate the protons of benzene ring of styrene moiety (P-5). The proton decoupled ¹³C NMR showed peaks at 164.31 to 177.41 ppm for ester carbons. The peaks appeared in the range of 51.72 to 68.87 ppm represent the carbons

of $-OCH_2$ groups. The peaks appeared in the range of 71.38 to 71.56 ppm indicate the carbons attached to the $-OH$ group. The peaks of all methyl and methylene carbons appear in the range of 14.02 to 41.30 ppm. The carbons of benzene ring showed peaks in the range of 125.35 to 132.89 ppm (for the polymer of P-5 only). (**Figures 3.3.6, 3.4.2, 3.4.3, 3.4.4, 3.4.5, 3.3.9, 3.4.6, 3.4.7, 3.4.8 and 3.4.9**)

3.4.5.2 Analysis of average molecular data

The experimental values of number average molecular weights (M_n), weight average molecular weights (M_w) and polydispersity indices (PDI) of the prepared polymers (P-1 to P-5) are given in **table 3.4.2**. From the experimental data, it is found that among the prepared five polymers, the copolymer P-5 (castor oil 90%, styrene 10%) has highest molecular weight followed by P-2 (castor oil 90%, MMA 10%). Homopolymer of castor oil (P-1) has lowest molecular weight among the five polymers. This signifies that when acrylate or styrene moiety is incorporated into the backbone of castor oil, the degree of polymerization increases.

3.4.5.3 Analysis of TGA data

The TGA values of the five polymers are given in **figure 3.4.10**. At 250 °C temperature the percentage weight loss of the polymers P-1 to P-5 are 21.56, 14.07, 19.46, 19.76 and 17.66 respectively. Whereas at 400 °C, the percentage weight loss of the polymers are 95.21, 73.05, 92.22, 93.42 and 78.44 respectively. The results are reflected in the figure 3.4.10 also. Among the five polymers, the homopolymer of castor oil (P-1) is thermally least stable and the polymer P-2 (castor oil 90% and MMA 10%) is thermally most stable followed by P-5. These TGA values confirm the suitability of the prepared additives as lubricating oil additives.

3.4.5.4 Analysis of viscosity index data

VI was calculated by dissolving the prepared polymers in two types of base oil (BO1 and BO2) in the concentration range of 1% - 5% (w/w). The experimental values of VI are given in **table 3.4.3**. From the experimental data, it is found that VI values increase with increasing the concentration of polymer in base oils. The lube oil viscosity decreases with increase in temperature but the expansion of polymer molecules takes place at high temperature due to increase the size of micelle. This increased in micelle size minimize the reduction of the viscosity of the polymer doped lube oil. At higher concentration, the total volume of polymer micelle in lube oil becomes higher and exerts higher thickening effect and improves the VI property.^{33, 34} Among the five polymers, polymer P-5 has higher effect on VI for both the

base oils followed by polymer P-2 and may be due to higher molecular weight distribution. Similar observation is already reported elsewhere.³⁵⁻³⁷

3.4.5.5 Analysis of pour point data

The polymer doped base oils (BO1 and BO2) at different concentration ranging from 1%–5% (w/w) were tested for pour point and experimental values are given in **table 3.4.4**. From the experimental values, it is found that all the prepared five polymers are effective as pour point depressant and the efficiency as pour point depressant (PPD) increases with increasing the concentration of polymer in both types of base oils (BO1 and BO2) up to 3% and after 3%, there is no any significant change in pour point. This indicates that at this concentration (3%) the effective interaction between the polymeric additives and paraffinic wax of base oil takes place and modifies the crystal size of waxes.³⁸⁻⁴⁰ Among the five polymers (P-1 to P-5), the polymer P-2 (CO, MMA) is more effective as PPD in both the base oils followed by P-3 (CO, DDA). The castor – acrylate copolymers (P-2 and P-3), due to their more polar character, interact strongly with paraffinic wax of base oil and disrupt the formation of wax crystals at low temperature.⁴¹ Among the four copolymers (P-2 to P-5), the polymer P-5 (castor, styrene) showed poor efficiency as PPD. It may be due to presence of phenyl group that reduces the adsorption of the additive molecule on the wax crystals.⁴² The homopolymer of castor oil (P-1) showed lower pour point but its efficiency as PPD is less than copolymers.

3.4.5.6 Analysis of tribological properties

The tribological properties of the lubricant compositions at different percentage composition (1% - 5%) were determined by measuring WSD values through FBWT apparatus applying 392 N load (40 kg) and shown in **figures 3.4.11** and **3.4.12**. The anti wear performance of the base oil is significantly improved when the additives are blended with it and is reflected in lower WSD values of the lubricant compositions. The WSD values gradually decrease with increasing the concentration of polymer doped base oil. Among the five polymers (P-1 to P-5), best performance as AW is observed in case of polymer P-2 (CO, MMA) followed by P-3 (CO, DDA). This indicates that the base oil blended with the polymer P-2 showed lowest values in WSD (39.92% and 44.95% in BO1 and BO2 oil respectively) followed by P-3 (36.35% and 43.61% in BO1 and BO2 oil respectively) at 5% (w/w/) concentration. The additives in lubricant composition form strong film between polar functional groups of the additives and metal surfaces through chemical and physical bonding.^{43 - 45} Due to presence of long hydrocarbon chain of the fatty acids and polar ester groups as well as polar hydroxyl group in CO, the polymers P-2 and P-3 form strong bond with metal atoms and exhibits

better AW property than polymer P-1, P-4 and P-5 which don't have any polar acrylate moiety. P-2 showed better AW property than P-3 and it may be due to more polarity of MMA than DDA.

3.4.5.7 Analysis of biodegradability test results

The results of SBT test are depicted in **figure 3.4.13**. From the SBT results, it was found that the degradation of the recovered samples taken every 15 days increases with increasing time. The homopolymer of castor oil (P-1) showed highest degradation and after 90 days' span the recovered sample showed 41.4% weight loss followed by P-3 (35.5% weight loss). Among the five polymers, P-5 showed least biodegradation and after 90 days' span the recovered sample showed 21.2% weight loss. Moreover, molecular weight of the recovered samples after 90 days of biodegradation was determined by GPC method and results (M_n and M_w values) were compared with the respective samples before biodegradation and given **table 3.4.5**. The IR spectra of the recovered samples after biodegradation are given in **figure 3.4.14**. Therefore, the lube oil additives prepared from castor oil has a significant biodegradation which is very important from the point view of green chemistry.

3.4.6 Conclusions

From the above study it was found that the homo and copolymers of castor oil showed better performance as viscosity index improver, pour point depressant and antiwear additive for lubricating oil. The copolymers P-2 and P-3 were found more efficient as PPD and AW. The oxy-rich property of castor oil molecules along with polar ends of acrylate moiety are the key reasons for exhibiting better PPD and AW performance of the polymeric additives P-2 and P-3. On the other hand, P-5 was found more efficient as VII than other polymers. The higher cross link density and higher molecular weight of the copolymer P-5 is responsible for showing higher viscosity index values. Moreover, due to better biodegradability the additives are environmentally benign also. Therefore, the above study is definitely a potential approach to formulate a cost effective and sustainable lubricant composition.

3.3.7 References

References are given in bibliography section of Chapter IV of Part III (Page No. 202 - 205).

3.3.8 Tables and figures

Table 3.4.1 Physical properties of the base oils

Base oil properties	<u>Base oil</u>	
	BO1	BO2
Density (g cm ⁻³) at 40 °C	0.83	0.84
Viscosity at 40 °C in c St	7.102	23.502
Viscosity at 100 °C in c St	1.850	3.98
Viscosity index	84.56	85.15
Pour point (°C)	-3	-6
Cloud point (°C)	-1	-4

Table 3.4.2 Polymer code, monomers, monomers ratio, molecular weight values of the polymers P-1, P-2, P-3, P-4 and P-5

Polymer code no.	Monomers	Monomer ratio(w/w)	<u>Molecular weight</u>		
			M _n	M _w	PDI
P-1	CO	-	7928	10022	1.26
P-2	CO, MMA	9:1	40879	50979	1.25
P-3	CO, DDA	9:1	17579	28736	1.64
P-4	CO, Dec	9:1	17824	24588	1.38
P-5	CO, Sty	9:1	40991	63691	1.55

CO = Homo polymer of Castor oil; MMA = methyl methacrylate; DDA = dodecyl acrylate; Dec = 1-decene; Sty = styrene; M_n = number average molecular weight; M_w = Weight average molecular weight; PDI = Polydispersity index

Table 3.4.3 Viscosity Index (VI) of polymer doped base oil

Polymer code	VI in BO1						VI in BO2					
	Concentration of the polymer (% in w/w)						Concentration of the polymer (% in w/w)					
	0	1	2	3	4	5	0	1	2	3	4	5
P-1	84.6	95	99.5	110.8	114	121	85.2	90.5	95.8	102	114	118
P-2	84.6	98.4	106	118	124.6	136	85.2	96.4	99	112	121	134
P-3	84.6	96.8	105	116	122	130	85.2	95.8	100	109	116	128
P-4	84.6	96	104	110	122.6	128	85.2	95	101	108	114	125
P-5	84.6	100	122.4	125	132	138	85.2	99.4	108	121	128	138

Table 3.4.4 Pour point values of polymer doped base oil

Sample Code	Pour point ($^{\circ}\text{C}$) in BO1						Pour point ($^{\circ}\text{C}$) in BO2					
	Concentration of the polymer (% in w/w)						Concentration of the polymer (% in w/w)					
	0	1	2	3	4	5	0	1	2	3	4	5
P-1	-3	-6	-8	-8	-7	-7	-6	-9	-10	-11	-10.5	-10
P-2	-3	-11	-13	-13.5	-12	-12	-6	-15	-16.5	-17	-17	-16
P-3	-3	-11	-12	-13	-12	-11	-6	-14	-16	-16.5	-16	-15
P-4	-3	-9	-10	-10	-10	-10	-6	-12	-14	-14.5	-14	-13
P-5	-3	-8	-8	-8	-7	-7	-6	-10	-12	-12	-12	-11

Table 3.4.5 Comparative molecular weight (determined by GPC)

Polymer code	Before biodegradation		After biodegradation	
	M_n	M_w	M_n	M_w
P-1	7928	10022	5822	7105
P-2	40879	50979	39172	48491
P-3	17579	28736	15768	26114
P-4	17824	24588	16205	22190
P-5	40991	63691	39432	61513

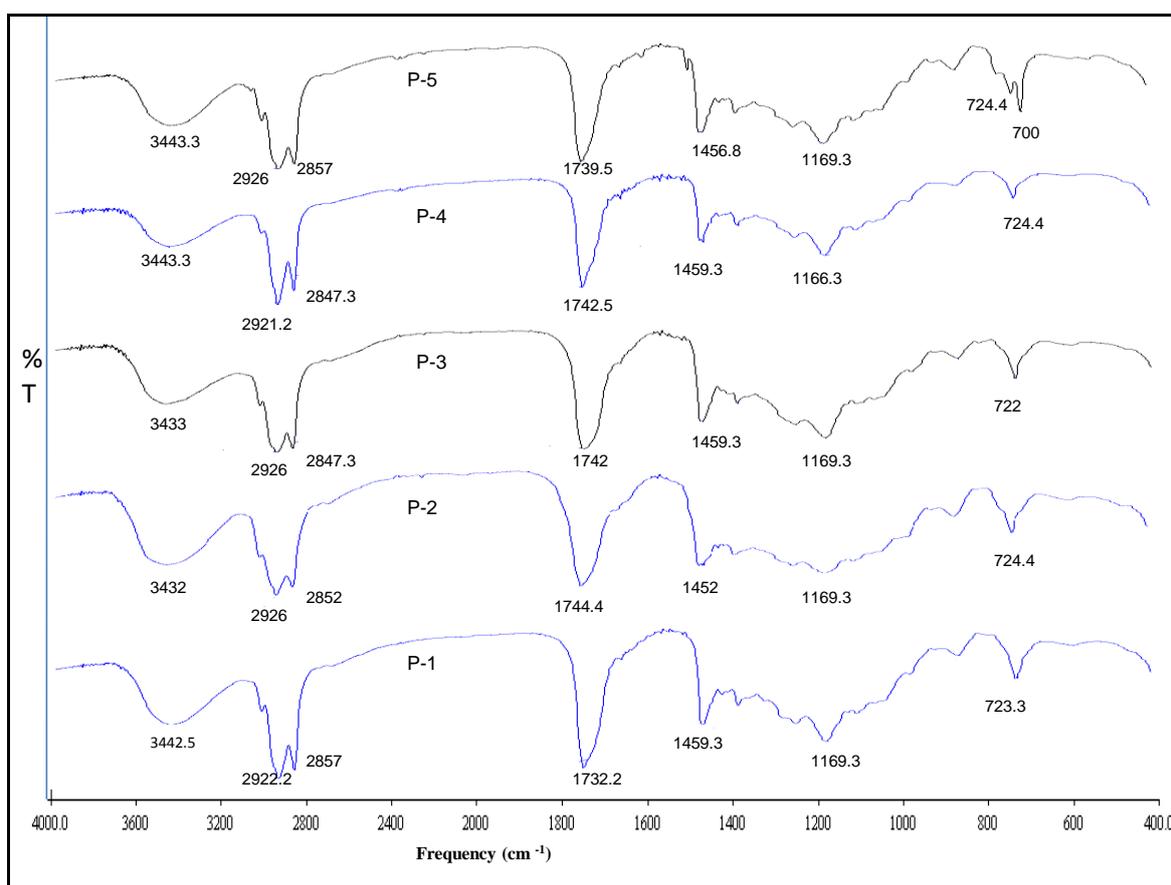


Figure 3.4.1 IR spectra of polymer P-1, P-2, P-3, P-4 and P-5

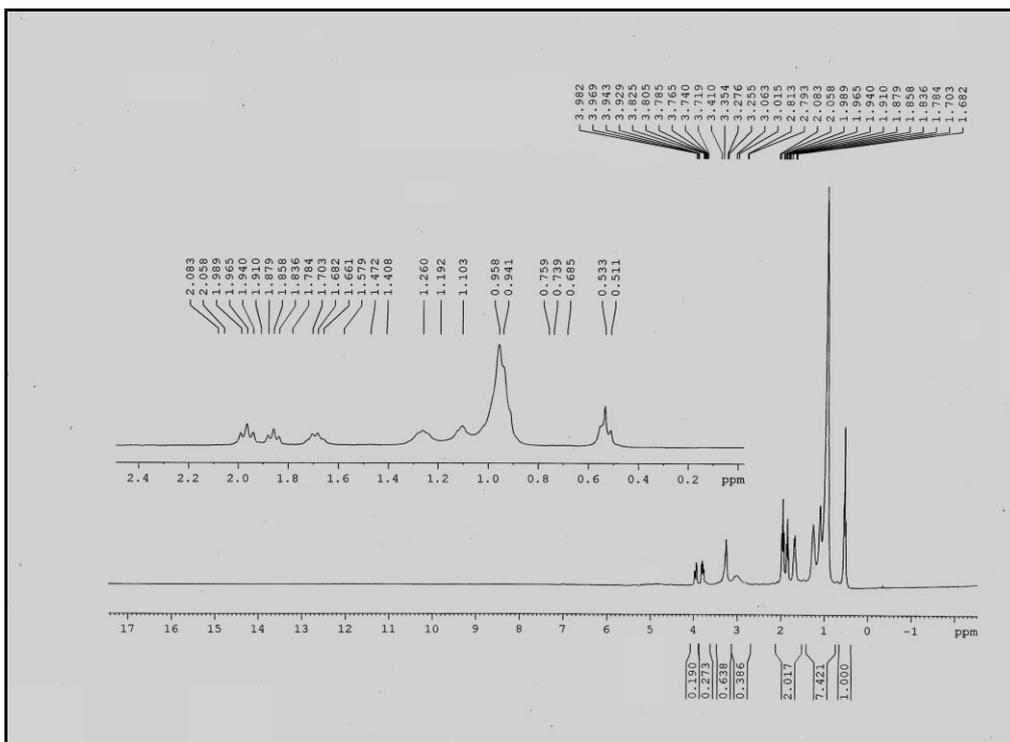


Figure 3.4.2 ^1H NMR spectra of P-2

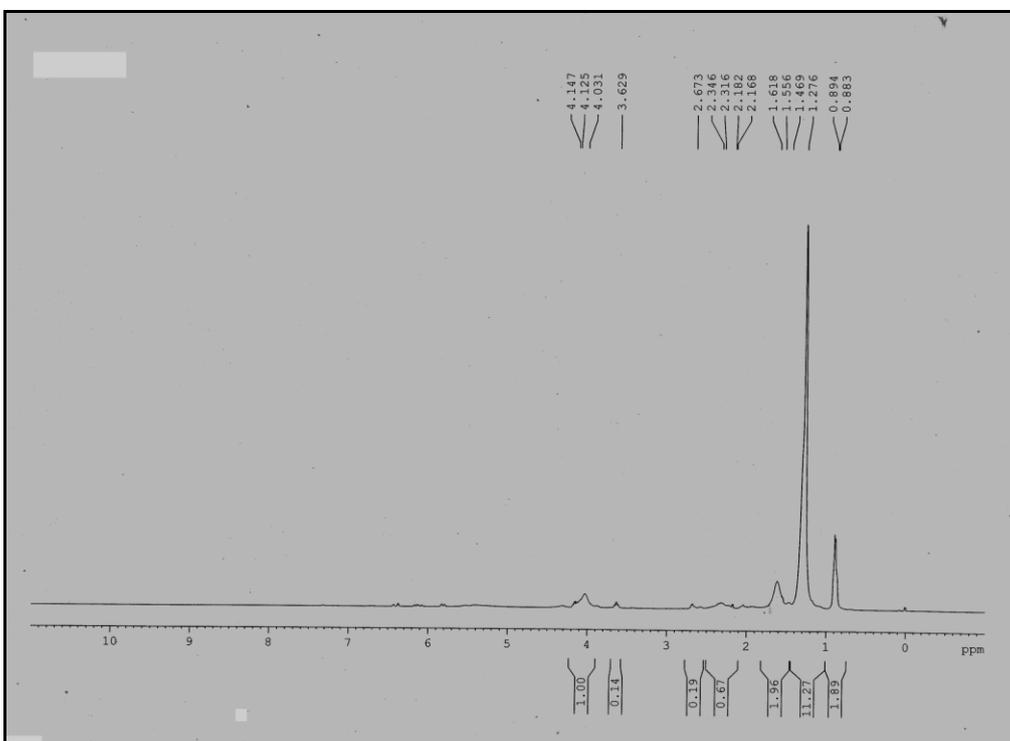


Figure 3.4.3 ^1H NMR spectra of P-3

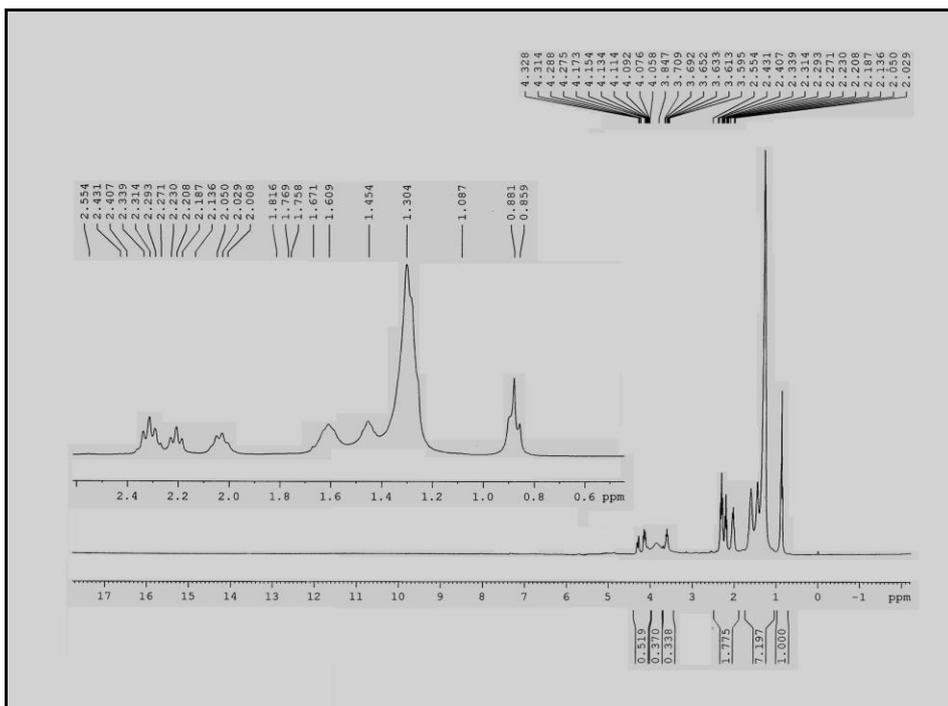


Figure 3.4.4 ^1H NMR spectra of P-4

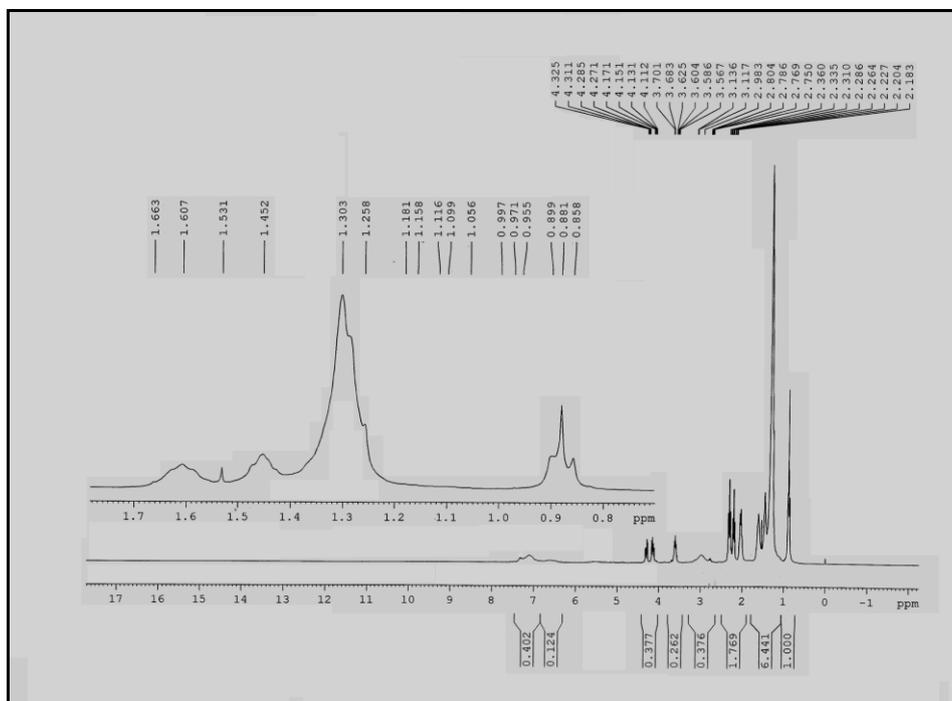


Figure 3.4.5 ^1H NMR spectra of P-5

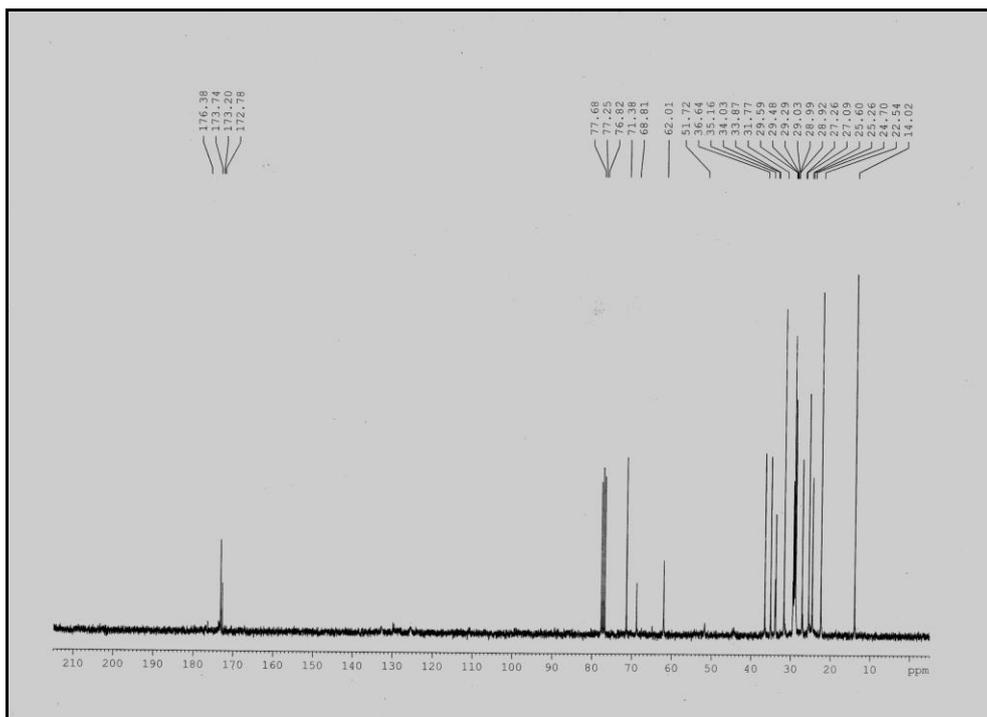


Figure 3.4.6 ^{13}C NMR spectra of P-2

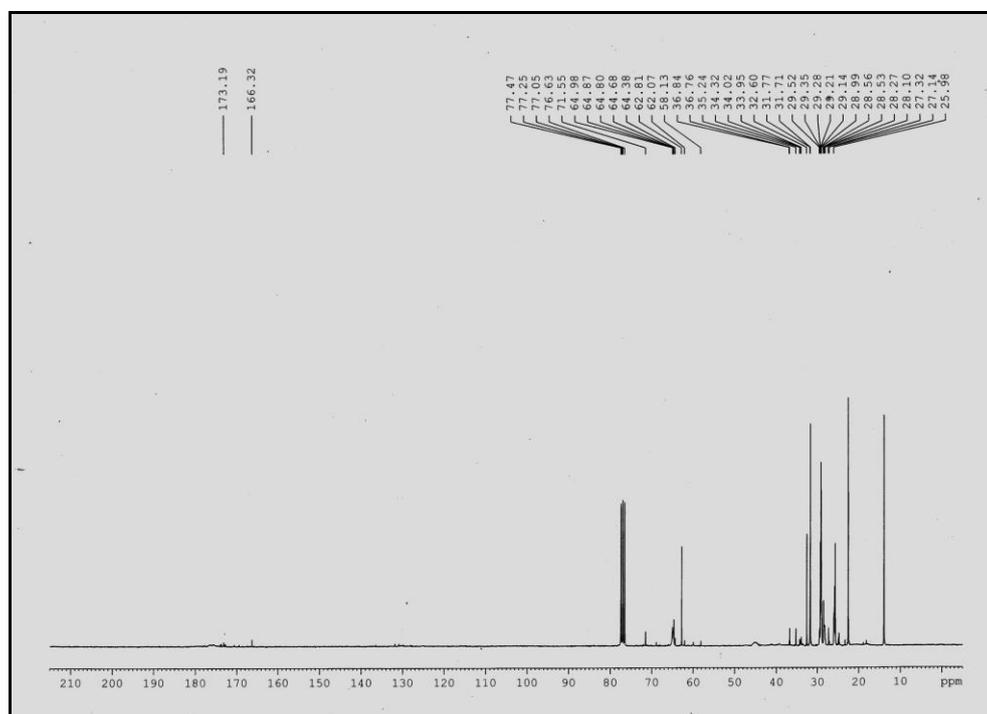


Figure 3.4.7 ^{13}C NMR spectra of P-3

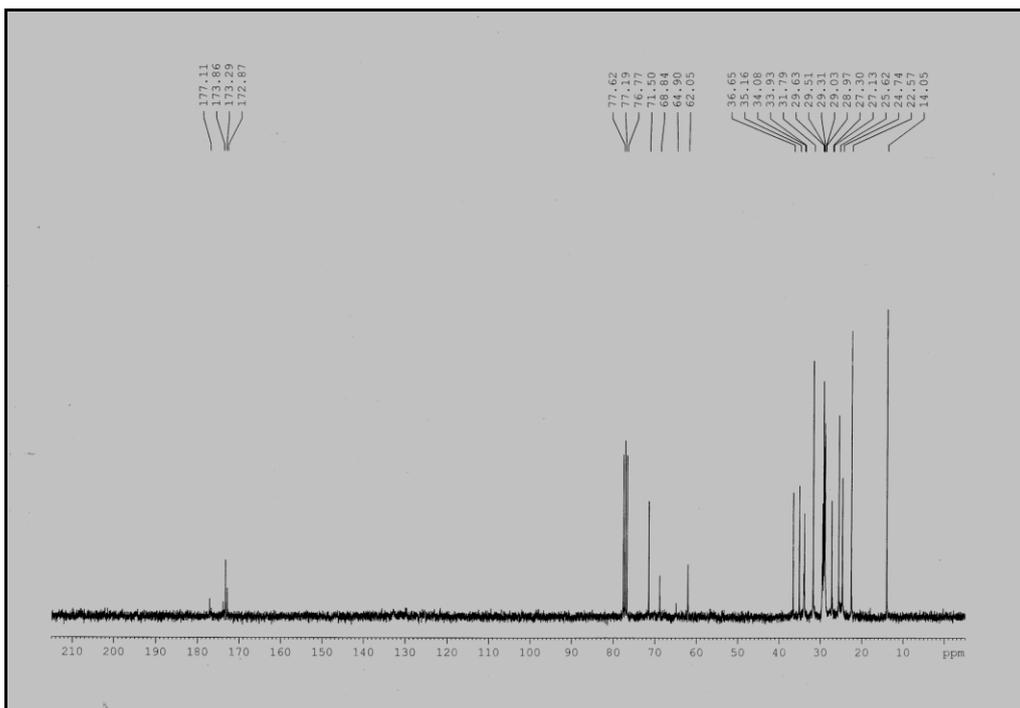


Figure 3.4.8 ^{13}C NMR spectra of P-4

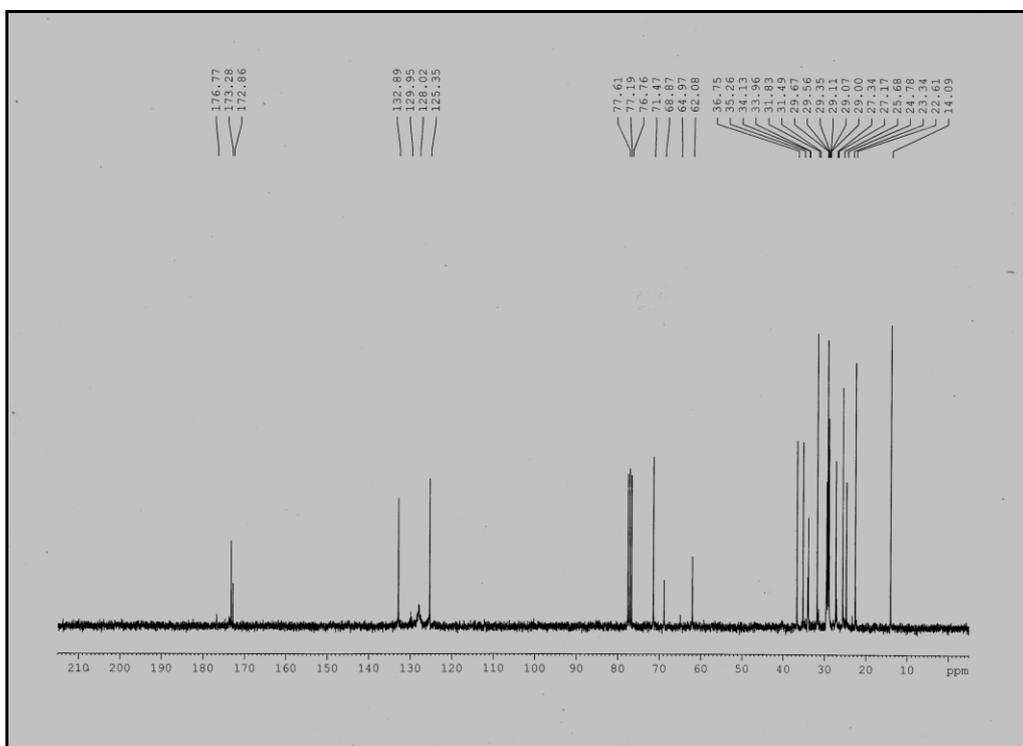


Figure 3.4.9 ^{13}C NMR spectra of P-5

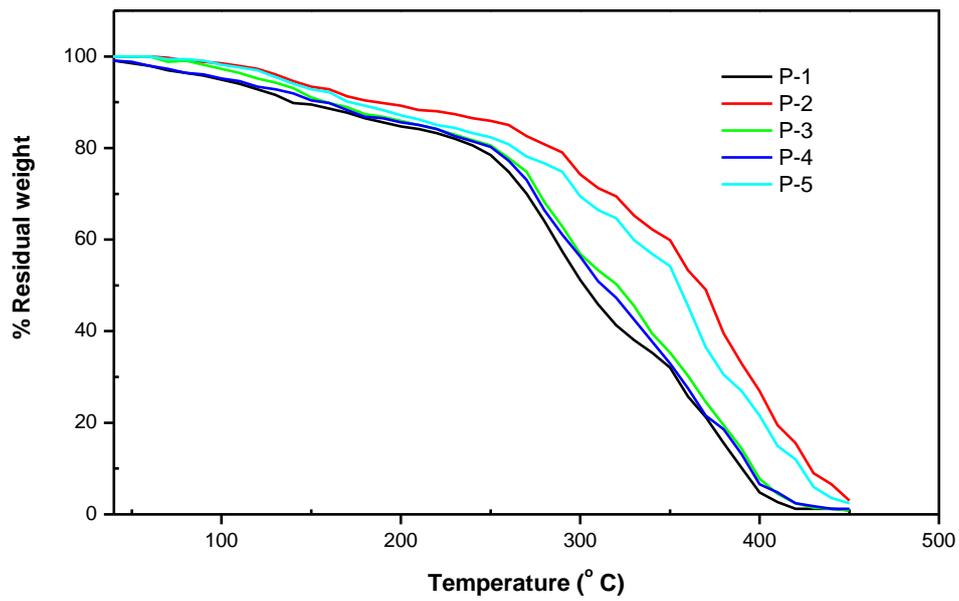


Figure 3.4.10 Thermal degradation of the prepared polymers P-1, P-2, P-3, P-4 and P-5

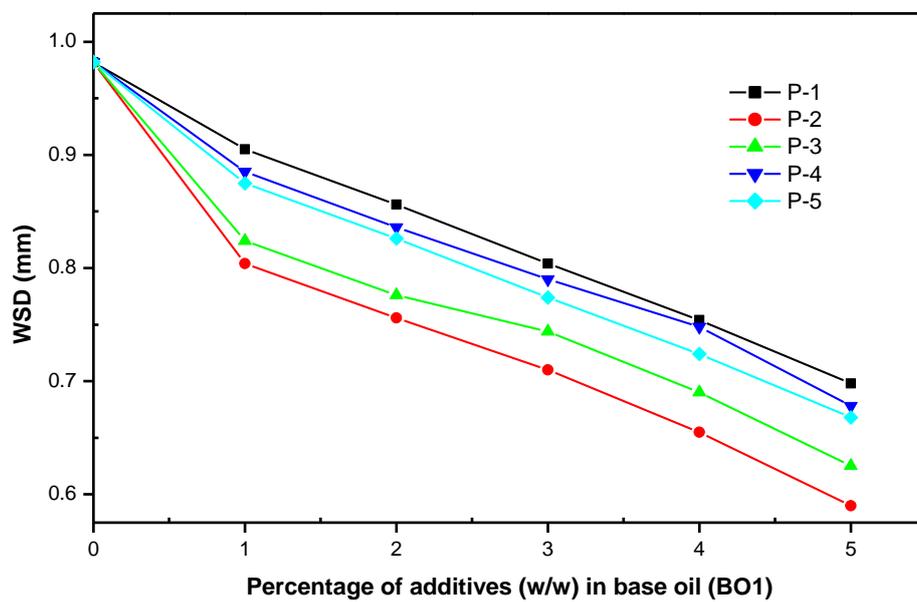


Figure 3.4.11 Wear scar diameter (WSD) of the base oil (BO1) blended with additives at different percentages (w/w) compositions

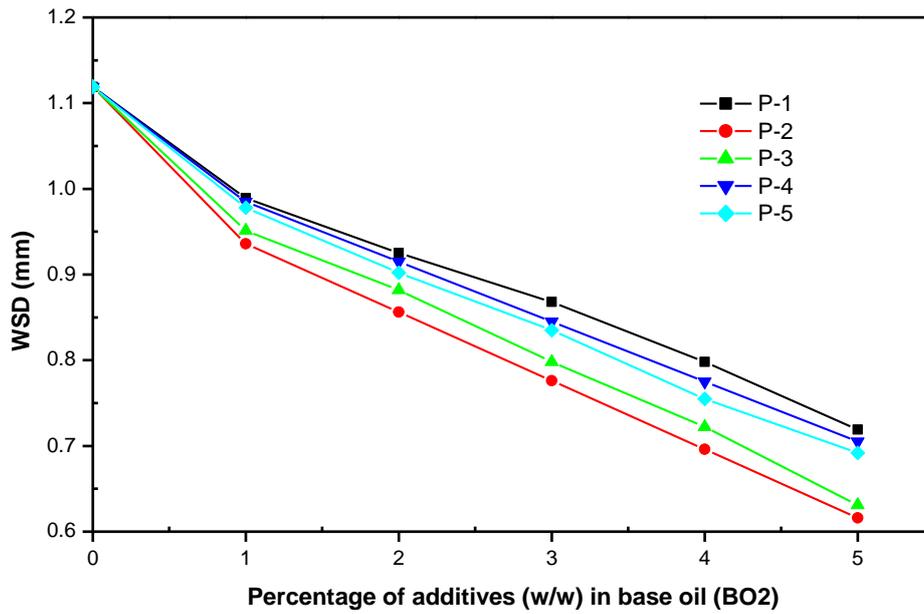


Figure 3.4.12 Wear scar diameter (WSD) of the base oil (BO2) blended with additives at different percentages (w/w) compositions

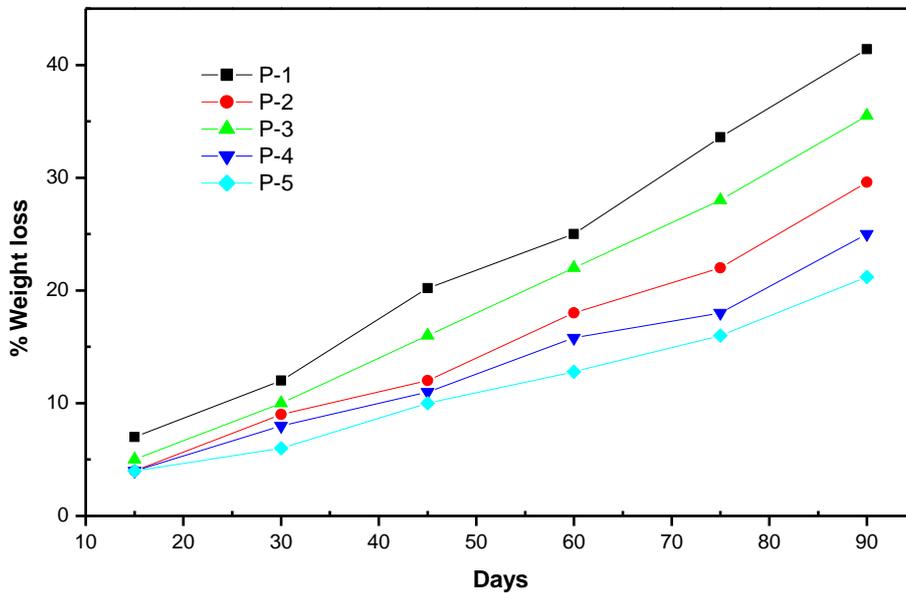


Figure 3.4.13 Results of biodegradability test (SBT) of the prepared additives

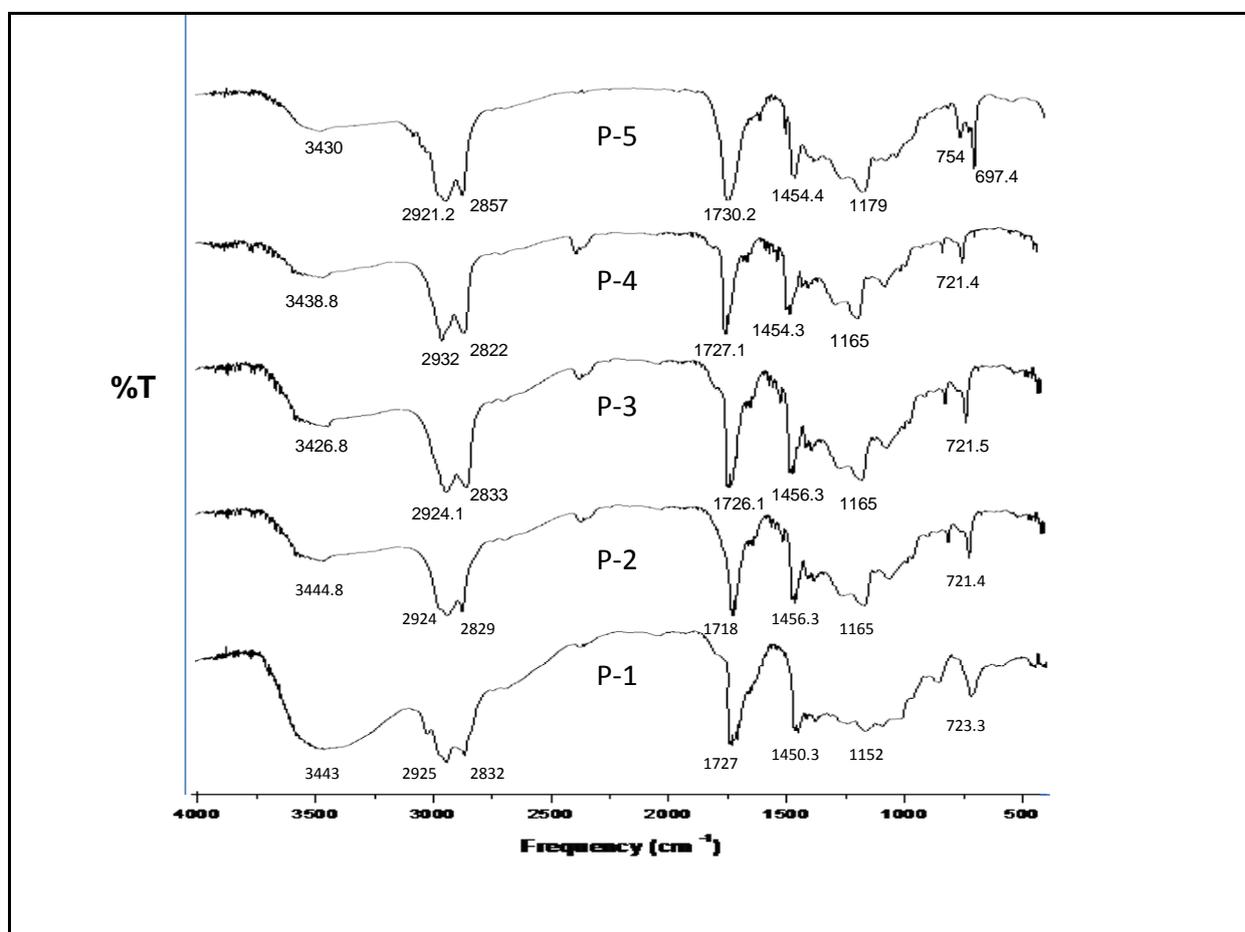


Figure 3.4.14 IR spectra of polymers P-1, P-2, P-3, P-4 and P-5 after biodegradable

BIBLIOGRAPHY

General introduction of the present investigation

1. Hsu, S. M. Molecular basis of lubrication. *Tribol. Int.* **2004**, 37(7), 553-559.
2. Bataille, P.; Sharifi-Sanjani, N.; Evin, E. Preparation and characterization of viscosity index improver for naphthenic and paraffinic base oils. *J. Sol. Chem.* **1994**, 23(2), 325-338.
3. Khonsari, M. M.; Booser, E. R. Applied Tribology: Bearing Design and Lubrication. John Wiley & Sons, New York, NY, **2001**.
4. Rudnick, L. R. Lubricant additives: Chemistry and Application, CRC press, **2003**.
5. Mortier, R. M.; Fox, M. F.; Orszulik, S. T. Chemistry and technology of lubricants. 3rd ed. Dordrecht, Springer, **2010**, 167-180.
6. Rizvi, S. Q. A. A comprehensive review of lubricant chemistry, technology, selection and design. ASTM international, West Conshohocken, PA., **2009**, 100-112.
7. Onyeji, L. I.; Aboje, A. A. The effect of additive on the viscosity index of lubricating oil (engine oil). *Int. J. Eng. Sci. Tech.* **2011**, 3(3), 1864-1869.
8. Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. Synthesis and evaluation of acrylate polymers in lubricating oil. *J. Chem. Eng. Data* **2011**, 56, 3752-3758.
9. Denis, J. Pour point depressants in lubricating oils. *Lubr. Sci.* **1989**, 1(2), 131-147.
10. Florea, M.; Catrinou, D.; Luca, P.; Balliu, S. The chemical composition on the pour point depressant properties of methacrylate copolymers used as additives for lubricating oils. *Lubr. Sci.* **1999**, 12(1), 31-44.
11. Soni, H. P.; Kiranbala; Bharambe, D. P. Performance- based on designing of wax crystal growth inhibitors. *Energy Fuels* **2008**, 22, 3930-3938.
12. Castro, L. V.; Vazquez, F. Copolymers as flow improvers for Mexican crude oil. *Energy Fuels* **2008**, 22, 4006-4011.
13. Garcia, M. C; Carbognani, L.; Urbina, A.; Orea, M. Paraffin deposition in oil production. oil composition and paraffin inhibitors activity. *Pet. Sci. Technol.* **1998**, 16, 1001-1021.

14. Al-Shafy, H. I.; Ismail, E. A. Studies on the influence of polymeric additives as flow improvers for waxy crude oil. *IOSR J. Eng.* **2014**, 4, 54-61.
15. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, 21, 19-30.
16. El-Gamal, I. M.; Atta, A. M.; Al- Sabbagh, A. M. Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* **1997**, 76, 1471-1478.
17. Ghosh, P.; Hoque, M. Synthesis and performance evaluation of vinyl acetate-maleic anhydride based polymeric additives for lube oil. *Pet. Sci. Technol.* **2015**, 33, 1182-1189.
18. Karmakar, G.; Ghosh, P. Green additives for lubricating oil. *ACS Sustainable Chem. Eng.* **2013**, 1, 1364-1370.
19. Ghosh, P.; Upadhyay, M.; Das, M. K. Studies on the additive performance of liquid crystal blended polyacrylate in lubricating oil. *Liq. Cryst.* **2014**, 41(1), 30-35.
20. Masabumi, M.; Hiroyasu, S.; Akihito, S.; Osamu, K. Prevention of oxidative degradation of ZnDTP by microcapsulation and verification of its antiwear performance. *Tribol. Int.* **2008**, 41, 197-204.
21. Otero, I.; López, E. R.; Reichelt, M.; Villanueva, M.; Salgado, J.; Fernández, J. Ionic liquids based on phosphonium cations as neat lubricants or lubricant additives for a steel/steel contact. *ACS Appl. Mater. Interfaces* **2014**, 6, 13115–13128.
22. Li, B.; Wang, X.; Liu, W.; Xue, Q. Tribochemistry and antiwear mechanism of organic –inorganic nanoparticles as lubricant additives. *Tribol. Lett.* **2006**, 22, 79-84.
23. Quinchia, L. A.; Delgado, M. A.; Reddyhoff, T.; Gallegos, C.; Spikes; H. A. Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers. *Tribol. Int.* **2014**, 69, 110–117.
24. Ahmed, N. S.; Nassar, A. M.; Abdel-Azim, A. A. A. Synthesis and evaluation of some detergents/dispersant additives for lube oil. *Int. J. Polym. Mater.* **2008**, 57, 114-124.
25. Smalheer, C. V.; Smith, R. K. “Lubricant Additives” Cleveland, Lensins-Hiles Co. **1967**.

26. Alema-Vazquez, L. O.; Villagomez-Ibarra, J. R. Polyisobutenylsuccinimides as detergents and dispersants in fuel: infrared spectroscopy application. *Fuel*, **2001**, 80, 965-968.
27. Ghosh, P.; Hoque, M. Mannich bases and phosphosulphurized Mannich bases: Synthesis characterization and performance evaluation as potential lube oil additives. *J. Sci. Ind. Res.* **2015**, 74, 150-154.
28. Abdel-Azim, A.; Nasser, A. M.; Ahmed, N. S.; Kamal, R. S. Multifunctional lube oil additives based on octadecene-maleic anhydride copolymer. *Pet. Sci. Technol.* **2011**, 29, 97–107.
29. Forbes, E. S.; Neustadter, E. L. The mechanism of action of polyisobutenyl succinimide lubricating oil additives. *Tribol. Int.* **1972**, 5(2), 72-77.
30. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Tech.* **2006**, 13, 398-403.
31. Changqiao, Z.; Congcong, G.; Fengfeng, G.; Jian, W.; Dawei, Z.; Yan, W.; Dawei, X. Synthesis of comb bipolymers and their pour point depressing properties. *J. Pet. Sci.* **2014**, 11, 155-160.
32. Latyshev, V. N.; Novikov, V. V.; Syrbu, S. A.; Kolbashov, M. A. Tribological properties of some cholesterical liquid-crystal additives. *J. Fric. Wear.* **2009**, 30(6), 411–414.
33. Ahmed, N. S.; Nassar, A. M.; Nasser, R. M.; Khattab, A. F.; Abdel-Azim, A. A. Synthesis and evaluation of some polymers as lubricating oil additives. *J. Dis. Sci. Technol.* **2012**, 33, 668-675.
34. Cai, G.; Zhang, L.; Ma, L.; Eli, W. Synthesis and characterization of polybutylacrylate viscosity index improver with anti-wear function. *Lubr. Sci.* **2015**, 27(4), 209-216.
35. Nassar, A. M.; Ahmed, N. S.; Abdel –Aziz, K. I.; El-Kafrawy, A. F.; Abdel-Azim, A. A. Synthesis and evaluation of detergent/dispersant additives from polyisobutylene succinimides. *Int. J. Polym. Mater.* **2006**, 55, 703–713.
36. Regueira, T.; Lugo, L.; Fandino, O.; Lopez, E. R.; Fernandez, J. Compressibilities and viscosities of reference and vegetable oils for their use as hydraulic fluids and lubricants. *Green Chem.* **2011**, 13, 1293-1302.
37. Ertugrul, D.; Filiz, K. Using cotton seed oil as an environmentally accepted lubricant additive. *Energy Sources.* **2004**, 26, 611-625.

38. Maleque, M. A.; Masjuki, H. H.; Sapuan, S. M. Vegetable based biodegradable lubricating oil additive. *Ind. Lubr. Tribol.* **2003**, 55(3), 137-143.

Part I

Chapter I

1. Mortier, R. M.; Fox, M. F.; Orszulik, S. T. Chemistry and Technology of Lubricants, 3rd edition. Springer publication, **2011**.
2. Pirro, D. M.; Wessol, A. A. Lubricants Fundamentals. New York: Marcel Dekker, **2001**, 37-43.
3. Wu, C.; Zang, J.; Li, W.; Wu, N. Molecular dynamics simulation guiding the improvement of EVA-type pour point depressant. *Fuel* **2005**, 84, 2039-2047.
4. Santos, J. C. O.; Santos, I. M. G.; Souza, A. G.; Sobrinho, E. V.; Fernandes V. J.; Silva, Jr. A. J. N. Thermoanalytical and rheological characterization of automotive mineral lubricants after thermal degradation. *Fuel* **2004**, 83, 2393-2399.
5. Xiangqiong, Z.; Heyang, S.; Wenqi, R.; Zhongyi, H.; Tianhui, R. Tribological study of trioctylthiotriazine derivative as lubricating oil additive. *Wear* **2005**, 258, 800-805.
6. Kajdas, C.; Majzner, M. Effectiveness of selected CHO compounds as antiwear additives to white mineral oils. *Tribol. Transac.* **2005**, 48, 93-99.
7. Aleman-Vazquez, L. O.; Villagomez-Ibarra, J. R. Polyisobutenylsuccinimides as detergents and dispersants in fuel: infrared spectroscopy application. *Fuel* **2001**, 80, 965-968.
8. Zhongyi, H.; Jinliang, L.; Xiangqiong, Z. Study of the tribological behaviours of S, P-containing triazine derivatives as additives in rapeseed oil. *Wear* **2004**, 257, 389-394.
9. Barnes, A. M.; Bartel, K. D.; Thibon, V. R. A. A review of zinc dialkyldithiophosphates (ZDDPS): Characterization and role in lubricating oil. *Tribol. Int.* **2001**, 34, 389-395.
10. Kapur, G. S.; Sarpal, A. S.; Mazumdar, S. K.; Jain, S. K.; Srivastava, S. P.; Bhatnagar A. K. Structure - performance relationships of viscosity index improvers: Micro structural determination of olefin copolymers by NMR spectroscopy. *Lubr. Sci.* **1995**, 8, 49-60.
11. Dean, E. W.; Baner, A. D.; Berglund, J. H. Viscosity index of lubricating oils. *Ind. Eng. Chem.* **1940**, 32, 102-107.

12. Eckert, R. J. A.; Covey, D. F. Developments in the field of hydrogenated diene copolymer as viscosity index improvers. *5th International Colloquium*, Technische Akademie, Esslingen, **1986**.
13. Abdel-Azim, A. A.; Huglin, M. B. Selective solvation of polystyrene in tetralin/cyclohexane mixtures. *Polymer* **1983**, 24, 1308-1312.
14. Abdel-Azim, A. A.; Huglin, M. B. *Proceedings of the second Egyptian conference of chemical engineering*, Cairo, Egypt, **1984**, March 18–20, 117–123.
15. Eckert, R. J. A.; Covey, D. F. Developments in the field of hydrogenated diene copolymers as viscosity index improvers. *Lubr. Sci.* **1988**, 1, 65–80.
16. Garcia, M. C.; Carbognani, L.; Urbina, A.; Orea, M. Paraffin deposition in oil production, oil composition and paraffin inhibitors activity. *Pet. Sci. Technol.* **1998**, 16, 1001-1021.
17. Huiyang, Z.; Weibang, Z.; Zhuomei, L. Synthesis of polymers with long side chain of *N*-alkyl esters and their effects on pour-point depression of oil. *J. Appl. Polym Sci.* **1991**, 43, 919-924.
18. Stohr, T.; Eisenberg, B.; Mullar, M., A new generation of high performance viscosity modifiers based on comb polymers. *SAE Int. J. Fuels Lubr.* **2009**, 1, 1511-1516.
19. Wuhua, C.; Zongchang, Z.; Caoyong, Y. The interaction of waxes with pour point depressants. *Fuel* **2010**, 89, 1127-1132.
20. Nasser, A. M. The behaviour of some acrylate copolymers as lubricating oil additives. LAP LAMBERT Academic Publishing, Germany, **2012**.
21. Florea, M.; Catrinou, D.; Luca, P.; Balliu, S. The influence of chemical composition on the pour-point depressant properties of methacrylate copolymers used as additives for lubricating oil. *Lubr. Sci.* **1999**, 12, 31-44.
22. Ghosh, P.; Das, T.; Das, M. Evaluation of poly (acrylates) and their copolymer as viscosity modifiers. *Res. J. Chem. Sci.* **2011**, 1, 18-25.
23. Ghosh, P.; Das, M. Study of the influence of some polymeric additives as viscosity index improvers and pour point depressants – synthesis and characterization. *J. Pet. Sci. Eng.* **2014**, 119, 79–84
24. Ruehrwein, R. A. *World Petroleum Congress, Prac.*, 3rd Congr. Hague, **1951**.
25. El-Gamal, I. M.; Atta, A. M.; Al-Sabbagh, A. M. Polymeric structures as a cold flow improvers for waxy residual fuel oil. *Fuel* **1997**, 76, 1471-1478.

26. El-Ghazawy, R. A.; Farag, R. K. Synthesis and characterization of novel pour point depressants based on maleic anhydride –alkyl acrylate terpolymers. *J. Appl. Polym. Sci.* **2010**, 115, 72-78.
27. Van Horne, W. L. Polymethacrylates as viscosity index improvers and pour point depressants. *Ind. Eng. Chem.* **1949**, 41, 952-959.
28. Jukic, A.; Rogosic, M.; Vidovic, E. Thermal stability of lubricating oil additives based on styrene and n-alkyl methacrylate terpolymers. *Polym.-Plastic Technol. Eng.* **2010**, 49, 74-77.
29. Nassar, A. M. The behaviour of polymers as viscosity index improvers. *Pet. Sci. Technol.* **2008**, 26, 514-522.
30. Jung, K-M.; Chun, B-H.; Park, S. H.; Chang, H. L.; Kim, S. H. Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricating oil. *J. Appl. Polym. Sci.* **2011**, 120, 2579-2586.
31. Jerbic, I. S.; Vukovic, J. P.; Jukic, A. Production and application properties of dispersive viscosity index improvers. *Ind. Eng. Chem. Res.* **2012**, 51, 11914-11923.
32. Mohammed, M. F.; Mahdi-Abd, M. Effect of temperature on lubricating oil and poly(methyl methacrylate) additive. *Diyala J. Eng. Sci.* **2012**, 5, 205-220.
33. Abdel-Azim, A. A. A.; Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. *Pet. Sci. Technol.* **2006**, 24, 887-894.
34. Jukic, A.; Vidovic, E.; Janovic, Z. Alkyl methacrylate and styrene terpolymers as lubricating oil viscosity index improvers. *Chem. Tech. Fuels Oils* **2007**, 43, 386-394.

Chapter II

1. Braga, J. W. B.; Junior dos Santos, A. A.; Martins, I. S. Determination of viscosity index in lubricant oils by infrared spectroscopy and PLSR. *Fuel* **2014**, 120, 171–178.
2. Soldi, R. A.; Oliveira, A. R. S.; Barbosa, R. V.; Cesar-Oliveira, M.A.F. Polymethacrylates: Pour point depressants in diesel oil. *Eur. Polym. J.* **2007**, 43, 3671–3678.
3. Ghosh, P.; Upadhyay, M.; Das, M. K. Studies on the additive performance of liquid crystal blended polyacrylate in lubricating. *Liq. Cryst.* **2014**, 41, 30–35.
4. Najman, M.; Kasrai, M.; Bancroft, G. M.; Davidson, R. Combination of ashless antiwear additives with metallic detergents: Interactions with neutral and overbased calcium sulphonates. *Tribol. Int.* **2006**, 39, 342-355.

5. Dean, E. W.; Davis, G. H. B. Viscosity variations of oils with temperature. *Chem. Met. Eng.* **1929**, 36, 618-619.
6. Akhmedov, A. I. Copolymer of alkyl methacrylates with styrene as viscosity index improvers for lubricating oils. *Chem. Tech. Fuels Oils* **1994**, 30, 34-37.
7. Mohamada, S. A.; Ahmed, N. S.; Hassanein, S. M.; Rashad, A. M. Investigation of polyacrylates copolymers as lube oil viscosity index improvers. *J. Pet. Sci. Eng.* **2012**, 100, 173–177.
8. Ahmed, N. S.; Nassar, A. M.; Nasser, R. M.; Khattab, A. F.; Abdel-Azim, A. A. A. Synthesis and evaluation of some polymeric compounds as pour point depressants and viscosity index improvers for lube oil. *Pet. Sci. Technol.* **2008**, 26, 1390–1402.
9. Ghosh, P.; Pantar, A. V.; Rao, U. S.; Sarma, A. S. Shear stability of polymers used as viscosity modifiers in lubricating oils. *Ind. J. Chem. Technol.* **1998**, 5, 309–314.
10. Denis, J. Pour point depressants in lubricating oils. *Lubr. Sci.* **1989**, 1, 131-147.
11. Florea, M.; Catrinoiu, D.; Luca, P.; Ballius, S. The influence of chemical composition on the pour point depressant properties of methacrylate copolymers used as additives for lubricating oil. *Lubr. Sci.* **1999**, 12, 31-44.
12. Khidr, T. T. The effect of commercial additives as pour point depressants for fuel oils. *Pet. Sci. Technol.* **2015**, 33, 975–983.
13. Zhang, H.; Liu, H.; Wang, S. A new alternating copolymerized derivative as a cold flow improver for diesel fuel. *J. Pet. Sci.* **2009**, 6, 82-85.
14. Rogosic, M.; Mencer, H. J.; Gomzi, Z. Polydispersity index and molecular weight distributions of polymers. *Eur. Polym. J.* **1996**, 32, 1337–1344.
15. Ghosh, P.; Das, T.; Nandi, D. Shear stability and thickening properties of homo and copolymer of methyl methacrylate. *American J. of polym. Sc.* **2011**, 1, 1-5.
16. Brahman, D.; Sinha, B. Partial molar volumes and viscosity *B*-coefficients of N, N'-Ethylene - bis(salicylideneiminato) cobalt (II) in binary mixtures of 1,4 dioxane + methanol at T= (298.15, 303.15, 308.15, 313.15) K. *J. Chem. Eng. Data*, **2011**, 56, 3073-3082.
17. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Tech.* **2006**, 13, 398-403.
18. Czech, Z.; Kowalczyk, A.; Kabatc, J.; Swiderska, J. Thermal stability of poly (2-ethyl hexyl acrylate) used as plasticizers for medical applications. *Polym. Bull.* **2013**, 70, 1911-1918.

19. Satapathy, H.; Banthia, A. K. Synthesis, characterisation, monomer reactivity ratio and thermal stabilities of homo and copolymers of 4-nonylphenyl methacrylate with styrene. *Pigm. Resin Technol.* **2007**, 36, 335-343.
20. Pourhossaini, M. R.; Farahani, E. V.; Gholamin, M.; Gholamin, M. Synthesis and characterization of olefin copolymers as viscosity modifier for engine oil. *Iranian Polym. J.* **2005**, 14, 549-557.
21. Nassar, A. M.; Ahmed, N. S.; Kamal, R. S.; Abdel-Azim, A. A. A. Preparation and evaluation of acrylate polymers as viscosity index improvers for lube Oil. *Pet. Sci. Technol.* **2005**, 23, 537-546.
22. Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. Synthesis and evaluation of acrylate polymers in lubricating oil. *J. Chem. Eng. Data* **2011**, 56, 3752-3758.
23. Nassar, A. M.; Ahmed, N. S.; Kamal, R. S.; Abdel-Azim, A. A. A.; El-Nagdy, E. I. Preparation and evaluation of acrylate polymers as viscosity index improves for lube oil. *Pet. Sci. Technol.* **2005**, 23, 537-546.
24. Jukic, A.; Vidovic, E.; Janovic, Z. Alkyl methacrylate and styrene terpolymers as lubricating oil viscosity index improvers. *Chem. Tech. Fuels Oils* **2007**, 43, 386-394.
25. Ghosh, P.; Talukdar, S. Studies on thermal and microwave assisted synthesis of polymyristyl acrylate and its evaluation as viscosity modifier in lubricating oil. *J. Sci. Ind. Res.* **2014**, 73, 656-660.
26. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, 21, 19-30.
27. Abdel-Azim, A. A. A.; Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. *Pet. Sci. Technol.* **2006**, 24, 887-894.

Chapter III

1. Ghosh, P.; Das, T. Copolymer of decyl acrylate and styrene: Synthesis, characterization and viscometric studies in different base stock. *Adv. Appl. Sci. Res.* **2011**, 2, 272-283.
2. Mortier, R. M.; Orszulik, S.Y. Chemistry and Technology of Lubricants, 2nd ed., Chapman & Hill, London, **1997**.

3. Miwa, T. K.; Rothfus, J. A.; Dimitroff, E. Extreme-Pressure lubricant tests on jojoba and sperm whale oils. *J. Am. Oil Chem. Soc.* **1979**, 56, 765-770.
4. Akhmedov, A. I. Copolymer of alkyl methacrylates with styrene as V. I. improvers for lubricating oils. *Chem. Tech. Fuels Oils* **1994**, 30, 34-37.
5. Jerbic, I. S.; Vukovic, J. P.; Jukic, A. Production and application properties of dispersive viscosity index improvers. *Ind. Eng. Chem. Res.* **2012**, 51, 11914–11923.
6. Jung, K-M.; Chun, B-H.; Park, S. H.; Lee, C. H.; Kim, S. H. Synthesis of methacrylate copolymers and their effects as pour point depressants for lubricating oil. *Int. J. Appl. Polym. Sci.* **2011**, 120, 2579-2586.
7. Ghosh, P.; Das, T.; Nandi, D.; Karmakar, G.; Mandal, A. Synthesis and characterization of biodegradable polymer – Used as a pour point depressant for lubricating oil. *Int. J. Polym. Mater.* **2010**, 59, 1008–1017.
8. Nassar, A. M.; Ahmed, N. S.; Abd El-Aziz, K. I.; Abdel-Azim, A. A. A.; El-Kafrawy, A. F. Synthesis and evaluation of detergent/dispersant additives from polyisobutylene succinimides. *Int. J. Polym. Mater.* **2006**, 55, 703–713.
9. Selezneva, I. E.; Levin, A. Ya.; Monin, S. V. Detergents- Dispersants additives for motor oils, alkylphenolates. *Chem. Tech. Fuels Oil* **1999**, 35, 389- 395.
10. Abdir, M. F.; Ashour, F. El-Z.; Ahmed, N. S.; Kamal, R. S.; El-Zahed, El- S. M. The effect of some additives on the rheological properties of engine lubricating oil. *Int. J. Eng. Res. Appl.* **2014**, 4, 169-183.
11. Al-Sabagh, A. M.; Khalil, T. M.; Sabaa, M. W.; Khidr, T. T.; Saad, G. R. Poly(n-alkyl itaconate-co-vinyl acetate) as a pour point depressant for lube oil in relation to rheological flow properties. *J. Dispersion Sci. Technol.* **2012**, 33, 1649-1660.
12. Abdel-Azim, A.A.A.; Abdel-Aziem, R.M. Polymeric additives for improving the flow properties and viscosity index of lubricating oils. *J. Polym. Res.* **2001**, 8, 111-118.
13. Abou El-Naga, H. H.; Abd El-Azim, W. M.; Ahmed, M. M. Polymeric additives for pour point depression of residual fuel oils. *J. Chem. Technol. Biot.* **1985**, 35, 241-247.
14. Pederson, K. S.; Ronningsen, H. P. Influence of wax inhibitors on wax appearance temperature, pour point and viscosity of waxy crude oil. *Energy Fuels* **2003**, 17, 321-328.
15. Castro, L. V.; Vazquez, F. Copolymers as flow improvers for Mexican crude oil. *Energy Fuels* **2008**, 22, 4006 – 4011.

16. Borthakur, A.; Laskar, N. C.; Mazumdar, R. K.; Rao, K. V.; Subramanyam, B. Synthesis and evaluation of alkyl fumarate – vinyl acetate copolymers in combination with alkyl acrylate as flow improvers for Borholla crude oil. *J. Chem. Technol. Biot.* **1995**, *62*, 75-80.
17. Rogosic, M.; Mencer, H. J.; Gomzi, Z. Polydispersity index and molecular weight distributions of polymers. *Eur. Polym. J.* **1996**, *32*, 1337–1344.
18. Marvel, C. S.; Riddle, E. H. The structure of vinyl polymers. *J. Am. Chem. Soc.* **1940**, *62*, 2666-2670.
19. Grassie, N.; Melville, H. W. The thermal degradation of polyvinyl compounds. *Proc. R. Soc. Lon. A* **1949**, *199*, 1-13.
20. Ghosh, P.; Karmakar, G. Synthesis and characterisation of polymyristyl acrylate as a potential additive for lubricating oil. *Am. J. Polym. Sci.* **2012**, *2*, 1-6.
21. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.* **2006**, *13*, 398–403.
22. Abdel-Azim, A. A. A.; Malcolm, B. H. Interaction parameters in ternary polystyrene solution at high temperature. *Polymer* **1984**, *25*, 803-807.
23. Abdel-Azim, A. A. A.; Malcolm, B. H. Viscometric behaviour of polystyrene in tetralin / cyclohexane mixture. *Polymer* **1983**, *24*, 1429-1433.
24. Nassar, A. M.; Ahmed, N. S.; Kamal, R. S.; Abdel-Azim, A. A. A.; El-Nagdy, E. I. Preparation and evaluation of acrylate polymers as viscosity index improvers for lube Oil. *Pet. Sci. Technol.* **2005**, *23*, 537–546.
25. El-Gamal, I. M.; Atta, A. M.; Al- Sabbagh, A. M. Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* **1997**, *76*, 1471-1478.
26. Nassar, A. M.; Ahmed, N. S. The behavior of α -olefins butyl acrylate copolymers as viscosity index improvers and pour point depressants for lube oil. *Int. J. Polym. Mater.* **2006**, *55*, 947–955.
27. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, *21*, 19-30.
28. Hassaneau, M. H. M.; Bartz, W. J.; Abou El-Naga, H. H. A study of the rheological behaviour of multigrade oil. *Lubr. Sci.* **1997**, *10*, 43-58.

29. Chou, C. C.; Lee, S. H. Rheological behaviour and tribological performance of a nanodiamond-dispersed lubricant. *J. Mater. Proc. Technol.* **2008**, 201, 542-547.
30. Punit, K.; Khonsari, M. M. On the role of lubricant rheology and piezo- viscous properties in line and point contact EHL. *Tribol. Int.* **2009**, 42, 1522-1530.
31. Ahmed, N. S.; Nassar, A. M.; Nassar, R. M.; Abdel Raouf, M. E.; El-Kafrawy, A. F. The rheological properties of lube oil with terpolymeric additives. *Pet. Sci. Technol.* **2015**, 32, 2115-2122.

Part II

Chapter I

1. Mortier, R. M.; Fox, M. F; Orszulik, S. T. Chemistry and Technology of Lubricants, 3rd edition, Springer publication, **2011**.
2. Akhmedov, A. I. Copolymers of alkyl methacrylates with styrene as V. I. Improvers for lubricating oils. *Chem. Tech. Fuel Oils* **1987**, 23, 147- 151.
3. Kapur, G. S.; Sarpal, A. S.; Mazumdar, S. K.; Jain, S. K.; Srivastava, S. P.; Bhatnagar, A. K. Structure-performance relationships of viscosity index improvers: Micro structural determination of olefin copolymers by NMR spectroscopy. *Lubr. Sci.* **1995**, 8, 49-60.
4. Mohamed, M. M.; Hamdi, H. A.; Mohamed, F. E. J. Multi- functional viscosity index improvers. *Chem. Tech. Biotech.* **1994**, 60, 283–289.
5. Jatti, V. S.; Singh, T. P. Copper oxide nano-particles as friction-reduction and antiwear additives in lubricating oil. *J. Mech. Sci. Tech.* **2015**, 29, 793-798.
6. Li, B.; Wang, X.; Liu, W.; Xue, Q. Tribochemistry and antiwear mechanism of organic – inorganic nanoparticles as lubricant additives. *Tribol. Lett.* **2006**, 22, 79 - 84.
7. Abdel – Azim, A. A. A.; Nasser, A. M.; Ahmed, N. S.; El- Kafrawy, A. F.; Kamal, R. S. Multifunctional additives viscosity index improvers, pour point depressants and dispersants for lube oil. *Pet. Sci. Technol.* **2009**, 27, 20 – 32.
8. Abdel – Azim, A.; Nasser, A. M.; Ahmed, N. S.; Kamal, R. S. Multifunctional lube oil additives based on octadecen – maleic anhydride copolymer. *Pet. Sci. Technol.* **2011**, 29, 97–107.
9. Du, T.; Wang, S.; Liu, H.; Song, C.; Nie, Y. The synthesis and characterization of ester of methacrylic acid and maleic anhydride as a lube oil pour point depressant. *Pet. Sci. Technol.* **2012**, 30, 212 – 221.

10. Atta, A. M.; El-Ghazawy, R. A.; Morsy, F. A.; Hebishy, A. M. S.; El-Morsy, A. Adsorption of polymeric additives based on vinyl acetate copolymers as wax dispersant and its relevance to polymer crystallization mechanism. *J. Chem.* **2015**, <http://dx.doi.org/10.1155/2015/683109>.
11. Khidr, T. T. Synthesis and evaluation of copolymers as pour point depressants. *Pet. Sci. Technol.* **2007**, *25*, 671 – 681.
12. Khidr, T. T. Pour point depressants additives for waxy gas oil. *Pet. Sci. Technol.* **2011**, *29*, 19- 28.
13. Zhang, H.; Liu, H.; Wang, S. A new alternating copolymerized derivative as cold flow improver for diesel fuel. *Pet. Sci.* **2009**, *6*, 82 - 85.
14. Feng, L.; Zhang, Z.; Wang, F.; Wang, T.; Yang, S. Synthesis and evaluation of alkyl acrylate – vinyl acetate – maleic anhydride terpolymers as cold flow improvers for diesel fuel. *Fuel Process. Technol.* **2014**, *118*, 42 - 48.
15. Aleman-Vazquez, L. O.; Villagomez-Ibarra, J. R. Polyisobutenylsuccinimides as detergents and dispersants in fuel: infrared spectroscopy application. *Fuel* **2001**, *80*, 965-968.
16. Kamal, R. S.; Ahmed, N. S.; Nasser, A. M. Study the efficiency of some compounds as lubricating oil additives. *Appl. Petrochem. Res.* **2013**, *3*, 1-8.
17. Ahmed, N. S.; Nassar, A. M.; Abdel-Azim, A. A. A. Synthesis and evaluation of some detergent/dispersant additives for lube oil. *Int. J. Polm. Mater.* **2008**, *57*, 114-124.

Chapter II

1. Ghosh, P.; Das, T. Copolymer of decyl acrylate and styrene: synthesis, characterization and viscometric studies in different base stock. *Adv. Appl. Sci. Res.* **2011**, *2*, 272-283.
2. Nassar, A. M.; Ahmed, N. S. Study the influence of some polymeric additives as viscosity index improver, pour point depressants and dispersants for lube oil, *Pet. Sci. Technol.* **2010**, *28*, 13-26.
3. Ghosh, P.; Das, T.; Nandi, D.; Karmakar, G.; Mandal, A. Synthesis and characterization of biodegradable polymer- used as a pour point depressant. *Int. J. Polym. Mater.* **2010**, *59*, 1008-1017.
4. Ghosh, P.; Upadhyay, M.; Das, M. K. Studies on the additives performance of liquid crystal blended polyacrylate in lubricating oil. *Liq. Cryst.* **2013**, *41*, 30-35.

5. Nassar, A. M.; Ahmed, N. S.; Abdel- Aziz, K. I.; EI-Kafrawy, A. F.; Abdel-Azim A. A. Synthesis and evaluation of detergents/dispersant additives from polyisobutylene succinimides. *Int. J. Polym. Mater.* **2006**, 55, 703-713.
6. Mohamed, M. M.; Hamid, H. A.; Mohamed, F. F. Multifunctional viscosity index improvers. *J. Chem.Technol. Biot.* **1994**, 60, 283-289.
7. Ford, J. F.; Wood, J. M. Phosphoramidates of alpha-olefin polymers, The British Petroleum Co. Limited, US Patent, 3, 562, 16, **1971**.
8. Ghosh, P.; Das, M.; Das, T. Synthesis, characterization and viscosity studies of acrylate based homo and copolymers. *Res. J. Chem. Environ.* **2010**, 14, 26-31.
9. Khidr, T.T. Pour point depressant, additives for waxy gas oil. *Pet. Sci. Technol.* **2011**, 29, 19-28.
10. Abdel Azim, A. A.; Huglin, M. B. Synthesis and evaluation of ethoxylated polyesters as viscosity index improvers and pour point depressant for lube oil. *Proceeding of the 2nd Egyptian Conference of Chemical engineering*, Egypt, March 18-20, **1984**.
11. Rogosic, M.; Mencer, H. J.; Gomzi, Z. Polydispersity index and molecular weight distributions of polymers. *Eur. Polym. J.* **1996**, 32, 1337-1344.
12. Dean, E. W.; Davis, G. H. B. Viscosity variations of oils with temperature. *Chem. Met. Eng.* **1929**, 36, 618-619.
13. Brahman, D.; Sinha, B. Partial molar volumes and viscosity *B*-coefficients of N, N'-
14. ethylene- bis(salicylideneiminato) cobalt (II) in binary mixtures of 1,4 dioxane + methanol at T= (298.15, 303.15, 308.15, 313.15) K. *J. Chem. Eng. Data.* **2011**, 56, 3073-3082.
15. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Tech.* **2006**, 13, 398-403.
16. Nikoleav, V. F.; Egorov, A. V.; Nikolaev, I. V.; Sultanova, R. B. A method of testing pour point of petroleum products on a refrigerated sloping surface. *Pet. Sci. Technol.* **2013**, 31, 276-283.
17. Ghosh, P.; Karmakar, G. Synthesis and characterisation of Polymyristyl acrylate as a potential additive for lubricating oil. *Am. J. Polym. Sci.* **2012**, 2, 1-6.
18. Abdel Azim, A. A.; Amal, M. N.; Nehal, S. A.; Rasha, S. K.; El-Nagdy, E. I. Preparation and evaluation of acrylate polymers as a viscosity index improvers for lube oil. *Pet. Sci. Technol.* **2005**, 23, 537-546.

19. Nassar, A. M. The behaviour of polymers as viscosity index improvers. *Pet. Sci. Technol.* **2008**, 26, 514–522.
20. Karmakar, G.; Ghosh, P. Atom transfer radical polymerization of soybean oil and its evaluation as a biodegradable multifunctional additive in the formulation of eco-friendly lubricant. *ACS Sustainable Chem. Eng.* **2016**, 4, 775–781
21. Abdel-Azim, A.; Huglin, M. B. Selective solvation of polystyrene in tetralin/cyclohexane mixtures. *Polymer* **1983**, 24, 1308-1312.
22. Abdel-Azim, A. A. A.; Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Preparation and evaluation of acrylate polymers as pour point depressants for lube Oil. *Pet. Sci. Technol.* **2006**, 24, 887–894.
23. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, 21, 19-30.
24. Ghosh, P.; Hoque, M., Nandi, D. Homo and copolymers of decyl methacrylate as performance additives for lube oil. *Pet. Sci. Technol.* **2015**, 33, 920-927.

Chapter III

1. Braun, J. Additives in Lubricants and Lubrication (2nd edition), Mang, T.; Dresel, W. (editors), Wiley-VCH, Weinheim, Germany **2007**, 89–94; ISBN: 978-3-527-31497-3.
2. Duangkaewmanee, S.; Petsom, A. Synergistic and antagonistic effects on oxidation stability of antioxidants in a synthetic ester based oil. *Tribol. Int.* **2011**, 44, 266–271.
3. Singh, N.; Thakre, G. D.; Chaterjee, A. K.; Singal, S. K. A systematic study on composition of low viscosity automotive lube oils with an emphasis on wear and frictional characteristics. *Int. J. Eng. Res. Appl.* **2014**, 4, 10-16.
4. Erdemir, A. Review of engineered tribological interfaces for improved boundary lubrication. *Tribol. Int.* **2005**, 38, 249-256.
5. Ghosh, P.; Das, T. Copolymer of decyl acrylate and styrene: Synthesis, characterization and viscometric studies in different base stocks. *Adv. Appl. Sci. Res.* **2011**, 2, 272-283.
6. Rizvi, S. Q. A. A comprehensive review of lubricant chemistry, technology, selection and design, ASTM International, West Conshohocken, PA, **2009**, 100 – 112.

7. Morgan, S.; Ye, Z.; Subramanian, R.; Zhu, S. Higher-molecular-weight hyper branched polyethylene containing cross linking structures as lubricant viscosity-index improvers. *Polym. Eng. Sci.* **2010**, 50, 911–918.
8. Li, W.; Li, Y.; H, Y.; Wang, Y. Synthesis and characterisation of HSIBR used as viscosity index improver for lubricants. *Lubr. Sci.* **2012**, 24, 188–197.
9. Shan, C. L. P.; Kuhlman, R. L.; Rath, G. L.; Kenny, P.; Hughes, M. M.; Cong, R. Viscosity index improver for lubricant compositions. US Patent, 8486878, **2013**.
10. Mohamada, S. A.; Ahmed, N. S.; Hassanein, S. M.; Rashad, A. M. Investigation of polyacrylates copolymers as lube oil viscosity index improvers. *J. Pet. Sci. Eng.* **2012**, 100, 173–177.
11. Abadir, M. F.; Ashour, F. El-Z.; Ahmed, N. S.; Kamal, R. S.; El-Zahed, El. S. M. The effect of some additives on the rheological properties of engine lubricating oil. *J. Eng. Res. Appl.* **2014**, 4, 169-183.
12. Van Home, W. L. Polymethacrylates as viscosity index improvers and pour point depressants. *Ind. Eng. Chem.* **1949**, 41, 952-959.
13. Garcia, M. C.; Carbognani, L.; Urbina, A.; Orea, M. Paraffin deposition in oil production.oil composition and paraffin inhibitors activity. *Pet. Sci. Technol.* **1998**, 16, 1001-1021.
14. Huiyang, Z.; Weibang, Z.; Zhuomei, L. Synthesis of polymers with long side chain of *N*-alkyl esters and their effects on pour-point depression of oil. *J. Appl. Polym. Sci.* **1991**, 43, 919-924.
15. Kumar, M. N. S. Preparation of *n*-alkylacrylate and vinyl acetate copolymer and its influence on low-temperature fluidity of diesel fuel. *Quart J. Technol.* **1989**, 15, 47-62.
16. Ghosh, P.; Das, T.; Das, M. Synthesis, characterization and viscosity studies of acrylate based homo and copolymers. *Res. J. Chem. Environ* **2010**, 14, 26-31.
17. Mellow, I. L.; Delpech, M. C.; Countinho, F. M. B.; Albino, F. F. M. Viscometric study of high cispolybutadiene in toluene solution. *J. Braz. Chem. Soc.* **2006**, 17, 194-199.
18. Dean, E. W.; Davis, G. H. B. Viscosity variation of oils with temperature. *Chem. Met. Eng.* **1929**, 36, 618-619.

19. Nikoleav, V. F.; Egorov, A. V.; Nikolaev, I. V.; Sultanova, R. B. A method of testing the pour point of petroleum products on a refrigerated sloping surface. *Pet. Sci. Technol.* **2013**, 31, 276-283.
20. Abdel-Azim, A. A.; Amal, M. N.; Nehal, S. A.; Rasha, S. K.; El- Nagdy, E. I. Preparation and evaluation of acrylate polymers as viscosity index improver for lube oil. *Pet. Sci. Technol.* **2005**, 23, 537-546.
21. Eckert, R. J. A.; Covey, D. F. Developments in the field of hydrogenated diene copolymers as viscosity index improvers. *Lubr. Sci.* **1988**, 1, 65-80.
22. Nassar, A. M. The behaviour of polymers as viscosity index improver. *Pet. Sci. Technol.* **2008**, 26, 514-522.
23. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.* **2006**, 13, 398–403.
24. Abdul-Azim, A. A. A.; Nasser, A. M.; Ahmed, N. S.; EI- Kafrawy, A. S.; Kamal, R. S. Multifunctional additives for viscosity index improver, pour point depressants and dispersants for lube oil. *Pet. Sci. Technol.* **2009**, 27, 20-32.
25. Ghosh, P.; Das, M., Study of the influence of some polymeric additives as viscosity index improvers and pour point depressants – Synthesis and characterization. *J. Pet. Sci. Eng.* **2014**, 119, 79–84.
26. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, 21, 19-30.
27. Machado, A. L. C.; Lucas, E. F.; Gonzalez, G. Poly (ethylene-co-vinyl) as a wax inhibitor of a Brazilian crude oil: oil viscosity, pour point and phase behaviour of organic solutions. *J. Pet. Sci. Eng.* **2001**, 32, 159 –165.

Chapter IV

1. Braun, J. Additives in Lubricants and Lubrication, 2nd edition, Chapter 6, (Mang T., Dresel W. eds.) Wiley-VCH, Weinheim, Germany, **2007**, 88–118.
2. Braga, J. W. B.; Junior dos Santos, A. A.; Martins, I. S. Determination of viscosity index in lubricant oils by infrared spectroscopy and PLSR. *Fuel* **2014**, 120, 171–178.

3. Mohamada, S. A.; Ahmed, N. S.; Hassanein, S. M.; Rashad, A. M. Investigation of polyacrylates copolymers as lube oil viscosity index improvers. *J. Pet. Sci. Eng.* **2012**, 100, 173–177.
4. Ghosh, P.; Das, T.; Das, M. Evaluation of Poly (acrylates) and their copolymer as viscosity modifiers. *Res. J. Chem. Sci.* **2011**, 1, 18-25.
5. Li, W.; Li, Y.; H, Y.; Wang, Y. Synthesis and characterisation of HSIBR used as viscosity index improver for lubricants. *Lubr. Sci.* **2012**, 24, 188–197.
6. Akhmedov, A. I.; Mamedova, D. A. 4-methyl-1-pentene oligomers as thickening agents for lube oils. *Chem. Tech. Fuels Oils* **2003**, 39:339–342.
7. Mohamed, M. M.; Hamid, H. A.; Mohamed, F. F. Multifunctional viscosity index improvers, *J. Chem. Technol. Biot.* **1994**, 60, 283-289.
8. Farag, R. K. Poly(cinnamoyloxy ethyl methacrylate -co - octadecylacrylate) as flow improver for Egyptian waxy crude oils. *Int. J. Polym. Mater.* **2008**, 57, 189-202.
9. Coutinho, J. A. P.; Dauphin, C.; Daridon, J. L. Measurements and modelling of wax formation in diesel fuels. *Fuel* **2000**, 79, 607-616.
10. Mortier, R. M.; Orszulik, S. T. *Chemistry and Technology of Lubricants*; Chapman & Hall: London, **1997**.
11. Ahmed, N. S.; Nassar, A. M.; Abdel-Azim, A. A. A. Synthesis and evaluation of some detergents/dispersant additives for lube oil. *Int. J. Polym. Mater.* **2008**, 57, 114-124.
12. Nehal, S. A.; Amal, M. N. *Lubrication and lubricants : tribology – fundamentals and advancements*. Rijeka, Croatia, **2013**, 55-76.
13. Abdel-Azim, A. A. A.; Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Multifunctional additives viscosity index improvers, pour point depressants and dispersants for lube oil. *Pet. Sci. Technol.* **2009**, 27, 20-32.
14. Alemán, L. O.; Vázquez, J. R.; Villagómez-Iberra. Poly isobutenyl succinimides as detergent and dispersants in fuel. *Fuel* **2001**, 80, 965 -968.
15. Kamal, R. S.; Ahmed, N. S.; Nasser, A. M. Study the efficiency of some compounds as lubricating oil additives. *Appl. Petrochem. Res.* **2013**, 3, 1-8.
16. Ghosh, P.; Hoque, M.; Nandi, D., Homo and copolymers of decylmethacrylate as performance additives for lube oil. *Pet. Sci. Technol.* **2015**, 33, 920-927.

17. Abdel-Azim, A. A.; Amal, M. N.; Nehal, S. A.; Rasha, S. K.; El- Nagdy, E. I. Preparation and evaluation of acrylate polymers as viscosity index improver for lube oil. *Pet. Sci. Technol.* **2005**, 23, 537-546.
18. Abdel- Azim, A. A. A.; Abdel-Aziem, R. M. Polymeric additives for improving the flow properties and viscosity index of lubricating oils. *J. Polym. Res.* **2001**, 8, 111-118.
19. Nassar, A. M. The behaviour of polymers as viscosity index improver. *Pet. Sci. Technol.* **2008**, 26, 514-522.
20. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.* **2006**, 13, 398–403.
21. Eckert, R. J. A.; Covey, D. F. Developments in the field of hydrogenated diene copolymers as viscosity index improvers. *Lubr. Sci.* **1988**, 1, 65-80.
22. El-Gamal, I. M.; Atta, A. M.; Al- Sabbagh, A. M. Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* **1997**, 76, 1471-1478.
23. Machado, A. L. C.; Lucas, E. F.; Gonzalez, G. Poly (ethylene-co-vinyl acetate) (EVA) as wax inhibitor of a Brazilian crude oil: Oil viscosity, pour point and Phase behaviour of organic solutions. *J. Pet. Sci. Eng.* **2001**, 32(2-4), 159-165.
24. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, 21, 19-30.
25. Nassar, A. M.; Ahmed, N. S.; Abdel –Aziz, K. I.; El-Kafrawy, A. F.; Abdel-Azim, A. A. A. Synthesis and evaluation of detergent/dispersant additives from polyisobutylene succinimides. *Int. J. Polym. Mater.* **2006**, 55, 703–713.
26. Ahmed, N. S.; Nassar, A. M.; Abdel-Hameed, H. S.; El-Kafrawy, A. F. Preparation, characterization and evaluation of some ashless detergent/dispersant additives for lubricating engine oil. *Appl. Petrochem. Res.* DOI 10.1007/s 13203-015-0110-5.

Chapter V

1. Ghosh, P.; Das, M.; Upadhaya, M.; Das, T.; Mandal, A. Synthesis and evaluation of acrylate polymers in lubricating oil. *J. Chem. Eng. Data* **2011**, 56, 3752-3758.
2. Braga, J. W. B.; Junior dos Santos, A. A.; Martins, I. S. Determination of viscosity index in lubricant oils by infrared spectroscopy and PLSR. *Fuel* **2014**, 120, 171–178.

3. Gravlin, G.; Swire, E. A.; Jones, S. P. Pour point depression of lubricating oil. *Ind. Eng. Chem.* **1953**, 45, 23-27.
4. Czech, Z.; Kowalczyk, A.; Kabatc, J.; Swiderska, J. Thermal stability of poly (2-ethyl hexylacrylate) used as plasticizers for medical applications. *Polym. Bull* **2013**, 70, 1911-1918.
5. Ghosh, P.; Upadhyay, M.; Das, M. K. Studies on the additive performance of liquid crystal blended polyacrylate in lubricating oil. *Liq. Cryst.* **2014**, 41, 30-35.
6. Habib, O. M. O.; Hassan, H. M.; Moawad, E. B.; El-Mekabaty, A. Synthesis of some novel antioxidant and anticorrosive additives for Egyptian lubricating oils. *Pet. Sci. Technol.* **2012**, 30, 2435–2449.
7. Ghosh, P.; Das, T.; Nandi, D. Synthesis, Characterization and viscosity studies of homopolymer of methyl methacrylate and copolymer of methyl methacrylate and styrene, *J. Sol. Chem.* **2011**, 40, 67-78.
8. Abdel-Azim, A.; Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Multifunctional lube oil additives based on octadecene - maleic anhydride copolymer. *Pet. Sci. Technol.* **2011**, 29, 97-107.
9. Ahmed, N. S.; Nassar, A. M.; Abdel-Azim, A. A. A. Synthesis and evaluation of some detergents/dispersant additives for lube oil, *Int. J. Polym. Mater.* **2008**, 57, 114-124.
10. Nassar, A. M.; Ahmed, N. S.; Abdel- Aziz, K. I.; EI-Kafrawy, A. F.; Abdel-Azim, A. A. A. Synthesis and evaluation of detergents/dispersant additives from polyisobutylene succinimides, *Int. J. Polym. Mater.* **2006**, 55, 703-713.
11. Nassar, A. M.; Ahmed, N. S. Study the Influence of some polymeric additives as viscosity index improvers, pour point depressants and dispersants for lube oil, *Pet. Sci. Technol.* **2012**, 28, 13-26.
12. Abdel-Azim, A. A. A.; Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Multifunctional additives viscosity index improvers, pour point depressants and dispersants for lube oil. *Pet. Sci. Technol.* **2009**, 27, 20-32.
13. Hus, S. M. Molecular basis of lubrication. *Tribol. Int.* **2004**, 37, 553-559.
14. Najman, M.; Kasrai, M.; Bancroft, G. M.; Davidson, R. Combination of ashless antiwear additives with metallic detergents. *Tribol. Int.* **2006**, 39, 342-355.
15. Pawlak, Z. *Tribochemistry of Lubricating oil*, (Elsevier B.V, Amsterdam), **2003**.

16. Santos, J. C. O.; Santos, V. J. F.; Souza, A. G.; Sobrinho, E. V.; Fernandes, V. J. J.; Silva, A. J. N. Thermo analytical and rheological characterization of automotive mineral lubricants after thermal degradation. *Fuel* **2004**, 83, 2393-2399.
17. Rundnick, L. R. Lubricant additives: Chemistry and applications,(Marcel Dekker, New York), **2003**.
18. Lamp, G. G.; Loance, C. M.; Gaynor, J. W. Indiana stirring oxidation test for lubricating oil. *Ind. Eng. Chem. Anal. Ed.* **1941**, 13, 317-321.
19. Kamal, R. S.; Ahmed, N. S.; Nasser, A. M. Study the efficiency of some compounds as lubricating oil additives. *Appl. Petrochem. Res.* **2013**, 3, 1-8.
20. Rose, D. J. Analysis of antioxidant behaviour in lubricating oils, A Ph.D thesis submitted to school of chemistry, the University of LEEDS, **1991**.
21. Nassar, A. M. A Ph.D thesis, department of chemistry, faculty of science, Ain Shams University, Cairo, **1996**.
22. Ahmed, N. S. A Ph.D thesis, department of chemistry, faculty of science, Ain Shams University, Cairo, **1996**.
23. Egharevba, F.; Maduako, A. U. C. Assessment of oxidation in automotive crankcase lube oil: Effects of metal and water activity. *Ind. Eng. Chem. Res.* **2002**, 41, 3473 - 3481.
24. Sarnavskaya, T. I.; Lebedev, E. V.; Gordash, Yu. T.; Shablii, V. I. Comparative evaluation of antioxidant properties of additives for synthetic lube oils, *Chem. Tech. fuels oils* **1975**, 11, 731-733.
25. Rundnick, L. R. Lubricant additives: Chemistry and applications, (Marcel Dekker, New York), **2009**.

Part III

Chapter I

1. Zeng, X.; Li, J.; Wu, X.; Ren, T.; Liu, W. The tribological behaviors of hydroxyl containing dithiocarbamate- triazine derivatives as additives in rapeseed oil. *Tribol. Int.* **2007**, 40 (3), 560–566.
2. Zeng, X.; Wu, H.; Yi, H.; Ren, T. Tribological behavior of three novel triazine derivatives as additives in rapeseed oil. *Wear* **2007**, 262 (5–6), 718–726.
3. Erhan, S. Z.; Sharma, B. K.; Liu, Z.; Adhvaryu, A. Lubricant base stock potential of chemically modified vegetable oils. *J. Agri. Food. Chem.* **2008**, 56 (19), 8919–8925.

4. Erhan, S. Z.; Asadauskas, S. Lubricant base stocks from vegetable oils. *Ind. Crop. Prod.* **2000**, 11 (2–3), 277–282.
5. Karmakar, G.; Ghosh, P. Soybean oil as a biocompatible multifunctional additive for lubricating oil. *ACS Sustainable Chem. Eng.* **2015**, 3, 19–25.
6. Singh, A. K. Development of Biodegradable Lubricant Chemical Business (ISSN 970-3136) 22 (4) April **2008**, 53-55.
7. Rizvi, S. Q. A. Additive chemistry and technology, Tribology data hand book. Booser, E. R. (Ed.), New York: CRC Press, **1997**, 1, 117-137.
8. Ertugrul, D.; Filiz, K. Using cotton seed oil as environmentally accepted lubricant additive. *Energ. sources* **2004**, 26, 611-625.
9. Guner, F. S.; Yagci, Y.; Erciyes, A. T. Polymer from triglycerides oils. *Prog. Polym. Sci.* **2006**, 31, 633-670.
10. Dinda, S.; Patwardhan, A. V.; Goyd, V. V.; Pradhan, N. C. Epoxidation of cottonseed oil by aqueous hydrogen peroxide catalyzed by liquid inorganic solids. *Bioresour. Technol.* **2008**, 99, 3737-3744.
11. Mofijur, M.; Masjuki, H. H.; Kalam, M. A.; Shahabuddin, M.; Hazrat, M. A.; Liaquat A. M. Palm Oil methyl ester and its emulsions effect on lubricant performance and engine components wear. *Energ. Procedia* **2012**, 14, 1748–1753
12. Fox, N. J.; Stachowiak, G. W. Vegetable oil-based lubricants—a review of oxidation. *Tribol. Int.* **2007**, 40, 1035–1046.
13. Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Oxidation, Friction reducing, and low temperature properties of epoxy fatty acid methyl esters. *Green Chem.* **2007**, 9 (5), 469–474.
14. Hwang, H.; Erhan, S. Z. Modification of epoxidized soybean oil for lubricant formulations with improved oxidative stability and low pour point. *J. Am. Oil. Chem. Soc.* **2001**, 78, 1179-1184.
15. Vinci, D.; Kersbulck, J.; Greaves, M. R.; Khelidj, N. High performance renewable base fluids derived from castor oil for industrial applications, solving friction problems. Synopsis 17th International Colloquium, *Tribol.* **2010**, 88.
16. Regueira, T.; Lugo, L.; Fandino, O.; Lopez, E. R.; Fernandez, J. Compressibilities and viscosities of reference and vegetable oils for their use as hydraulic fluids and lubricants. *Green Chem.* **2011**, 13, 1293–1302.

17. Joseph, P. V.; Sharma, D. K., Improvement of thermo-oxidative stability of non – edible vegetable oil of Indian origin for biodegradable lubricant application. *Lubr. Sci.*, **2010**, 22, 149–161.
18. Mendoza, G.; Igartua, A.; Fernandez-Diaz, B.; Urquiola, F.; Vivanco, S.; Arguizoniz, R. Vegetable oils as hydraulic fluids for agricultural applications. *Grasasy Aceites*, **2011**, 62, 29 – 38.
19. Suhane, A.; Sarviya, R. M.; Rehman, A.; Khaira, H. K. Experimental study of castor oil based lubricant for automotive applications. *Int. J Eng. Res. Appl.* **2014**, 4, 104-107.
20. Maleque, M. A.; Masjuki, H. H.; Sapuan, S. M. Vegetable based biodegradable lubricating oil additives. *Ind. Lubr. Tribol.* **2003**, 55, 137-143.
21. Ghosh, P.; Das, T.; Karmakar, G.; Das, M. Evaluation of acrylate-sunflower oil copolymer as viscosity index improvers for lube oils. *J. Chem. Pharm. Res.* **2011**, 3, 547–556.
22. Li, W.; Jiang, C.; Chao, M.; Wang, X. Natural garlic oil as a high performance, environmentally friendly, extreme pressure additive in lubricating oils. *ACS Sustainable Chem. Eng.* **2014**, 2, 798–803.
23. Quinchia, L. A.; Delgado, M. A.; Valencia, C.; Franco, J. M.; Gallos, C. Viscosity modification of high oleic sunflower oil with polymeric additives for the design of new biolubricant formulations. *Environ. Sci. Technol.* **2009**, 43, 2060-2065.
24. Nassar, A. M.; Ahmed, N. S.; Nasser, R. M. Jojoba polymers as lubricating oil additives. *Petroleum & Coal* **2015**, 57, 120-129.
25. Bisht, R. P. S.; Sivasankaran, G. A.; Bhatia, V. K. Additive properties of Jojoba oil for lubricating formulations. *Wear* **1993**, 161, 193-197.
26. Ghosh, P.; Das, T.; Karmakar, G.; Das, M. Evaluation of acrylate-sunflower oil copolymer as viscosity index improvers for lube oils. *J. Chem. Pharm. Res.* **2011**, 3, 547-556.
27. Ghosh, P.; Karmakar, G. Evaluation of sunflower oil as a multifunctional lubricating oil additive. *Int. J. Ind. Chem.* **2014**, 5, 7-17.
28. Karmakar, G.; Ghosh, P. Green additives for lubricating oil. *ACS Sustainable Chem. Eng.* **2013**, 1, 1364-1370.
29. Gast, L. E.; Croston, C. B.; Schneider, W. J.; Teeter, H. M. Synthetic lubricants from polyhydroxystearic acids. *J. Ind. Eng. Chem.* **1954**, 46, 2205-2208.

30. Wu, X.; Zhang, X.; Yang, S.; Chen, H.; Wang, D. The study of epoxidized rapeseed oil used as a potential biodegradable lubricant. *J. Am. Oil Chem. Soc.* **2000**, *77*, 561-563.
31. Gunera, F. S.; Yagci, Y.; Erciyas, A. T. Polymers from triglyceride oils. *Prog. Poly. Sci.* **2006**, *31*, 633–670.
32. Pellegriono, M. Grand challenges in polymer chemistry: energy, environment, health. *Front. Chem.* **2013**, *1*, 1-4.

Chapter II

1. Rizvi, S. Q. A. A Comprehensive Review of Lubricant Chemistry, Technology, Selection and Design, ASTM International, West Conshohocken, PA, **2009**, 100.
2. Fustin, C. A.; Abetz, V.; Gohy, J. F. Triblock terpolymer micelles: a personal outlook. *Eur. Phys. J. E. Soft Matter* **2005**, *16*, 291-302.
3. Breiner, U.; Krappe, U.; Abetz, V.; Stadler, R. Cylindrical morphologies in asymmetric ABC triblock copolymers. *Macromol. Chem. Phys.* **1997**, *198*, 1051-1083.
4. Ghosh, P.; Das, T.; Karmakar, G.; Das, M. Evaluation of acrylate- sunflower oil copolymer as viscosity index improvers for lube oil. *J. Chem. Pharm. Res.* **2011**, *3*, 547-556.
5. Maleque, M. A.; Masjuki, H. H.; Sapuan, S. M. Vegetable based biodegradable lubricating oil additives. *Ind. Lubr. Tribol.* **2003**, *55*, 137-143.
6. Valdes, A. F.; Garcia, A. B. A study of the evolution of the physicochemical and structural characteristics of olive and sunflower oils after heating at frying temperatures. *Food Chem.* **2006**, *98*(2), 214-219.
7. Mohamed, M. M.; Hamid, H. A.; Mohamed, F. F. Multifunctional viscosity index improvers. *J. Chem. Technol. Biot.* **1994**, *60*, 283-289.
8. Kupareva, A.; Maki-Arvela, P.; Grenman, H.; Eranen, K.; Sjöholm, R.; Reunanen, M.; Murzin, D.Y. Chemical characterization of lube oils. *Energy Fuels* **2013**, *27*, 27-34.
9. Zhang, H.; Liu, H.; Wang, S. A new alternating copolymerized derivative as a cold flow improver for diesel fuel. *J. Pet. Sci.* **2009**, *6*, 82-85.
10. Ghosh, P.; Das, T.; Nandi, D.; Karmakar, G.; Mandal, A. Synthesis and characterization of bio gradable polymer – Used as a pour point depressant for lubricating oil. *Int. J. Polym. Mater* **2010**, *59*, 1008 – 1017.

11. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.* **2006**, 13, 398–403.
12. Ghosh, P.; Das, M.; Upadhyay, M.; Das, T.; Mandal, A. Synthesis and evaluation of acrylate polymers in lubricating oil. *J. Chem. Eng. Data* **2011**, 56, 3752–3758
13. Al-Sabagh, A. M.; Sabaa, M. W.; Saad, G. R.; Khidr, T. T.; Khalil, T. M. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egypt. J. Pet.* **2012**, 21, 19-30.
14. Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties. *Bioresour. Technol.* **2008**, 99, 7333–7340.
15. Sharma, B. K.; Adhvaryu, A.; Erhan, S. Z. Friction and wear behavior of thioether hydroxy vegetable oil. *Tribol. Int.* **2009**, 42, 353–358.
16. Chevallier, V.; Petitjean, D.; Bouroukha, M.; Dirand, M. Mixtures of numerous different n-alkane: 2. Studies by X- ray diffraction and differential thermal analysis with increasing temperatures. *Polymer* **1999**, 40, 2129-2137.
17. Srivastava, S. P.; Tandon, R. S.; Verma, P. S.; Saxena, A. K.; Joshi, G. C.; Phatak, S. D. Crystallization behaviour of n-paraffin in Bombay-High middle-distribution wax/gel. *Fuel* **1992**, 71, 533-537.
18. Khidr, T. T. Synthesis and evaluation of copolymers as pour point depressants. *Pet. Sci. Technol.* **2007**, 25, 671-681.
19. Chen, W.; Zhao, Z.; Yin, C. The interaction of waxes with pour point depressants. *Fuel* **2010**, 89, 1127-1132.
20. Khidr, T. T. Pour point depressant additives for waxy gas oil. *Pet. Sci. Technol.* **2011**, 29, 19-28.
21. Hassaneau, M. H. M.; Bartz, W. J.; Abou El-Naga, H. H. A study of the rheological behaviour of multigrade oil. *Lubr. Sci.* **1997**, 10, 43-58.
22. Hewson, R. W.; Kapur, N.; Gaskel, P. H. A model for film forming with Newtonian and shear – thinning fluids. *J. Non-Newtonian Fluids Mech.* **2009**, 162, 21-28.
23. Carbone, G.; Scaraggi, M.; Mangialardi, L. EHL squeeze at pin – pulley interface in CVTs: Influence of lubricant rheology. *Tribol. Int.* **2009**, 42, 862 – 868.
24. Mortier, R. M.; Orszulik, S. T. Chemistry and Technology of Lubricants, Springer Science and Business Media, **2012**.

25. Ahmed, N. S.; Nassar, A. M.; Nassar, R. M.; Abdel Raouf, M. E.; El-Kafrawy, A. F. The rheological properties of lube oil with terpolymeric additives. *Pet. Sci. Technol.* **2014**, *32*, 2115 - 2122.

Chapter III

1. Adhvaryu, A.; Erhan, S. Z.; Perez, J. M. Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants. *Wear* **2004**, *257*, 359–367.
2. Shanta, S. M.; Molina, G. J.; Soloiu, V. Tribological Effects of Mineral-Oil Lubricant Contamination with Biofuels: A Pin-on-Disk Tribometry and Wear Study. *Adv. Tribol.* **2011**, doi:10.1155/2011/820795
3. Kumar, G. S.; Balamurugan, A.; Vinu, S.; Radhakrishnan, M.; Senthilprabhu, G. Tribological and emission studies on two stroke petrol engine lubricated with sunflower methyl ester. *J. Sci. Ind. Res.* **2012**, *71*, 562–565.
4. Liew, W. Y. H.; Dayou, S.; Dayou, J.; Siambun, N. J.; Ismail, M. A. B. The effectiveness of palm oil methyl ester as lubricant additive in milling and four-ball tests. *Int. J. Surf. Sci. Eng.* **2014**, *8*, 153–172.
5. Samarth, N. B.; Mahanwar, P. A. Modified vegetable oil based additives as a future polymeric material—Review. *Open J Org. Polym Mater.* **2015**, *5*, 1–22.
6. Sharma, B. K.; Adhvaryu, A.; Erhan, S. Z. Friction and wear behavior of thioether hydroxyl vegetable oil. *Wear* **2009**, *42*, 353–358.
7. Liu, W.; Hu, L.; Zhang, Z. Friction and wear of the film formed in the immersion test of oil containing antiwear and extreme pressure additives. *Thin Solid Films* **1995**, *271*, 88–91.
8. Li, W.; Jiang, C.; Chao, M.; Wang, X. Natural garlic oil as a high-performance, environmentally friendly, extreme pressure additive in lubricating oils. *ACS Sustainable Chem. Eng.* **2014**, *2*, 798–803.
9. Mofijur, M.; Masjuki, H. H.; Kalam, M. A.; Shahabuddin, M.; Hazrat, M. A.; Liaquat, A. M. Palm oil methyl ester and its emulsions effect on lubricant performance and engine components wear. *Energ. Procedia* **2012**, *14*, 1748–1753.
10. Liu, Z.; Sharma, B. K.; Erhan, S. Z.; Biswas, A.; Wang, R.; Schuman, T. P. Oxidation and low temperature stability of polymerized soybean oil-based lubricants. *Thermochim. Acta* **2015**, *601*, 9–16.

11. Adhvaryu, A.; Erhan, S. Z.; Liu, Z. S.; Perez, J. M. Oxidation kinetic studies of unmodified and genetically modified vegetable oils using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochim. Acta* **2000**, 364 (1-2), 87-97.
12. Fox, N. J.; Stachowiak, G. W. Vegetable oil-based lubricants—A review of oxidation. *Tribol. Int.* **2007**, 40 (7), 1035–1046.
13. Sharma, B. K.; Adhvaryu, A.; Liu, Z.; Erhan, S. Z. Chemical modification of vegetable oils for lubricant applications. *J. Am. Oil Chem. Soc.* **2006**, 83, 129-136.
14. Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Oxidation, friction reducing, and low temperature properties of epoxy fatty acid methyl esters. *Green Chem.* **2007**, 9 (5), 469–474.
15. Sharma, B. K.; Liu, Z.; Adhvaryu, A.; Erhan, S. Z. One-pot synthesis of chemically modified vegetable oils. *J. Agric. Food Chem.* **2008**, 56 (9), 3049–3056.
16. Biswas, A.; Sharma, B. K.; Willett, J. L.; Erhan, S.Z.; Cheng, H.N. Soybean oil as a renewable feedstock for nitrogen-containing derivatives. *Energ. Environ. Sci.* **2008**, 1, 639–644.
17. Shashidhara, Y. M.; Jayaram, S. R. Vegetable oils as a potential cutting fluid-An evolution. *Tribol. Int.* **2010**, 43 (5–6), 1073–1081.
18. Erhan, S. Z.; Sharma, B. K.; Liu, Z.; Adhvaryu, A. Lubricant base stock potential of chemically modified vegetable oils. *J. Agric. Food Chem.* **2008**, 56 (19), 8919–8925.
19. Campanella, A.; Rustoy, E.; Baldessari, A.; Baltanás, M. A. Lubricants from chemically modified vegetable oils. *Bioresour. Technol.* **2010**, 101 (1), 245–254.
20. Sharma, B. K.; Doll, K. M.; Erhan, S. Z. Ester hydroxy derivatives of methyl oleate: Tribological, oxidation and low temperature properties. *Bioresour. Technol.* **2008**, 99, 7333–7340.
21. Lathi, P. S.; Mattiasson, B. Green approach for the preparation of biodegradable lubricant base stock from epoxidized vegetable oil. *Appl. Catal. B- Environ.* **2007**, 69, 207–212.
22. Ogunniyi, D. S. Castor oil: A vital industrial raw material. *Bioresour. Technol.* **2006**, 97, 1086–1091.
23. Mutlu, H.; Meier, M. A. R. Castor oil as a renewable resource for the chemical industry. *Eur. J. Lipid Sci. Technol.* **2010**, 112 (1), 10–30.

24. Kunduru, K. R.; Basu, A.; Zada, M. H.; Domb, A. J. Castor oil-based biodegradable polyesters. *Biomacromolecules* **2015**, 16 (9), 2572–2587.
25. Azambujaa, M. A.; Diasb, A. A. Use of castor oil-based polyurethane adhesive in the production of glued laminated timber beams. *J. Mater. Res.* **2006**, 9 (3), 287–291.
26. brahim, S.; Ahmad, A.; Mohamed N. S. Characterization of novel castor oil - based polyurethane polymer electrolytes. *Polymer* **2015**, 7, 747–759.
27. Singh, A. K. Castor oil based lubricants reduces smoke emission in two stroke engines. *Ind. crop. prod.* **2011**, 33, 287–295.
28. Borugadda, V.; Goud, V. Improved low-temperature properties of chemically modified high free fatty acid castor oil-methyl esters: Blending and optimization study. *J. Energy Eng.* **2016**, 142, DOI: 10.1061/(ASCE)EY.1943-7897.0000283.
29. Quinchia, L. A.; Delgado, L. A.; Reddyhoff, T.; Gallegos, C.; Spikes, H. A. Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers. *Tribol. Int.* **2014**, 69, 110–117.
30. Chincholkar, D. S.; Salpute, S. T.; Kumbhar N. R. Castor oil as green lubricant-A review. *Int. J. Eng. Res. Technol.* **2012**, 1(5), 1–3.
31. Madankar, C. S.; Pradhan, S.; Naik, S. N. Parametric study of reactive extraction of castor seed (*Ricinus communis* L.) for methyl ester production and its potential use as bio lubricant. *Ind. Crop. Prod.* **2013**, 43, 283–290.
32. Majumdar, S.; Kumar, D.; Nirvan, Y. P. S. Acrylate grafted dehydrated castor oil alkyd—A binder for exterior paints. *J. Coatings Technol.* **1998**, 70, 27–33.
33. Karmakar, G.; Ghosh, P. Soybean oil as a biocompatible multifunctional additive for lubricating Oil. *ACS Sustainable Chem. Eng.* **2015**, 3, 19–25.
34. Chandure, A. S.; Umare, S. S. Synthesis, characterization and biodegradation study of low molecular weight polyesters. *Int. J. Polym. Mater.* **2007**, 56, 339–353.
35. Tanveer, S.; Sharma, U. C.; Prasad, R. Rheology of multigrade engine oils. *Indian J. Chem. Technol.* **2006**, 13, 180–184.
36. Karmakar, G.; Ghosh, P. Green Additives for Lubricating Oil. *ACS Sustainable Chem. Eng.* **2013**, 1, 1364–1370.
37. Morgan, S.; Ye, Z.; Subramanian, R.; Zhu, S. Higher-molecular-weight hyperbranched polyethylenes containing crosslinking structures as lubricant viscosity-index improvers. *Polym. Eng. Sci.* **2010**, 50, 911–918.

38. Soni, H. P.; Kiranbala, Bharambe, D. P. Performance – based designing of wax crystal growth inhibitors. *Energy Fuels* **2008**, *22*, 3930–3938.
39. El-Gamal, I. M.; Atta, A. M.; Al- Sabbagh, A. M. Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* **1997**, *76*, 1471–1478.
40. Behbahani, T. J. Experimental investigation of the polymeric flow improver on waxy oils. *Petroleum & Coal* **2014**, *56*, 139–142.
41. Eckermann, D. I. B.; Vogelpohi I. A. Deasphaltization and demetalling of heavy crude oil and distillation residues with CO₂. *Chem. Eng. Technol.* **1990**, *13*, 258–264.
42. Tan, Y.; Huang, W.; Wang, X. Molecular orbital indexes criteria for friction modifiers in boundary lubrication. *Tribol. Int.* **2002**, *35*, 381–384.
43. Masjuki, H. H.; Maleque, M. A. Investigation of the anti-wear characteristics of palm oil methyl ester using a four-ball tribometer test. *Wear* **1997**, *206*, 179–186.
44. Matthew, T. S.; Nader, S.; Bigyan, A.; Lambert, A. D. Influence of fatty acid composition on the tribological performance of two vegetable-based lubricants. *J. Synth. Lubr.* **2007**, *24*, 101–110.

Chapter IV

1. Tamada, I. S.; Lopes, P. R. M.; Montagnolli, R. N.; Bidoia, E. D. Biodegradation and toxicological evaluation of lubricant oils. *Braz. Arch. Biol. Technol.* **2012**, *55*, 951–956.
2. Kayode, J.; Oyedeji, A. A.; Olowoyo, O. Evaluation of the effects of pollution with spent lubricating oil on the physical and chemical properties of soil. *Pac. J. Sci. Technol.* **2009**, *10*, 387–391.
3. Boyde, S. Green lubricants: Environmental benefits and impacts of lubrication. *Green Chem.* **2002**, *4*, 293–307.
4. Mobarak, H. M.; Mohamad, E. N.; Masjuki, H. H.; Kalam, M. A.; Al-Mahmud, K. A. H.; Habibullah, M.; Ashraful, A. M. The prospects of biolubricants as alternatives in automotive applications. *Renew. Sustain. Energy Rev.* **2014**, *33*, 34–43.
5. Adhvaryu, A.; Erhan, S. Z.; Perez, J. M. Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants. *Wear* **2004**, *257*, 359–367.
6. Samarth, N. B.; Mahanwar, P. A. Modified vegetable oil based additives as a future polymeric material—review. *Open J. Org. Polym. Mater.* **2015**, *5*, 1-22.

7. Liu, Z.; Sharma, B. K.; Erhan, S. Z.; Biswas, A.; Wang, R.; Schuman, T. P. Oxidation and low temperature stability of polymerized soybean oil-based lubricants. *Thermochim. Acta* **2015**, 601, 9–16.
8. Adhvaryu, A.; Erhan, S. Z.; Liu, Z. S.; Perez, J. M. Oxidation kinetic studies of unmodified and genetically modified vegetable oils using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochim. Acta* **2000**, 364 (1-2), 87-97.
9. Sulek, M. W.; Kulczycki, A.; Malysa, A. Assessment of lubricity of compositions of fuel oil with bio components derived from rape-seed. *Wear* **2010**, 268, 104–108.
10. Sukjit, E.; Dearn, K. D. Enhancing the lubricity of an environmentally friendly Swedish diesel fuel MK1. *Wear* **2011**, 271, 1772–1777.
11. Becker, R.; Knorr, A. An evaluation of antioxidants for vegetable oils at elevated temperatures. *Lubr. Sci.* **1996**, 8, 95-117.
12. Sharma, B. K.; Adhvaryu, A.; Liu, Z.; Erhan, S. Z. Chemical modification of vegetable oils for lubricant applications. *J. Am. Oil Chem. Soc.* **2006**, 83, 129-136.
13. Xia, Y.; Larock, R. C. Vegetable oil-based polymeric materials: Synthesis, properties, and applications. *Green Chem.* **2010**, 12, 1893-1909.
14. Ronda, J. C.; Lligadas, G.; Galia, M.; Cadiz, V. Vegetable oils as platform chemicals for polymer synthesis. *Eur. J. Lipid Sci. Tech.* **2011**, 113, 46-58.
15. Karmakar, G.; Ghosh, P. Atom transfer radical polymerization of soybean oil and its evaluation as a biodegradable multifunctional additive in the formulation of eco-friendly lubricant. *ACS Sustainable Chem. Eng.* **2016**, 4, 775–78.
16. Raghunanan, L.; Narine, S. S. Engineering green lubricants I: Optimizing thermal and flow properties of linear diesters derived from vegetable oils. *ACS Sustainable Chem. Eng.* **2016**, 4, 686–692.
17. Nagendramma, P.; Kaul, S. Development of ecofriendly biodegradable lubricants: An overview. *Renew. Sustain. Energ. Rev.* **2012**, 16, 764–774.
18. Naughton, F. C. Production, chemistry, and commercial applications of various chemicals from castor Oil. *J. Am. Oil Chem. Soc.* **1974**, 51, 65-71.
19. Ibrahim, S.; Ahmad, A.; Mohamed, N. S. Characterization of novel castor oil- based polyurethane polymer electrolytes. *Polymer* **2015**, 7, 747–759.
20. Mutlu, H.; Meier, M. A. R. Castor oil as a renewable resource for the chemical industry. *Eur. J. Lipid Sci. Tech.* **2010**, 112 (1), 10–30.

21. Kunduru, K. R.; Basu, A.; Zada, M. H.; Domb, A. J. Castor oil-based biodegradable polyesters. *Biomacromolecules* **2015**, 16 (9), 2572–2587.
22. Patel, M.; Suthar, B. Interpenetrating polymer networks from castor oil based polyurethanes and poly(methyl acrylate). *Eur. Polym. J.* **1987**, 23, 399–402.
23. Singh, A. K. Castor oil based lubricants reduces smoke emission in two stroke engines. *Ind. Crop. Prod.* **2011**, 33, 287–295.
24. Sánchez, R.; Fiedler, M.; Kuhn, E.; Franco, J. M. Tribological characterization of green lubricating greases formulated with castor oil and different biogenic thickener agents: a comparative experimental study. *Ind. Lubr. Tribol.* **2011**, 63, 446–452.
25. Quinchia, L. A.; Delgado, L. A.; Reddyhoff, T.; Gallegos, C.; Spikes, H. A. Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers. *Tribol. Int.* **2014**, 69, 110–117.
26. Chincholkar, D. S.; Salpute, S. T.; Kumbhar N. R. Castor oil as green lubricant-A review. *Int. J. Eng. Res. Technol.* **2012**, 1(5), 1–3.
27. Madankar, C. S.; Pradhan, S.; Naik, S. N. Parametric study of reactive extraction of castor seed (*Ricinus communis* L.) for methyl ester production and its potential use as bio lubricant. *Ind. Crop. Prod.* **2013**, 43, 283–290.
28. Goodrum, J.; Geller, D. Influence of fatty acid methyl esters from hydroxylated vegetable oils on diesel fuel lubricity. *Bioresour. Technol.* **2005**, 96, 851–855.
29. Pena, R.; Romero, R.; Martinez, S.; Ramos, M.; Martinez, A.; Natividad, R. Transesterification of castor oil: effect of catalyst and co-solvent. *Ind. Eng. Chem. Res.* **2009**, 48, 1186–1189.
30. Hincapie, G.; Mondragon, F.; Lopez, D. Conventional and in situ transesterification of castor seed oil for biodiesel production. *Fuel* **2011**, 90, 1618–1623.
31. Karmakar, G.; Ghosh, P. Soybean oil as a biocompatible multifunctional additive for lubricating oil. *ACS Sustainable Chem. Eng.* **2015**, 3, 19–25.
32. Chandure, A. S.; Umare, S. S. Synthesis, characterization and biodegradation study of low molecular weight polyesters. *Int. J. Polym. Mater.* **2007**, 56, 339–353.
33. Mohamada, S. A.; Ahmed, N. S.; Hassanein, S. M.; Rashad, A. M. Investigation of polyacrylates copolymers as lube oil viscosity index improvers. *J. Pet. Sci. Eng.* **2012**, 100, 173–177.
34. Tanveer, S.; Prasad, R. Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.* **2006**, 13, 398–403.

35. Nassar, A. M. The behavior of polymers as viscosity index improvers. *Pet. Sci. Technol.* **2008**, 26, 514-522.
36. Abdel Azim, A.; Abdel Azim, R. M. Polymeric additives for improving the flow properties and viscosity index of lubricating oils. *J. Polym. Res.* **2001**, 8, 111-118.
37. Mohamed, M. M.; Abou El Naga, H. H.; El Meneir, M. F. Multifunctional viscosity index improvers. *J. Chem. Tech. Biotechnol.* **1994**, 60, 283-289.
38. El-Gamal, I. M.; Atta, A. M.; Al- Sabbagh, A. M. Polymeric structures as cold flow improvers for waxy residual fuel oil. *Fuel* **1997**, 76, 1471-1478.
39. Pedersen, K. S. Influence of wax inhibitors on wax appearance temperature, pour point and viscosity of waxy crude oils. *Energy Fuels* **2003**, 17, 321-328.
40. Castro, L.; Vazquez, F. Copolymers as flow improvers for Mexican crude oil. *Energy Fuels* **2008**, 22, 4006-4011.
41. Kuzmic, A. E.; Radosevic, M.; Bogdanic, G.; Srca, V.; Vukovic, R. Studies on the influence of long chain acrylic esters polymers with polar monomers as crude oil flow improver additives. *Fuel* **2008**, 87, 2943–2950.
42. Abdel-Azim, A. A. A.; Nassar, A. M.; Ahmed, N. S.; Kamal, R. S. Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. *Pet. Sci. Technol.* **2006**, 24, 887–894.
43. Sharma, B. K.; Adhvaryu, A.; Erhan, S. Z. Friction and wear behavior of thioether hydroxy vegetable oil. *Tribol. Int.* **2009**, 42, 353–358.
44. Trindade, E. D.; Zuleta Durango, A.; Sinatora, A. Friction and wear performance of MoDTC-containing and ester-containing lubricants over steel surfaces under reciprocating conditions. *Lubr. Sci.* **2015**, 27, 217-229.
45. Kalam, M .A.; Masjuki, H. H.; Shahabuddin, M.; Mofijur, M. Tribological characteristics of amine phosphate and octylated / butylated diphenylamine additives infused bio-lubricant. *Energ. Educ. Sci. Technol. Part A: Energ. Sci. Res.* **2012**, 30, 123–136.

A

Acid number, 98

Additive, 9, 32, 98

AIBN, 17, 18, 136, 159

Alternaria alternate, 120

Antioxidant, 2, 100

Antiwear, 4, 112, 137

ASTM D, 20, 83, 138

B

Base oil, 56, 83, 138

Biodegradability, 120, 155, 161

Boron nitride, 5

BZP, 17, 25

C

COF, 138

Copolymer, 2, 33, 142

Corrosion inhibitors, 2

Castor oil, 7, 136, 157

D

1-Decene, 54, 83, 159

Detergent, 5, 55

Dean Stark apparatus, 17, 71

Disc diffusion method, 116

Dispersant, 2, 5, 55

Diethylenetriamine, 96

Dodecyl acrylate, 116, 136

Dodecylamine, 51, 83

E

Esterification, 33, 56

Extreme pressure, 2, 113

Ethylenediamine, 96

F

Fatty acid, 5, 112

Four Ball Wear Test, 118, 138

Friction modifier, 2

Fungal pathogens, 7

G

Graphite, 5

GPC, 19, 57, 83

H

Homopolymer, 18, 21, 113, 149

Huggins equation, 72

Hydroquinone, 17, 116

I

Ionic liquid, 4

Isooctanol, 56

Intrinsic viscosity, 72

J

Jojoba oil, 112

K

Kinematic viscosity, 20, 112, 160

L

Liquid crystal, 4

Lubricant, 4, 142

Lubricating oil, 16, 157

M

Mahua oil, 111

Mark-Houwink-Sakurada (MHS) equation, 72

Maleic anhydride, 73, 83

Mannich base, 6, 94

N

Nanoparticle, 4

Number average molecular weight, 19, 61, 144

Newtonian fluid, 38, 122

Non-newtonian fluids, 38, 122

O

Octyl acrylate, 117, 124

Octyl amine, 82

P

P- Cresol, 96

Phosphorous pentasulphide, 52, 96

Percent weight loss, 26

Polydispersity index, 34, 117, 137

PDI, 119, 140, 162

Polyisobutylene, 2

Polymethacrylate, 2, 13

Pour-point depressants, 3, 13, 118

Photo micrographic image, 84, 141

R

Radical polymerization, 136

Rape seed oil, 111

Ricinoleic acid, 135

S

Shear Stability Index, 19

Soil burial test, 161

Soya bean oil, 113

Sunflower oil, 113, 114

T

Terpolymer, 114

Triethylenetetramine, 96

Thermogravimetric analysis, 36, 117, 140

Thickening effect, 140

TMS, 18

Triglyceride, 111

V

Vegetable oil, 111, 135

Vinyl acetate, 33, 71, 158

Viscometric molecular weight, 72

Viscosity index, 2, 59, 73, 137

Viscosity modifier, 2, 55

W

Wear scar diameter, 118, 138, 160

Weight average molecular weight, 40, 144, 160

X

XRD, 116, 121, 122

Z

Zinc dialkyl dithio phosphate, 4

Zinc dithio phosphate, 5

Reprint of published papers

This article was downloaded by: [North Bengal University]

On: 08 July 2015, At: 02:26

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: 5 Howick Place, London, SW1P 1WG



Petroleum Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lpet20>

Homo- and Copolymers of Decyl Methacrylate as Performance Additives for Lube Oil

P. Ghosh^a, M. Hoque^a & D. Nandi^a

^a Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India

Published online: 01 Jun 2015.



[Click for updates](#)

To cite this article: P. Ghosh, M. Hoque & D. Nandi (2015) Homo- and Copolymers of Decyl Methacrylate as Performance Additives for Lube Oil, *Petroleum Science and Technology*, 33:8, 920-927, DOI: [10.1080/10916466.2015.1034364](https://doi.org/10.1080/10916466.2015.1034364)

To link to this article: <http://dx.doi.org/10.1080/10916466.2015.1034364>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Homo- and Copolymers of Decyl Methacrylate as Performance Additives for Lube Oil

P. Ghosh,¹ M. Hoque,¹ and D. Nandi¹

¹*Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India*

Homopolymer of decyl methacrylate and its copolymer with styrene at different concentrations using two types of initiators (benzoyl peroxide [BZP] and azobisisobutyronitrile [AIBN]) were synthesized. All the prepared polymers are characterized by FT-IR and NMR. The molecular weight was determined by gel permeation chromatography. The performance of the prepared polymers in different base oils were evaluated as viscosity modifier, also known as viscosity index improver and pour point depressant. The molecular weight of homopolymer prepared by using BZP initiator is higher than homopolymer prepared by using AIBN initiator but molecular weight of copolymers prepared by BZP are lower than copolymers prepared by AIBN initiator. The thermogravimetric analysis value of the prepared polymers was determined by standard ASTM method and it is found that the thermal stability of copolymers decrease with increasing the styrene content.

Keywords: homopolymer, copolymer, viscosity modifier, pour point depressant, thermal stability

INTRODUCTION

Base oil is the major component of lubricating oil. Some additives are to be added to the base oil to meet the requirement of modern lubricating oil. Additives are the chemical substances which when added to the base oil they can enhance the properties already present or add some new properties. Some of the important additives added in lube oil are viscosity index improver (VII), pour point depressant (PPD), antiwear, antioxidant, and dispersant, among others.

VIIs are long chain, high molecular weight polymers and are used to resist the change of viscosity and function by increasing the relative viscosity of oil more at high temperatures than at low temperatures (Dean et al., 1929). It is believed that polymer molecules in cold oil adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the polymer molecules tend to straighten out and the interaction between these long molecules and the oil produces a proportionally greater thickening effect. As the temperature increases, the solubility improves and the polymer coils expand to some maximum size and in so doing donate more and more viscosity. The process of coil expansion is entirely reversibly as coil contraction occurs with decreasing temperature (Akhmedov, 1994). The viscosity index is an indicator which indicates the change in viscosity when the temperature is changed. A higher viscosity index indicates the less change in viscosity of oil for a given temperature changes (Ahmed et al., 2008). Most of the lubricating oils

Address correspondence to P. Ghosh, Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling 734013, India. E-mail: pizy12@yahoo.com

contain viscosity modifier that are composed of very large viscosity-controlling molecules (Ghosh et al., 1998).

The pour point of oil is the lowest temperature at which the oil stops its flowing. Most of base oil contains some dissolved paraffinic wax. The complete removal of wax from oil is difficult and expensive. At low temperature, the wax crystallizes to form a rigid structure that trap the oil in small packets in the structure. With sufficient formation of these crystal structures, the oil will no longer capable to flow. To overcome this problem some high molecular weight polymers are used as PPD. The high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent the oil flow at low temperature (Zhang et al., 2009).

In this present work, we have prepared homopolymers of decylmethacrylate and its copolymers with styrene at different percentage composition by using two types of initiators (BZP and AIBN) and investigated the efficiency of the polymers as VII and PPD in two types of base oil. Shear stability, which is an indicator to indicate the amount of viscosity of oil, which may be lost during operation, for each of the polymer have also been investigated. Finally a comparison of the efficiency of the polymers in terms of their performances in lube oil is investigated and reported herein.

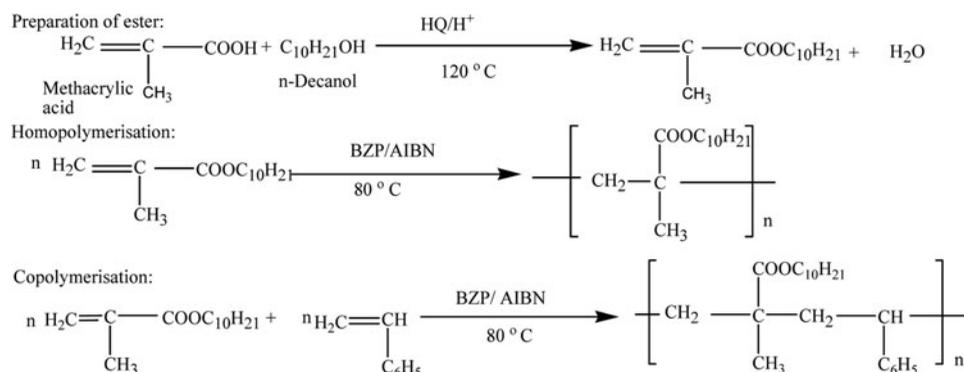
EXPERIMENTAL

Preparation of Monomer and Its Purification

Decyl methacrylate (DAMA) was prepared by reacting methacrylic acid with decyl alcohol in the molar ratio of 1.1:1 in the presence of conc. H_2SO_4 as a catalyst, 0.25% (w/w) hydroquinone with respect to the reactants as polymerization inhibitor, and toluene as solvent by using Dean Stark apparatus. The process of esterification and its purification were carried out by the procedure as reported in the earlier publication (Ghosh et al., 2011).

Preparation of Copolymers and Homopolymers

The polymers were prepared by free radical polymerization (Scheme 1) of different percentage ratios of styrene with DAMA (Table 1) in presence of different initiators (BZP and AIBN). The process and purification of polymer was carried out by the procedure as reported in our earlier publication (Ghosh et al., 2011).



SCHEME 1

TABLE 1
Percentage of Styrene, Molecular Weight, TGA Values, and PSSI Values (in Base Oil BO2 at 2% and 5% Conc.)
of the Prepared Homo- and Copolymers (P-1 to P-10)

Polymer Code No.	% of Styrene(w/w)	Molecular Weight			TGA Values		PSSI Values (% Polymer, w/w)	
		Mn	Mw	PDI	Decom. temp, °C	PWL	2	5
P-1	—	21,112	58,917	2.7906	170/350	28/82	60	63
P-2	2.5	19,121	40,571	2.1217	250/412	16/81	50	51.4
P-3	5	19,842	39,918	2.0117	250/410	15/81	43.8	55
P-4	7.5	22,982	56,121	2.4419	210/352	14/85	55.8	68
P-5	10	23,245	68,712	2.9559	190/306	31/90	57.6	70
P-6	—	20,482	49,682	2.4256	248/315	20/76	50.9	60
P-7	2.5	21,592	58,982	2.7316	280/382	20/78	44	56
P-8	5	27,457	77,688	2.8294	275/350	18/82	48	52
P-9	7.5	28,946	81,556	2.8175	275/336	19/88	65	68
P-10	10	30,345	93,842	3.0925	172/300	20/92	64	77.6

Polymer P-1 to P-5 is prepared by BZP (benzoyl peroxide) initiator, P-6 to P-10 is prepared by AIBN (azobisisobutyronitrile) initiator; Mn is number average molecular weight; Mw is weight average molecular weight; PDI is polydispersity index; Decom. temp. is decomposition temperature; PWL is percent weight loss; PSSI is permanent shear stability index.

Measurements

Spectroscopic measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells at room temperature within the wave number range of 400–4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

Determination of the molecular weight

The number average molecular weight (Mn) and weight average molecular weight (Mw) were measured by GPC method (Water 2414, polystyrene calibration) in HPLC grade THF (0.4%, w/v) at 40°C.

Determination of thermo gravimetric analysis (TGA) data

TGA data was measured on Shimadzu TGA-50 system, at a heating rate of 10°C / min. The mass loss was evaluated between 24°C and 600°C.

Determination of shear stability

Shear stability of the polymer blended lube oil is one of the essential criteria that determine the suitability of the additive in a lubricant formulation. The shear stability of the doped VMs has a strong influence on multigrade engine oil's ability to retain its viscosity under shearing conditions,

experienced by the lubricant when it is used. The loss of viscosity of a lubricant under shearing condition can be of two types, temporary viscosity loss (TVL) and permanent viscosity loss (PVL). The PVL values are generally expressed in terms of permanent shear stability index (PSSI). The PVL/PSSI value was determined as per ASTM D-3945 method by the following relation (Ghosh et al., 2011).

$$\text{PVL}(\%) = (V_i - V_s)/V_i \times 100$$

$$\text{PSSI}(\%) = (V_i - V_s)/(V_i - V_o) \times 100$$

Where V_i = kinematic viscosity of lube oil with polymer before shearing at 100°C, V_s = kinematic viscosity of lube oil with polymer after shearing at 100°C, and V_o = kinematic viscosity of lube oil at 100°C. The higher the PVL/PSSI value is, the lower the shear stability of the polymer is.

Performance evaluation as VIs

Viscosity index was calculated by dissolving prepared polymer in two base oils BO1 and BO2 through the viscosity index test according to ASTM D 2270-10. The kinematic viscosity of the polymer doped base oil was determined at 40°C and 100°C. Different concentrations of additives [ranging from 1% to 5% (w/w)] were used, to study the effect of additive concentration on VI.

Performance evaluation as PPDs

PPDs were determined in polymer doped different base oils (BO1 and BO2) through the pour point test according to the ASTM D 97-09 method using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging from 1% to 5% (w/w).

RESULTS AND DISCUSSION

Spectroscopic Analysis

The homopolymer of decylmethacrylate exhibited IR absorption band at 1735.8 cm^{-1} for the ester carbonyl group. The peak at 2854.5 cm^{-1} and 2924 cm^{-1} is the characteristic of CH_3CH_2 - group. The peaks at 1465.8, 1404, 1229, 1211, and 1149.5 cm^{-1} due to CO stretching vibration and absorption bands at 1064.6, 710, and 690 cm^{-1} were due to bending of C-H bond. In the IR spectrum of copolymer, the ester carbonyl group at 1735.8 cm^{-1} shifted to 1728.1 cm^{-1} in the copolymer. Peaks at 748.3 cm^{-1} and 702 cm^{-1} were attributed to the C-H bond of the phenyl group of styrene. In the ^1H NMR of homopolymer, the methyl protons appears in the range of 0.890–1.285 ppm, the methylene protons in the range of 1.615–1.934 ppm for all alkyl groups. A broad peak at 3.928 ppm indicates the protons of $-\text{OCH}_2$ group. Absence of any peak in the range of 5–6 ppm confirms the polymerization. In the ^{13}C NMR of homopolymer, the peak at 177.54 ppm indicates the presence of ester carbon. The peaks at 65.03 ppm and 64.88 ppm confirm the presence of $-\text{OCH}_2$ carbon. Peaks in the range of 14.16–45.12 ppm represent all sp^3 carbon atoms of alkyl groups. No peak in the range of 120–150 ppm indicates the absence of sp^2 carbon atoms and confirms the polymerization. In the ^1H NMR of copolymer, a multiplet in the range of 3.933–4.15 ppm indicates the $-\text{OCH}_2$ protons. A broad peak at 7.014–7.329 ppm appears due to the protons of phenyl group. All the sp^3 protons appear in the range of 0.9–1.942 ppm. Absence of peaks in the range of 5–6 ppm indicates that the polymerization was carried out successfully. In the ^{13}C NMR of copolymer, the peaks in the range

of 176.8–177.79 ppm confirm the presence of ester carbons. The phenyl carbons appear in the range of 125.04–128.56 ppm. The $-OCH_2$ carbon peaks appear at 64.86 ppm and 65.02 ppm. Peaks in the range 14.12–54.41 ppm represent all the sp^3 carbons.

Molecular Weight

The experimental values of M_n and M_w for the polymer P-1 to P-10 (determined by GPC) are given in Table 1. The data indicated that molecular weight of homopolymer prepared by BZP (P-1) initiator is higher than homopolymer prepared by AIBN initiator (P-6). But the copolymers prepared by BZP have lower molecular weight than the copolymers prepared by AIBN. Moreover, it is also seen that with increasing the percentage of styrene in copolymers the molecular weight as well as PDI values increases.

Analysis of TGA Data

The TGA values of all the polymers are given in Table 1. From the experimental data, it is found that the homopolymer prepared by BZP initiator (P-1) is thermally less stable than homopolymer prepared by AIBN initiator. It may be due to higher molecular weight and higher PDI value of P-1. From the values, it is also observed that thermal stability of copolymers (P-2, P-3, P-4, and P-5) is more than homopolymer, P-1. Similarly, the copolymers P-7, P-8, and P-9 are thermally more stable than homopolymer, P-6 except P-10, which is thermally less stable than P-6. It may be because of the higher PDI value P-10, that may lead to more degradation. The higher thermal stability of copolymers may be due to the presence of phenyl group. On the other hand, the homopolymer containing only the ester group may easily undergo degradation by producing gaseous products (Czech et al., 2013). Moreover, it is also observed that with increasing the styrene content in the feed of copolymers, the thermal stability decreases which is also reflected in their higher PDI value.

Analysis of Shear Stability

PSSI values were calculated in polymer doped base oil (BO2) at 2% (w/w) and 5% (w/w) concentrations at 100°C. The experimental values are given in Table 1. From the values, it is found that homopolymer P-1 is less shear stable (higher PSSI value) than homopolymer P-6. It may be due to higher molecular weight of P-1. The copolymers P-2, P-3, P-4, and P-5 are more shear stable than P-1 at low concentration but at higher concentration P-4 and P-5 is less shear stable. In case of copolymers prepared by AIBN initiator, P-7 and P-8 are more shear stable than homopolymer P-6 but P-9 and P-10 are less shear stable than P-6. It may be due to higher PDI value of P-9 and P-10. Moreover, it is also found that at a higher concentration polymer–base oil blend is less shear stable than at lower concentration. From the Table 1, it is observed that with increasing the styrene content in copolymers the shear stability decreases (higher PSSI value) which may be due to their increased PDI values. (Pourhossaini et al., 2005).

Analysis of Viscosity Index Data

VI was calculated by dissolving the prepared polymers at the concentration of 1–5% (w/w) to the two types of base oil (BO1 and BO2). The experimental values of VI are given in Table 2. From the experimental data, it is found that for all the polymers VI values increase with increasing the

TABLE 2
Viscosity Index of Polymer Doped Base Oil

Sample	VI in BO1					VI in BO2				
	Concentration of the Polymer,% in w/w					Concentration of the Polymer,% in w/w				
	1	2	3	4	5	1	2	3	4	5
P-1	96	114	123	144	153	96	104	109	118	128
P-2	91	96	98	107	122	92	98	110	112	107
P-3	96	108	115	126	128	108	116	118	120	126
P-4	112	120	128	138	162	104	105	119	128	136
P-5	112	122	134	156	162	108	114	116	124	138
P-6	103	105	123	130	136	98	102	112	114	118
P-7	99	102	106	116	125	106	110	108	119	126
P-8	101	104	115	122	132	106	108	114	122	132
P-9	99	118	128	148	163	105	122	138	142	143
P-10	102	124	124	142	160	102	115	132	142	142

concentration of polymer in base oils. With increasing temperature, the lube oil viscosity decreases but the expansion of polymer molecules take place at high temperature due to increase in solvation power and increased size of micelle. This increased in micelle size minimize the reduction of the viscosity of the polymer doped lube oil. Therefore, with increasing the concentration of polymer in lube oil leads to an increase in the total volume of polymer micelle in lube oil, thus exerting higher thickening effect and improves the VI property (Tanveer et al., 2006). Between the two homopolymers (P-1 and P-6), P-1 (prepared by BZP initiator) has greater effect on VI for both the base oils than P-6 (prepared by AIBN initiator). It may be due to higher molecular weight of P-1. From the experimental values, it is also found that the performance of the prepared copolymers as VI increases by increasing the styrene content. It may be due to increase of the molecular weight with increasing styrene content. In case of P-5 and P-10 (% of styrene 10), the molecular weight has increased but VI remain approximately same with P-4 and P-9 respectively. It may be due to higher PDI value and hence reduces the solubility (Nassar et al., 2005). The VI value is somewhat better in case of copolymers prepared by AIBN initiator than copolymers prepared by BZP initiator. The lower decomposition temperature of AIBN compared to BZP may be responsible for giving higher molecular and hence the VI (Ghosh et al., 2014). All the polymers are more effective in BO1 (lower viscous) than BO2 as VM.

Analysis of Pour Point Data

The polymer doped base oils (BO1 and BO2) at different concentrations ranging from 1% to 5% (w/w) were tested for pour point and experimental values are given in Table 3. From the values, it is observed that all the polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oil. It may be due to decrease in solvation power. The efficiency as PPD of homopolymer, P-1 (prepared by BZP initiator) is better than homopolymer P-2 (prepared by AIBN initiator). It may be due to higher PDI value of P-1 (Al-Sabagh et al., 2012). The copolymers P-2, P-3, P-4, and P-5 are less efficient as PPD than the homopolymer P-1. It may be due to presence of phenyl group in the copolymers that reduces the adsorption of the polymer molecule on the wax crystals (Abdel-Azim et al., 2006). From the experimental values, it is clear that there is no significant change of pour point with increasing the styrene content among the copolymers of P-2, P-3, P-4, and P-5 (prepared by BZP initiator). The

TABLE 3
Pour Point of Polymer Doped Base Oil

Sample	Pour Point in BO1, °C Concentration of the Polymer,% in w/w					Pour Point in BO2, °C Concentration of the Polymer,% in w/w				
	1	2	3	4	5	1	2	3	4	5
P-1	-10	-10	-8	-7	-7	-12	-12	-10	-9	-9
P-2	-7.4	-7.4	-6	-5.5	-5.5	-8.8	-8.8	-7.5	-7.5	-7.5
P-3	-7.8	-7.8	-6.8	-6.8	-6	-9.6	-9.6	-9	-9	-9
P-4	-9.4	-9.4	-7.5	-7	-7	-10	-10	-9	-9.5	-9
P-5	-9	-9	-8	-8	-8	-8	-8	-7.5	-7.5	-7.5
P-6	-9	-9	-8	-7	-7	-10	-11	-10	-10	-10
P-7	-15	-15	-13	-10	-10	-12	-12	-10	-10	-9.5
P-8	-12	-12	-10	-10	-10	-12	-12	-10	-10	-10
P-9	-9.4	-9.4	-8.5	-7.5	-7.5	-10	-9.5	-9.5	-9.5	-8.5
P-10	-9	-10	-8	-7	-7	-9.4	-9	-8.5	-8	-8

copolymer P-7 and P-8 (prepared by AIBN initiator) are more efficient as PPD than homopolymer P-6 (prepared by AIBN initiator) but P-9 and P-10 are less efficient compare to homopolymer. With increasing the styrene content among the copolymers P-7, P-8, P-9, and P-10, it is found that PPD property gradually decreases and may be due to increase of percentage of phenyl group. By comparing the PPD property of copolymers, prepared by BZP initiator and AIBN initiator, it is seen that copolymers prepared by AIBN initiator are more effective as PPD. The lower decomposition temperature of AIBN compare to BZP may be responsible for this observation.

CONCLUSION

From the above study, it is found that all the prepared decyl methacrylate based polymers are effective as VM and PPD. The homopolymer prepared by BZP initiator is more effective as VM and PPD than the homopolymer prepared by AIBN initiator. The efficiency of the copolymers as VM increases with increasing the styrene content up to 7.5% of styrene but at 10% of styrene, it does not increase. The performance as VM of the copolymers prepared by AIBN initiator is better than the copolymers prepared by BZP initiator. The efficiency of the copolymers as PPD prepared by AIBN initiator decreases with increasing styrene content. Therefore, a critical observation can be made from the present study that initiator and percentage of styrene has a significant role in relation to the performance of the additive as VM and PPD.

ACKNOWLEDGMENTS

The authors thank IOCL, India, for supplying base oil.

FUNDING

The authors thank UGC, New Delhi, for financial support.

REFERENCES

- Abdel-Azim, A. A. A., Nassar, A. M., Ahmed, N. S., and Kamal, R. S. (2006). Preparation and evaluation of acrylate polymers as pour point depressants for lube oil. *Pet. Sci. Technol.* 24:887–894.
- Ahmed, N. S., Nassar, A. M., Nasser, R. M., Khattab, A. F., and Abdel-Azim, A. A. A. (2008). Synthesis and evaluation of some polymeric compounds as pour point depressants and viscosity index improvers for lube oil. *Pet. Sci. Technol.* 26:1390–1402.
- Akhmedov, A. I. (1994). Copolymer of alkyl methacrylates with styrene as V. I. improvers for lubricating oils. *Chem. Technol. Fuels Oils* 30:34–37.
- Al-Sabagh, A. M., Sabaa, M. W., Saad, G. R., Khidr, T. T., and Khalil, T. M. (2012). Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egyptian J. Pet.* 21:19–30.
- Czech, Z., Kowalczyk, A., Kabatc, J., and Swiderska, J. (2013). Thermal stability of poly(2-ethyl hexyl acrylate) used as plasticizers for medical applications. *Polym. Bull.* 70:1911–1918.
- Dean, E. W., and Davis, G. H. B. (1929). Viscosity variations of oils with temperature. *Chem. Met. Eng.* 36:618–619.
- Ghosh, P., Das, T., and Nandi, D. (2011). Shear stability and thickening properties of homo and copolymer of methyl methacrylate. *Am. J. Polym. Sci.* 1:1–5.
- Ghosh, P., Das, M., Upadhyay, M., Das, T., and Mandal, A. (2011). Synthesis and evaluation of acrylate polymers in lubricating oil. *J. Chem. Eng. Data* 56:3752–3758.
- Ghosh, P., Pantar, A. V., Rao, U. S., and Sarma, A. S. (1998). Shear stability of polymers used as viscosity modifiers in lubricating oils. *Ind. J. Chem. Technol.* 5:309–314.
- Nassar, A. M., Ahmed, N. S., Kamal, R. S., Abdel-Azim, A. A. A., and El-Nagdy, E. I. (2005). Preparation and evaluation of acrylate polymers as viscosity index improves for lube oil. *Pet. Sci. Technol.* 23:537–546.
- Pourhossaini, M. R., Farahani, E. V., Gholamin, M., and Gholamin, M. (2005). Synthesis and characterization of olefin copolymers as viscosity modifier for engine oil. *Iranian Polym. J.* 14:549–557.
- Tanveer, S., and Prasad, R. (2006). Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.* 13:398–403.
- Zhang, H., Liu, H., and Wang, S. (2009). A new alternating copolymerized derivative as a cold flow improver for diesel fuel. *J. Pet. Sci.* 6:82–85.

Mannich bases and Phosphosulphurized Mannich bases: Synthesis, characterization and performance evaluation as potential lube oil additives

P Ghosh* and M Hoque

Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling-734013, India

Received 15 September 2014; revised 31 December 2014; accepted 30 January 2015

With increasing demands being placed on lubricants for automotive engines and transmissions, it has become necessary to improve the function of lubricants. Modern lubricants are formulated from a range of base fluids and chemical additives to improve their function or to add some new performance properties in them. In this study, some Mannich bases were prepared by using p-cresol, formaldehyde and different polyethylene polyamines. Phosphosulphurized Mannich bases were also prepared by the using P_2S_5 . Structure of the prepared compounds has been confirmed by infrared spectroscopy, NMR and molecular weight determination. The performance of the prepared Mannich bases as well as their Phosphosulphurized derivatives was investigated as antioxidants and detergents/dispersants. It was found that the efficiency of additive performance increases with increasing the number of -NH groups in the amines used.

Keywords: Mannich base, antioxidants, detergents/dispersants, additives.

Introduction

Modern engine oil contains a wide range of additives, which are blended with base oil to form a complete package capable of meeting demanding performance¹. The functions of lubrication additives include improvement of the viscosity index, pour point, oxidative or thermal stability, anti wear performance of the base oil, to minimize rust and corrosion, to lessen the deposition of harmful chemicals on lubricated parts and so on². Dispersant additive contains a polar head group with an oil soluble hydrocarbon tail, keeps metal surfaces clean by preventing deposition of oxidation products of internal combustion engines^{3, 4}. The main functions of detergents in engine oils are acid neutralisation, oxidation inhibition and rust prevention⁵. These functions provide engine cleanliness and extended trouble free operation⁶. The most important mode of lubricant degradation is oxidation. Additives that reduce the oil oxidation are called antioxidants, which act to retard oxidation of lubricating oil, thus preventing the formation of corrosive products. Antioxidants act in two different ways, by inhibition of peroxides or as radical scavengers, which react with peroxy radicals, thus preventing further propagation of the free radical chain⁷. In the present work, some Mannich bases were prepared by using

p-cresol, formaldehyde and different amines, and finally the Mannich bases were treated with P_2S_5 to synthesize phosphosulphurized Mannich bases. The efficiency of the prepared compound was investigated as antioxidant and detergents/dispersants additive for lube oil.

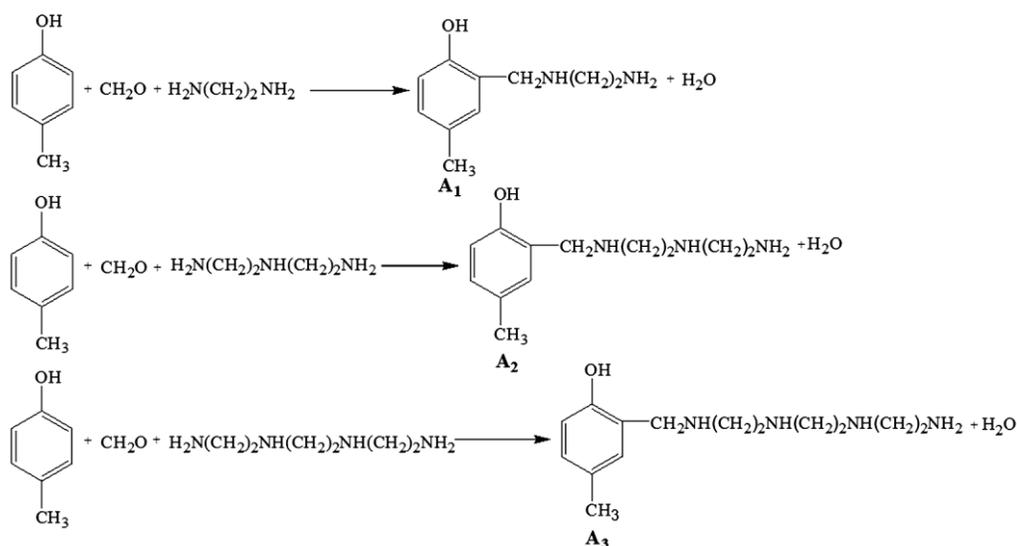
Materials and Methods

Preparation of Mannich bases

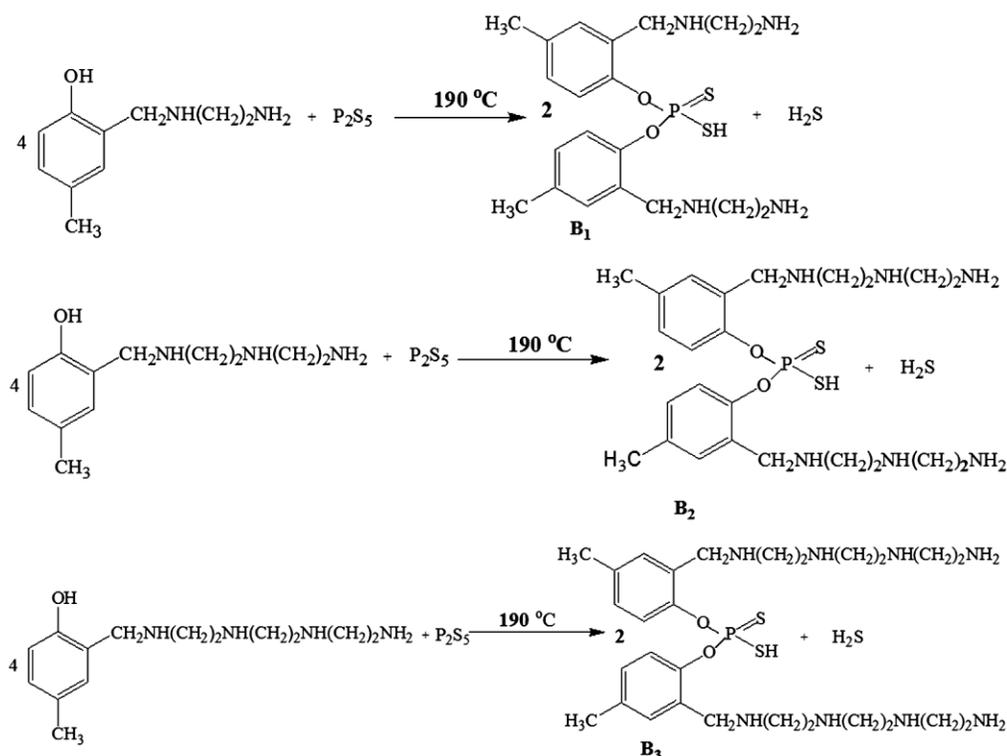
In a 5 necked round bottom flask, fitted with a mechanical stirrer, a ground joint thermometer, a condenser and a dropping funnel, the appropriate amount of p-cresol in methanol and aqueous solution of polyethylene polyamines were added. A formaldehyde (37%) solution was added drop wise during 1 hour at room temperature under nitrogen atmosphere. When the addition of formaldehyde is completed, the temperature of the mixture was raised to reflux temperature for 3 hour. The mixture was then cooled to room temperature. The upper layer was separated from the lower viscous layer (product). The product was dissolved in benzene and washed three times with distilled water to remove the excess of amine and formaldehyde. The molar ratio of p-cresol, formaldehyde and amines were taken as 1:1:1 ratio. The prepared three Mannich bases with ethylenediamine, diethylenetriamine and triethylenetetramine have been designated by A_1 , A_2 and A_3 respectively.

*Author for correspondence
E-mail: pizy12@yahoo.com

Scheme 1



Scheme 2



Preparation of Phosphosulphurization Mannich Bases

A four necked round bottom flask, fitted with a mechanical stirrer, thermometer, condenser and inlet for passing nitrogen gas was used for the reaction.

The reactions were carried out with four moles of prepared Mannich bases and one mole

of P₂S₅ in methanol. The reaction mixture was maintained at 185-190 °C with continuous stirring for 4 hour. Three products of phosphosulphurized Mannich bases have been prepared using three Mannich bases to give B₁, B₂ and B₃ respectively.

Measurements

Spectroscopic Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wave number range (400 to 4000) cm^{-1} . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and tetramethylsilane (TMS) as reference material.

Determination of the molecular weight

The mean molecular weight of the prepared six additives was determined by using Gel Permeation Chromatography (GPC, Model number-water 2414). In this method the samples were dissolved in tetrahydrofuran (0.4%, w/v) (used as mobile phase) in the Water GPC system (polystyrene calibration) at 40 °C.

Performance evaluation of the prepared compounds as lube oil additives

As Antioxidant

The lube oil sample and its blends containing 2% additive (w/w) of each of the prepared additives were subjected to severe oxidation condition in presence of copper and iron strips at 165.5 °C for 72 hours using Indiana test method of oxidation⁸. The oxidation stabilities of the lube oil blends is expressed in terms of variation of viscosity ratio and change in total acid number and it was determined by taking samples at intervals of 24 hour and up to 72 hour of oxidation and the samples were tested for:

Variation of viscosity ratio V/V_0

The variation of viscosity ratio was determined using Ubbelohde OB Viscometer using ASTM D-2270 method, where V = Kinematic viscosity at 40°C of sample after oxidation, V_0 = Kinematic viscosity at 40°C of sample before oxidation.

Change in total acid number ($\Delta T.A.N$)

The change in total acid number was calculated according to ASTM D 664-95 standard test method where $\Delta T.A.N$ = total acid number of sample after oxidation – total acid number of sample before oxidation.

As Dispersant

Spot method was applied to determine dispersancy⁹. Drops of oxidized 2% additive (w/w) and lube oil mixture were taken from the Indiana oxidation apparatus after each 24 h intervals of oxidation and up to 72 h to make spots on filter paper

(Durieux 122) and dispersancy of the sample were measured as follows:

$$\% \text{ Dispersancy} = \frac{\text{Diameter of black spot}}{\text{Diameter of the total spot}} \times 100$$

The efficiency of dispersants has been classified as follows:

Values up to 30%, no dispersancy; 30-50%, medium; 50-60%, good; 60-70%, very good and above 70% excellent dispersancy performance.

Results and Discussion

Determination of molecular weight

The molecular weight of the prepared Mannich bases and Phosphosulphurized Mannich bases were determined by GPC and values are given in table 1.

Spectroscopic Analysis

IR spectrum of prepared Mannich bases: The –NH and –OH group regions are overlapping in the range of 3600-3200 cm^{-1} . Peak for the presence of C-N linkage appeared at 1250 and 1103 cm^{-1} . In case of ¹H-NMR, the disappearance of –CHO proton peak at δ 9.92 ppm and appearance of benzylic –CH₂ peak at δ 3.8 ppm supports the IR observation. ¹³C NMR also confirms the formation of benzylic –CH₂ proton, (appearance of peak at δ 47 ppm). The IR peaks at 2400 cm^{-1} (–SH group), 1018 cm^{-1} (P-O bond), 686,624 and at 463 cm^{-1} (P=S bond) and in the range 1100 – 1050 cm^{-1} (Ar-O bonds) indicates the formation of phosphosulphurized Mannich base.

Performance Analysis of Mannich Bases

The prepared compounds A₁, A₂ and A₃ were added to the lube oil samples and the oxidation stability as well as detergency/ dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

Table 1—Theoretical and determined mean molecular weights of compounds A₁, A₂, A₃, B₁, B₂ and B₃

Prepared compounds	Theoretical	Determined
A ₁	180	189
A ₂	223	228
A ₃	266	276
B ₁	454	462
B ₂	540	546
B ₃	626	635

As antioxidants

The prepared Mannich bases A_1 , A_2 and A_3 were added to the lube oil samples in 2% concentration by weight and the blends were subjected to severe oxidation condition as described in experimental section. The oxidation stability is expressed in terms of increase in kinematic viscosity ratio (v/v_0), and change in total acid number ($\Delta T.A.N$), compared with lube oil samples free from additives. Results are given in figures 1 and figure 2, which indicate the followings: The additives A_1 , A_2 and A_3 exert better oxidation resistance properties to the additive doped lube oil than the additive free oil. It may be due to the presence of phenolic or amino groups in their structures, which act as chain breaking inhibitors (antioxidants) by donation of labile hydrogen from groups (-OH or -NH) to stabilize the chain radicals; i.e., these inhibitors destroy the peroxide radicals and thus, the oxidation chain is broken¹⁰. The presence of amine part present in the prepared Mannich bases neutralizes some of the acidic products formed during oxidation. The kinematic viscosity ratio (V/V_0) and

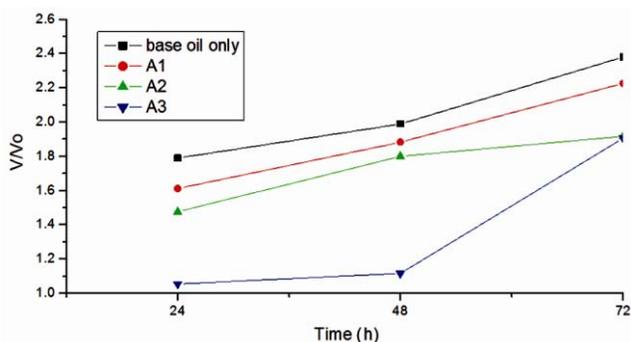


Fig. 1—Variation of V/V_0 with oxidation time of lube oil without and with Mannich bases additives A_1 , A_2 and A_3

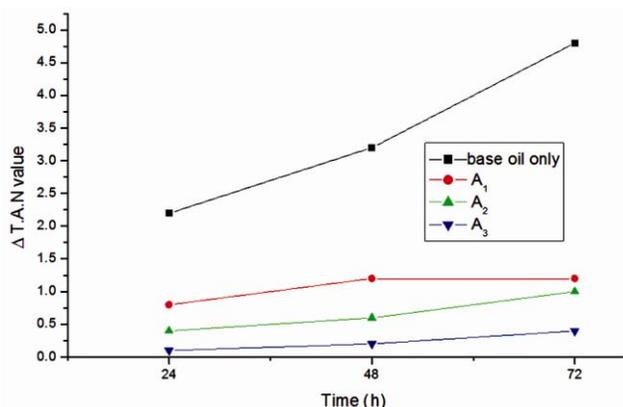


Fig. 2—Variation of $\Delta T.A.N$ with oxidation time of lube oil without and with Mannich bases additives A_1 , A_2 and A_3

total acid number change ($\Delta T.A.N$) decrease with increasing the number of -NH groups present in the amines used. The performances of the additives follow the order $A_3 > A_2 > A_1$. figure 1 and figure 2

As Dispersants/ Detergents

The base oil with 2% (w/w) additives were subjected to severe oxidation conditions using the Indiana test method as described in experimental section, in which the efficiency of the dispersant additive increases the diameter of the black spot. This is due to the enhanced capability of the doped oil to carry the oxidation products to a longer distance from the centre of the spot. It may be due to the fact that the -NH groups form hydrogen bonds with the polar end of alcohol, aldehyde, ketone, acids etc which are formed during oxidation. The values of dispersants are given in table 2. From the data, it is clear that dispersancy increases with increasing the number of -NH groups present in the prepared additive. The highest dispersancy was found in case of A_3 due to presence of higher number of -NH groups.

Performance analysis of phosphosulphurized Mannich bases

The prepared compounds B_1 , B_2 and B_3 were added to the lube oil samples and the oxidation stability as well as detergency/ dispersancy of all samples under evaluation were determined and compared with lube oil sample without any additives.

As antioxidants

Mannich bases were treated with P_2S_5 to produce the additives B_1 , B_2 and B_3 . The prepared additives were added to the base oil and subjected to severe oxidation conditions using the Indiana test method discussed in experimental section. The oxidation stability is expressed in terms of change in total acid number and increase in kinematic viscosity ratio and

Table 2—Dispersancy of the base oil and its blends containing additives A_1 , A_2 , A_3 , B_1 , B_2 and B_3 after different oxidation period

Sample	Dispersancy time,(in hour)		
	24	48	72
Base oil only	42	40	35
Base oil +additive A_1	45	53	55.5
Base oil +additive A_2	63.6	66	68
Base oil + additive A_3	66.6	71	75.75
Base oil+ additive B_1	60	62	66
Base oil+ additive B_2	63	71	74
Base oil+ additive B_3	64	71	77

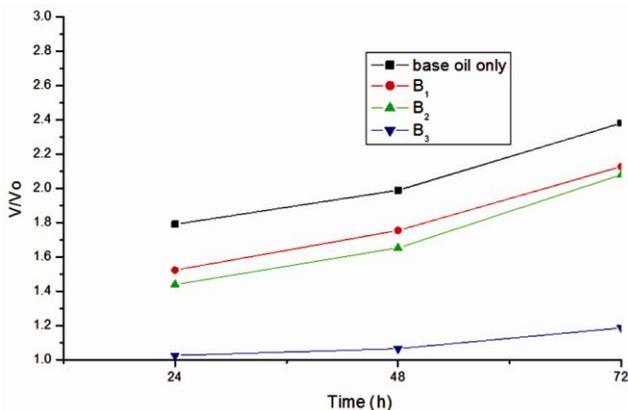


Fig. 3—Variation of V/Vo with oxidation time of lube oil without and with Phosphosulphurized Mannich bases additives B₁, B₂ and B₃

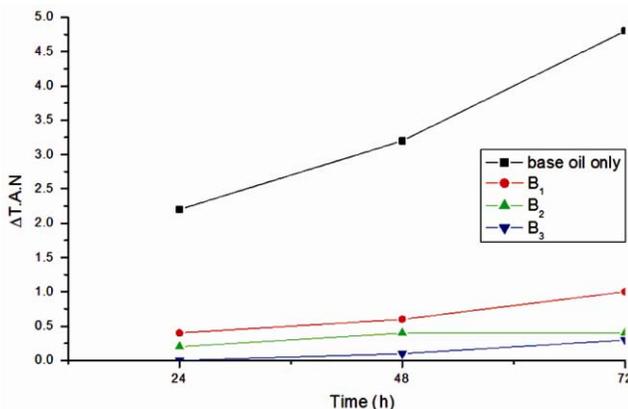


Fig. 4—Variation of ΔT.A.N with oxidation time of lube oil without and with phosphosulphurized Mannich bases additives B₁, B₂ and B₃

compared with the additive free lube oil. Results are given in figure 3 and figure 4 which indicate the followings. With increasing the number of –NH groups, the oxidation stability increases and therefore B₃ gave better results than others. In comparison to Mannich bases, phosphosulphurized Mannich bases gave somewhat better results. It is due to presence of phosphorous and Sulphur. The sulphur and phosphorous compounds combine with metal to form sulphide and phosphide films that prevent the contact between metal surfaces and lube oil, and hence interfere with the catalytic action of metal on lube oil oxidation process¹¹. figure 3 and figure 4

As dispersants/detergents

The dispersancy values of phosphosulphurized Mannich bases are not very much different from those of dispersancy of Mannich bases. The values are

given in table 2. The dispersancy capability mainly depends on the number of –NH groups present on the prepared additives. That is why B₃ has highest dispersancy capacity than B₂ and B₁.

Conclusions

This comparative study indicated that addition of very small amount of prepared additives to lube oil enhances the efficiency as antioxidant and dispersant. It is also found that phosphosulphurized Mannich bases are more efficient as antioxidant than Mannich bases only. The performance of all the prepared additives increases with increasing number of –NH groups present in the additives.

Acknowledgement

Authors thank to UGC, New Delhi for financial support and thank also to IOCL, India for supplying base oil.

References

- Ghosh P, Das M, Upadhaya M, Das T & Mandal A, Synthesis and evaluation of acrylate polymers in Lubricating oil, *J Chem Eng Data*, **56** (2011) 3752-3758.
- Ghosh P, Das T & Nandi D, Synthesis, Characterization and viscosity studies of homopolymer of methyl methacrylate and copolymer of methyl methacrylate and styrene, *J Sol Chem*, **40** (2011) 67-78.
- Abdel-Azim A, Nassar AM, Ahmed NS & Kamal RS, Multifunctional Lube oil Additives based on Octadecene-Maleic anhydride Copolymer, *Petrol Sci Technol*, **29** (2011) 97-107.
- Ahmed NS, Nassar AM & Abdel-Azim AAA, Synthesis and evaluation of some detergents/dispersant additives for lube oil, *Int J Polym Mater*, **57** (2008) 114-124.
- Nassar AM, Ahmed NS, Abdel Aziz KI, El-Kafrawy AF & Abdel-Azim AAA, Synthesis and evaluation of detergents/dispersant additives from polyisobutylene succinimides, *Int J Polym Mater*, **55** (2006) 703-713.
- Najman M, Kasrai M, Bancroft GM & Davidson R, Combination of ashless antiwear additives with metallic detergents. *Tribol Int*, **39** (2006) 342-355.
- Rundnick LR, *Lubricant additives: Chemistry and applications*, (Marcel Dekker, New York) 2003.
- Lamp GG, Loance CM & Gaynor JW, Indiana stirring oxidation test for lubricating oil. *Ind Eng Chem Anal Ed*, **13** (1941) 317-321.
- Kamal RS, Ahmed NS & Nassar AM, Study the efficiency of some compounds as lubricating oil additives, *Appl Petrochem Res*, **3** (2013) 1-8.
- Rose DJ, Analysis of Antioxidant Behaviour in Lubricating oils, A Ph.D thesis submitted to School of Chemistry, The University of LEEDS (1991).
- Sarnavskaya TI, Lebedev EV, Gordash Yu T & Shablii VI, Comparative evaluation of antioxidant properties of additives for synthetic lube oils, *Chem Technol of fuels and oils*, **11** (1975) 731-733.

This article was downloaded by: [North Bengal University]

On: 14 August 2015, At: 23:19

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: 5 Howick Place, London, SW1P 1WG



Petroleum Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/lpet20>

Synthesis and Performance Evaluation of Vinyl Acetate-Maleic Anhydride Based Polymeric Additives for Lubricating Oil

P. Ghosh^a & M. Hoque^a

^a Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India

Published online: 14 Aug 2015.



[Click for updates](#)

To cite this article: P. Ghosh & M. Hoque (2015) Synthesis and Performance Evaluation of Vinyl Acetate-Maleic Anhydride Based Polymeric Additives for Lubricating Oil, *Petroleum Science and Technology*, 33:11, 1182-1189, DOI: [10.1080/10916466.2015.1049357](https://doi.org/10.1080/10916466.2015.1049357)

To link to this article: <http://dx.doi.org/10.1080/10916466.2015.1049357>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Synthesis and Performance Evaluation of Vinyl Acetate-Maleic Anhydride Based Polymeric Additives for Lubricating Oil

P. Ghosh¹ and M. Hoque¹

¹*Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling, India*

Copolymer of vinyl acetate with maleic anhydride was synthesised and the prepared copolymer was esterified with different long chain alcohols (octyl, decyl, and dodecyl alcohol). The performance of the polymeric additives in different base oils was evaluated as viscosity modifier (VM), also called viscosity index improver and pour point depressant by standard ASTM methods. Intrinsic viscosity and viscometric molecular weight of the polymers were determined by Huggins and Mark-Houwink equation, respectively. It was found that the efficiency of the polymers as a VM increases with increasing the alkyl chain length of the used alcohol. Whereas, the efficiency as a pour point depressant increases with decreasing alkyl chain length of the used alcohol of the polymers.

Keywords: viscosity modifier, pour point depressant, copolymer, intrinsic viscosity, viscometric molecular weight

INTRODUCTION

Lubricant comprises a base fluid and a package of additives. The basic function of lubricant is to lubricate modern engines to prolong its lifetime. Base fluids also known as base oils, the basic building block of a lubricant, are a complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with low volatility and high viscosity index. The percentage of different hydrocarbon components determines the characteristics of the base oil (Ghosh and Das, 2011). Additives are the specific chemical compounds when added to base oil, impart new and useful properties to the oil. Some additives enhance the properties already present and some act to reduce the rate at which undesirable changes take place in the product during its service life (Rizvi, 2009). The most important additive is viscosity index improver (VII). The degree of susceptibility of viscosity of a fluid with rise in temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI). A higher VI value signifies a lesser effect of temperature on viscosity. VII or viscosity modifier (VM) are additives that resist the change of viscosity of oil with change in temperature. The performance of VII mainly depends on the behavior of polymer molecule in the base stock, polymer solubility, molecular weight, and resistance to shear degradation (Abadir et al., 2014).

Pour point is the lowest temperature at which the lube oil loses its flow ability. The freezing of lube oil is caused by the formation of crystal network of paraffinic wax present in the lube oil.

Address correspondence to P. Ghosh, Natural Product and Polymer Chemistry Laboratory, Department of Chemistry, University of North Bengal, Darjeeling 734013, India. E-mail: pizy12@yahoo.com

The pour point of a lube oil can be lowered with additives, called pour point depressant (PPDs), also known as cold flow improvers. The PPD additive works by destroying the wax crystal network and thereby lowering the pour point. The flow property at low temperature is thus maintained (Van Home, 1949).

In this present work, we have prepared maleic anhydride–vinyl acetate copolymer. Due to insolubility of the copolymer in lube oil, it was esterified with three types of long chain alcohol (1-octanol, 1-decanol, and 1-dodecanol) to get the corresponding esterified polymeric products. We investigated the efficiency of each of them as VM and PPD in three types of base oil.

EXPERIMENTAL

Materials

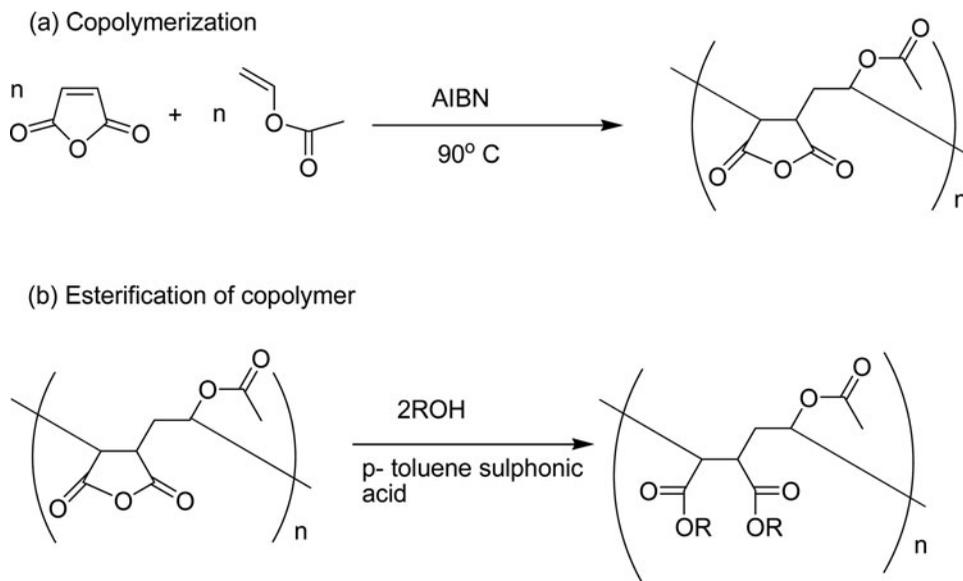
Maleic anhydride (99%, LOBA Chemie, India) and vinyl acetate (99%, S D Fine Chemicals, India) were used without further purification. Azobisisobutyronitrile (AIBN; 98%, Spectrochem Pvt. Ltd., India) was used without purification. Toluene (SRL) was purified by distillation and used as solvent for polymerisation as well as esterification of polymer. P-Toluene sulfonic acid (98%, LOBA chemie) was used as catalyst after complete drying. 1-octanol (99%, LOBA chemie, India), 1-decanol (99%, S D Fine Chemicals, India), and 1-dodecanol (98%, S D Fine Chemicals, India) were used in esterification without further purification.

Preparation of Maleic Anhydride-Vinyl Acetate Copolymer

The copolymerization of maleic anhydride and vinyl acetate was carried out in a three necked round bottom flask fitted with a magnetic stirrer and an inlet for the introduction of nitrogen. Vinyl acetate and maleic anhydride was mixed in the molar ratio of 1:1 in the presence of AIBN (0.5% w/w, with respect to the monomer) as an initiator and toluene was used as a solvent. The reactants were mixed and temperature was kept constant at 90°C for half an hour and then AIBN was added and heated for 6 h at 90°C. After the reaction is over, the product was put into cold methanol and filtered to obtain the copolymer.

Esterification of the Copolymer With Different Alcohols

The prepared copolymer was reacted separately with 1-octanol, 1-decanol, and 1-dodecanol in presence of catalytic amount of p-toluene sulfonic acid to prepare three esterified products, A, B, and C of the copolymer, respectively. In a four-necked round-bottom flask fitted with a mechanical stirrer, an efficient condenser with Dean-Stark apparatus, a thermometer and a nitrogen gas inlet. The dried copolymer was esterified with different alcohols in the presence of p-toluene sulfonic acid as a catalyst and toluene as a solvent. The copolymer and alcohol were taken in 1:1 (w/w) ratio. Reaction mixture was slowly heated up to 130°C until all water of esterification was removed. The ester was purified by washing with distilled water and drying over Na₂SO₄. Finally methanol was added to precipitate the product and was filtrated and dried (Scheme 1).



SCHEME 1 ROH = C₈H₁₇OH (octyl alcohol) gives polymeric additive A; ROH = C₁₀H₂₁OH (decyl alcohol) gives polymeric additive B; ROH = C₁₂H₂₅OH (dodecyl alcohol) gives polymeric additive C.

Measurements

Spectroscopic Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the range 400–4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl₃ was used as solvent and tetramethylsilane (TMS) as reference material.

Determination of Intrinsic Viscosity and Viscometric Average Molecular Weight of Additives

Viscometric properties were determined at 40°C in toluene solution using an Ubbelohde OB viscometer. The time flow was counted at eight different concentrations (g/c.c) of the polymer solution. Intrinsic viscosity and viscometric molecular weight were determined by Huggins (Eq. [1]) and Mark-Houwink-Sakurada equation (Eq. [2]), respectively (Ghosh et al., 2010).

$$\text{Huggins equation (H), } \eta_{sp}/C = [\eta]_h + K_h[\eta]_h^2 C \quad (1)$$

Where C is the mass concentration, $\eta_{sp} = \eta_r - 1$, η_{sp} is the specific viscosity, $\eta_r = t/t_0$, η_r is the relative viscosity or viscosity ratio, t is the flow of time of the polymer solution, and t₀ is the flow of time of the pure solvent. $[\eta]_h$ = intrinsic viscosity, respective to Huggins equation, K_h is the Huggins coefficient. According to Mark-Houwink-Sakurada (Eq. [2]), the value of intrinsic viscosity changes with the molecular weight of the additive in a solvent as:

$$[\eta] = KM^a \quad (2)$$

TABLE 1
Base Oil Properties

Property	Base Oil		
	BO1	BO2	BO3
Density at 40°C, g cm ⁻³	0.83	0.84	0.87
Viscosity at 40°C, cSt	7.102	23.502	107.120
Viscosity at 100°C, cSt	1.850	3.98	10.322
Viscosity index	84.56	85.15	81.5
Pour point, °C	-3	-6	-0.5
Cloud point, °C	-8	-10	-8

Where $[\eta]$, the intrinsic viscosity, can be calculated by using Huggins equation, and parameters K and a depend on the type of polymer, solvent, and temperature. For the determination of viscosity average molecular weight, the constants, $K = 0.00387$ dl/g and $a = 0.725$ were used in Mark-Houwink-Sakurada equation (Mellow et al., 2006).

Determination of Thermogravimetric Analysis Data

Thermogravimetric analysis (TGA) data was recorded on Shimadzu TGA-50 system, at a heating rate of 10°C/min. The mass loss was calculated between 24°C and 600°C.

Performance Evaluation of the Polymers as VMs

VI was calculated by dissolving prepared polymer in three different base oils (BO1, BO2, and BO3) through the viscosity index test according to ASTM D 7042 method (Dean and Davis, 1929). The kinematic viscosity of the polymer doped base oil was determined at 40°C and 100°C. Different concentrations ranging from 1% to 5% (w/w) were used to study the effect of additive concentration on VI.

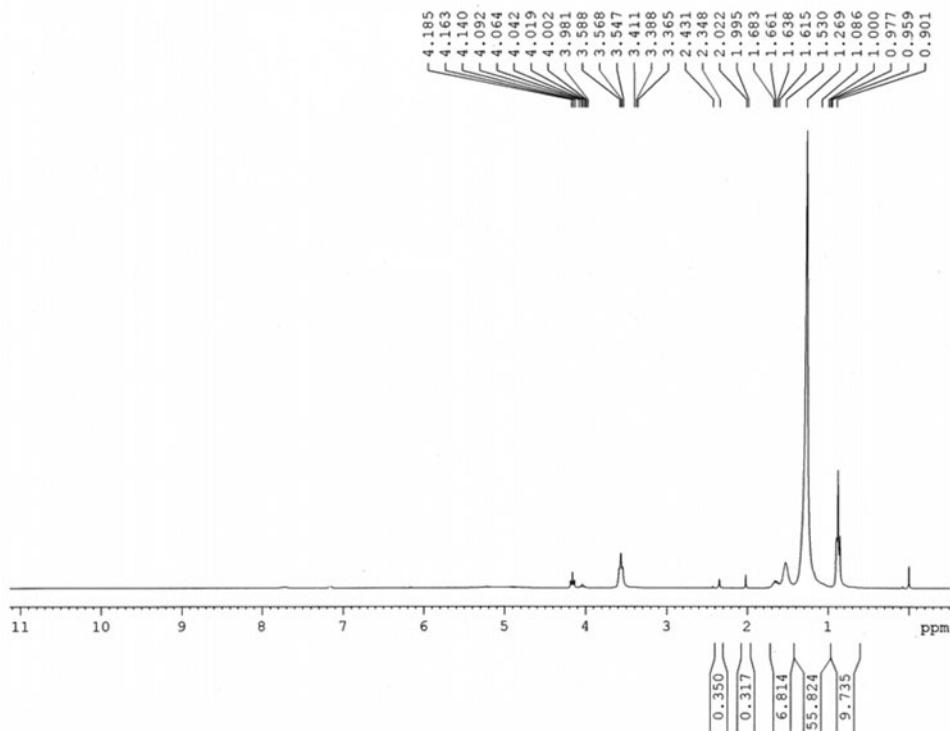
Performance Evaluation of the Polymers as PPDs

Pour point of the additive doped base oils (BO1, BO2, and BO3) were recorded through the pour point test according to the ASTM D 97-09 method (Nikolaev et al., 2013) using the cloud and pour point tester model WIL-471 (India). The effect of additive concentration on pour point was investigated by using different doping concentrations ranging from 1% to 5% (w/w). The properties of the three base oils are given in Table 1.

RESULTS AND DISCUSSION

Spectroscopic Analysis

The spectroscopic data (IR and NMR) of the three polymers A, B, and C are similar. In the IR spectra, peak at 1735.8 cm⁻¹ indicates the presence of ester carbonyl group. The peaks at 2854.5 cm⁻¹ and 2925 cm⁻¹ are the characteristic of CH₃CH₂- group. The peaks at 1466 cm⁻¹, 1404 cm⁻¹, 1373 cm⁻¹,

FIGURE 1 ^1H NMR of polymer A.

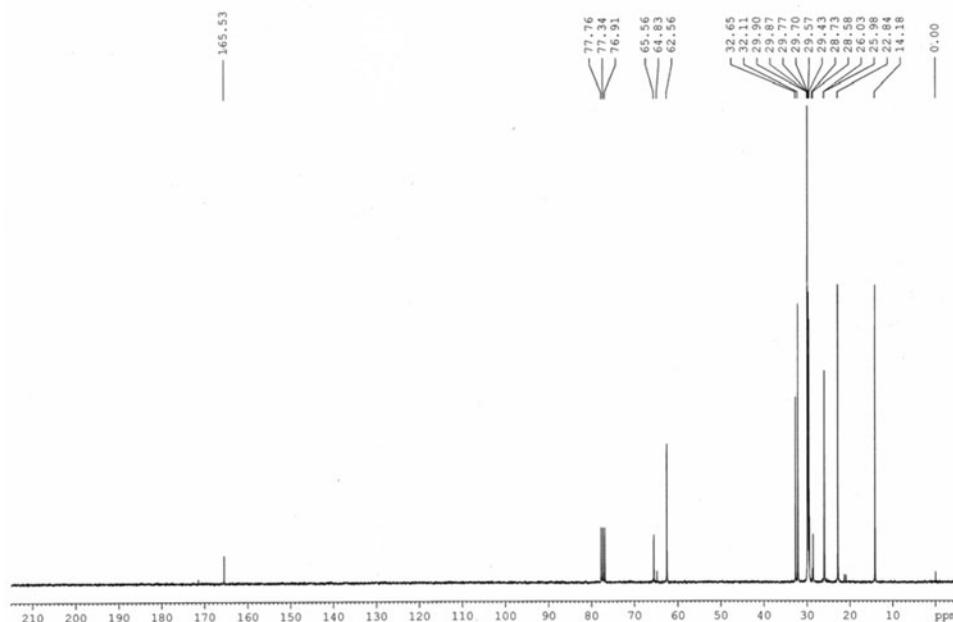
1211 cm^{-1} , and 1156 cm^{-1} due to CO stretching vibration and absorption bands at 818 and 725 cm^{-1} were due to bending of C—H bond. The disappearance of two anhydride peaks at 1782 cm^{-1} and 1851.5 cm^{-1} indicate that esterification of copolymer was carried out successfully.

In the ^1H NMR, a broad peak in the range of 3.365–3.981 ppm indicates the protons of $-\text{COCH}_3$ group. Another broad peak ranging from 4.002–4.185 ppm indicates the protons of $-\text{OCH}_2$ groups. The hydrogen attached to sp^3 carbons appear in the range of 0.901–2.431 ppm. Absence of any peak in the range of 5–6 ppm indicates the disappearance of C=C bond and confirms the polymerisation (Figure 1).

In ^{13}C NMR, the peak at 165.53 ppm indicates the presence of ester carbonyl group. The peaks at 62.56 ppm indicate the presence of $-\text{COCH}_3$ methyl carbon. The peaks at 64.83 and 65.56 ppm confirm the presence of all $-\text{OCH}_2$ carbons. The peaks ranging from 14.18–32.65 ppm represents all other sp^3 carbons. No peak in the range of 120–150 ppm indicates the absence of sp^2 carbons and confirms the polymerization (Figure 2).

Molecular Weight and TGA Data Analysis

The experimental values of intrinsic viscosity and viscometric molecular weight of polymer A, B, and C are given in Table 2. From the values, it is seen that by increasing the alkyl chain length of the alcohol used in esterification, the molecular weight increases. From TGA values of all the

FIGURE 2 ^{13}C NMR of polymer A.

three polymers (Table 2), it is seen that polymer A is thermally less stable than polymers B and C. Polymers B and C are thermally almost equal stable.

Analysis of VI Data

VI was calculated by dissolving the prepared polymers at a concentration range of 1–5% (w/w) in different base oil. The values are given in Table 3. From the experimental data, it is found that VI values increase with increasing the concentration of polymer in base oil. The higher concentration of polymer increases the total volume of polymer micelles in the oil solutions and hence increases the VI (Abdel-Azim et al., 2005). The VI value of polymer C is higher than polymer B and B is higher than A in all the three base oils. The lube oil viscosity decreases with increasing temperature but

TABLE 2
Intrinsic Viscosity, Viscometric Molecular Weight, and Thermogravimetric Analysis Data of Polymers A, B, and C

Polymer	$[\eta]_h$	$[M]_h$	Deco.Temp., °C	PWL
A	4.12	14,973	180/306	32/91
B	4.38	16,220	198/ 355	26/88
C	4.52	16,916	203/365	25/87

A = esterified product of maleic anhydride–vinyl acetate copolymer with 1-octanol; B = esterified product of maleic anhydride–vinyl acetate copolymer with 1-decanol; C = esterified product of maleic anhydride–vinyl acetate copolymer with 1-dodecanol; $[\eta]_h$ = intrinsic viscosity respective to Huggins; $[M]_h$ = viscometric molecular weight according to Mark-Houwink–Sakurada equation; Deco. Temp. = decomposition temperature; PWL = percentage weight loss.

TABLE 3

Viscosity Index of Polymers A, B, and C at Different Concentrations in Different Base Oils (BO1, BO2, and BO3)

Polymer	Base Oil	Viscosity Index of Polymer Doped Base Oil, % (w/w)					
		0%	1%	2%	3%	4%	5%
A	BO1	84.6	90	96	96	100	104
	BO2	85.2	92	95	95	100	103
	BO3	81.5	87	92	92	98	105
B	BO1	84.6	93	97	97	104	106
	BO2	85.2	95	98	100	106	108
	BO3	81.5	88	90	96	96	105
C	BO1	84.6	96	96	99	108	112
	BO2	85.2	98	98	102	110	112
	BO3	81.5	89	94	94	102	107

expansion of polymer molecules increase with increasing temperature. As a result, the hydrodynamic volume increases and micelle size of the solvated polymer molecule also increase and resists the reduction of the viscosity of lube oil with temperature (Tanveer and Prasad, 2006; Nassar, 2008). This effect is greater in case of polymer C which may be due to its higher molecular weight (Table 3).

Analysis of Pour Point Data

The polymer doped base oils (BO1, BO2, and BO3) at different concentration ranging from 1% to 5% (w/w) were tested for pour point and experimental values are given in Table 4. From the values, it is observed that all the three polymers can be effectively used as pour point depressant and pour point increases with increasing the concentration of polymer in base oil. It may be due to decrease in solvation power (Abdul-Azim et al., 2009). Among the three polymers (A, B, and C), the polymer A is more efficient as PPD in all the three base oils. It may be due to presence of short alkyl chain in polymer A. The interaction between the short alkyl chain length and paraffin in the lube oil is more effective than long alkyl chain length and wax crystal formation is inhibited (Al-Sabagh et al., 2012). From the experimental pour point values, it is also observed that all the three polymers are more effective in base oil, BO1 (i.e., in the lower viscous base oil).

TABLE 4

Pour Point of Polymers A, B, and C at Different Concentrations in Different Base Oils

Polymer	Base Oil	Pour Point of Polymer Doped Base Oil, % (w/w)					
		0%	1%	2%	3%	4%	5%
A	BO1	-3	-10	-12	-9	-9	-9
	BO2	-6	-12	-12	-10	-10	-10
	BO3	-0.5	-6	-7	-6	-5	-5
B	BO1	-3	-10	-10	-9	-8	-8
	BO2	-6	-10	-10	-10	-9	-9
	BO3	-0.5	-6	-6	-5	-5	-5
C	BO1	-3	-9	-9	-7	-7	-7
	BO2	-6	-9	-10	-8	-8	-8
	BO3	-0.5	-6	-4	-4	-4	-3

CONCLUSION

In this study we found that all the prepared three polymers are effective as VM and PPD. Among the three polymers, polymer C is more efficient than B and B is more efficient than A as VM. This indicates that with increasing the alkyl chain length of alcohols used in esterification, the VM property increases. The PPD property of polymer A is higher than polymers B and C, it indicates that with decreasing the alkyl chain length of alcohols used in esterification, the PPD property improves. Therefore, alkyl chain length has a significant role in polymerization to enhance the property of VM and PPD for lube oil polymeric additives.

FUNDING

The authors thank UGC, New Delhi, for financial support and thank also to IOCL, India, for providing base oil.

REFERENCES

- Abadir, M. F., Ashour, F. El-Z., Ahmed, N. S., Kamal, R. S., and El-Zahed, El. S. M. (2014). The effect of some additives on the rheological properties of engine lubricating oil. *J. Eng. Res. Appl.* 4:169–183.
- Abdel-Azim, A. A., Amal, M. N., Nehal, S. A., Rasha, S. K., and El-Nagdy, E. I. (2005). Preparation and evaluation of acrylate polymers as viscosity index improver for lube oil. *Pet. Sci. Technol.* 23:537–546.
- Abdul-Azim, A. A. A., Nasser, A. M., Ahmed, N. S., El-Kafrawy, A. S., and Kamal, R. S. (2009). Multifunctional additives for viscosity index improver, pour point depressants and dispersants for lube oil. *Pet. Sci. Technol.* 27:20–32.
- Al-Sabagh, A. M., Sabaa, M. W., Saad, G. R., Khidr, T. T., and Khalil, T. M. (2012). Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. *Egyptian J. Pet.* 21:19–30.
- Dean, E. W., and Davis, G. H. B. (1929). Viscosity variation of oils with temperature. *Chem. Met. Eng.* 36:618–619.
- Ghosh, P., and Das, T. (2011). Copolymer of decyl acrylate and styrene: Synthesis, characterization and viscometric studies in different base stocks. *Adv. Appl. Sci. Res.* 2:272–283.
- Ghosh, P., Das, T., and Das, M. (2010). Synthesis, characterization and viscosity studies of acrylate based homo and copolymers. *Res. J. Chem. Environ.* 14:26–31.
- Mellow, I. L., Delpach, M. C., Countinho, F. M. B., and Albino, F. F. M. (2006). Viscometric study of high cis-polybutadiene in toluene solution. *J. Braz. Chem. Soc.* 17:194–199.
- Nassar, A. M. (2008). The behaviour of polymers as viscosity index improver. *Pet. Sci. Technol.* 26:514–522.
- Nikolaev, V. F., Egorov, A. V., Nikolaev, I. V., and Sultanova, R. B. (2013). A method of testing the pour point of petroleum products on a refrigerated sloping surface. *Pet. Sci. Technol.* 31:276–283.
- Rizvi, S. Q. A. (2009). A comprehensive review of lubricant chemistry, technology, selection, and design., West Conshohocken, PA: ASTM International.
- Tanveer, S., and Prasad, R. (2006). Enhancement of viscosity index of mineral base oils. *Ind. J. Chem. Technol.* 13:398–403.
- Van Home, W. L. (1949). Polymethacrylates as viscosity index improvers and pour point depressants. *Ind. Eng. Chem.* 41:952–959.