

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC ADDITIVES FOR LUBRICATING OIL

Thesis Submitted for the Degree of Doctor of
Philosophy (~~Science~~) of the
University of North Bengal
2011

Submitted by

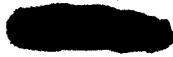
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Dedicated to My Parents

DECLARATION

I hereby declare that the thesis entitled “ SYNTHESIS AND CHARACTERIZATION OF POLYMERIC ADDITIVES FOR LUBRICATING OIL” completed and written by me has not previously formed the basis for the award of any Degree or Diploma or other similar title of this or any other University or examining body.

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Certificate from the Supervisor

This is to certify that the thesis entitled, "**Synthesis and Characterization of Polymeric Additives for Lubricating Oil**", submitted by Sri Tapan Das, who got his name registered on 25.09.2008 for the Ph.D. (Science) Degree of the University of North Bengal, is entirely based upon his work and carried out under my supervision and that neither this thesis nor any part of it has been submitted for any Degree / Diploma or any other academic award anywhere before.

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ACKNOWLEDGEMENT

The present thesis embodied the results of research carried out by the author at the Department of Chemistry, University of North Bengal, Dist. Darjeeling, West Bengal.

The author at the very first opportunity offers his heartfelt gratitude and sincerest thanks to Dr. Pranab Ghosh, Associate Professor in chemistry, Department of Chemistry, University of North Bengal, under whose guidance, constructive criticism and close attention, the present work was carried out.

The author is thankful to Indian Oil Corporation, Dhakuria, Kolkata and also to Bharat Petroleum Corporation, Matigara, Siliguri for supplying Lubricating oils used throughout the investigation.

The author acknowledges his indebtedness to Dr. A. K. Nanda, Associate Professor, Department of Chemistry, University of North Bengal, to take NMR spectra of a number of compounds mentioned in the thesis. Sincere thanks are also accorded to all teachers in the department of chemistry for their constant inspiration and helpful suggestions.

The author pays deep regards to his beloved parents, his brothers, sisters, sisters - in -law, brother- in- law for their constant co-operation and encouragement.

The author acknowledges his friends Dr. Amitabha Chakroborty, Dr Vivek Bagchi, Dr. Arjun Ghosh, Dr. Biplab Sarkar, Sri Uttam Mondal, Sri Amritendu Chatterjee, Sri Mrinmoy Jha and Sri Sanjay Dey for their valuable suggestions and timely help in supplying valuable papers related to my work.

The author is thankful to his colleagues and other research scholars of this laboratory for various helps rendered during the whole work of the study.

Last but not the least author's friend Shrabani Sarkar owes his loving acknowledgment, who helped him in all the way she could and was a source of inspiration. Her support and help, without which it would not have been possible for him to concentrate in his studies and bring out this work. He once again thanks her for the same.

LIST OF PUBLISHED / COMMUNICATED RESEARCH PAPERS

1. Synthesis Characterization and Viscosity Studies of Homopolymer of Methyl Methacrylate and Copolymer of Methyl Methacrylate and Styrene. Pranab Ghosh, **Tapan Das** and Debabrata Nandi. *Journal of Solution Chemistry*, **40**: 67-78, 2011.
2. Synthesis of Copolymers and Homopolymers of Methyl Methacrylate and Styrene and Studies on their Viscometric Properties in Three Different Solvents. Pranab Ghosh, **Tapan Das** and Debabrata Nandi. *Research Journal of Chemistry and Environment*, **13(1)**: 10-25, 2009.
3. Synthesis and Characterization of Homopolymer of Decyl Acrylate and its Copolymer with Styrene and Evaluation of their Performance as a Pour Point Depressant in Lubricating Oil. Pranab Ghosh and **Tapan Das**, Accepted for publication in *Malaysian Polymer Journal* for early issue of 2011.
4. Copolymer of Decyl Acrylate and Styrene – Synthesis, Characterization and Viscometric Studies in Different Base-stocks. Pranab Ghosh and **Tapan Das**, Submitted to *Jordan Journal of Chemistry* on 6th June 2010, Article No. JJCART00134.
5. Synthesis, Characterization and Viscosity Studies of Acrylate Based Homo and Copolymers. Pranab Ghosh, Moumita Das and **Tapan Das**, *Research Journal of chemistry and Environment*, **14(4)**: 26-31, 2010.
6. Synthesis and characterization of biodegradable polymer – Used as Pour Point Depressant for Lubricating Oil. Pranab Ghosh, **Tapan Das**, Debabrata Nandi, Gobinda Karmakar and Amitava Mandal, *International Journal of Polymeric Materials*, **59**: 1008-1017, 2010.

LIST OF PUBLISHED RESEARCH PAPERS IN THE PROCEEDINGS OF NATIONAL/INTERNATIONAL SEMINAR/ CONFERENCE/WORKSHOP

1. Preparation, Characterization and Evaluation of Acrylate Polymers as Pour Point Depressant for Lube Oil. **Tapan Das**, Debabrata Nandi and Pranab Ghosh, Page-45, Proceeding of “ NCAM- 2008” 6-8 March, 2008- Chemistry Department, U.P.A. College, Varanashi, U.P. India.
2. Synthesis and Characterization of Polymeric Additive for Lubricating Oil. Pranab Ghosh, **Tapan Das** and Debabrata Nandi, Page 19 as P1, proceeding of “National Workshop on Recent Trends in Polymer Science”, 20-25 October 2008- IASST, Paschim Boragaon, Guahati, (Assam), India.
3. Copolymer of Sunflower Oil with Alkyl Acrylate- Synthesis, Characterization and Performance Evaluation in Lubricating Oil. **Tapan Das**, Debabrata Nandi, Gobida Karmakar and Pranab Ghosh, Page 55 as P-27, proceeding of “ International Symposium on Frontiers of Functional Materials”,6-7 January, 2009- Department of Chemistry, University of.Calcutta, WB, India.
4. Synthesis and Characterization and Viscometric studies of Homo and Copolymer of Decyl Acrylate. **Tapan Das**, Debabrata Nandi, Gobida Karmakar and Pranab Ghosh, proceeding of “11th CRSI National Symposium in Chemistry” 6-8 February 2008. NCL, Pune, India.

LIST OF ORAL PRESENTATION IN THE NATIONAL SEMINAR/ CONFERENCE/ WORKSHOP

1. Preparation, Characterization and Evaluation of Acrylate Polymers as Pour Point Depressant for Lube Oil. **Tapan Das**, presented in the national seminar “ NCAM-2008” 6-8 March, 2008- Chemistry Department, U.P.A. College, Varanashi, U.P. India and have won the **Young Scientist Award (Position-1)** in the event.
2. Synthesis and Characterization of Polymeric Additive Lubricating Oil. **Tapan Das**, presented in the “National Workshop on Recent Trends in Polymer Science”, 20-25 October 2008- IASST, Paschim Boragaon, Guahati, (Assam), India.
3. Copolymer of Sunflower Oil with Alkyl Acrylate- Synthesis, Characterization and Performance Evaluation in Lubricating Oil. **Tapan Das** presented in the seminar “TSSRA” 6th December 2008- Department of Chemistry, University of North Bengal, Darjeeling, WB, India.

Abbreviations

1. MA- Methyl acrylate
2. PMA- Poly(Methyl acrylate)
3. MMA- Methyl methacrylate
4. PMMA- Poly(Methylmethacrylate)
5. VA- Vinyl acetate
6. PPD- Pour point depressant
7. VI- Viscosity index
8. VII- Viscosity index improvers
9. VM- Viscosity modifier
10. DA- Decyl acrylate
11. PDA-Poly(decyl acrylate)
12. IDA- Isodecyl acrylate
13. PIDA- Poly(isodecyl acrylate)
14. DDA- Dodecyl acrylate
15. PDDA- Poly(dodecyl acrylate)
16. SB- Schulz-Blaschke
17. SC- Solomon- Ciute
18. DC- Deb –Chanterjee
19. TGA- Thermo gravimetric analysis
20. IR- Infra red
21. NMR- Nuclear magnetic resonance
22. GPC- Gel permeation chromatography
23. BZP- Benzoyl peroxide
24. SEC- Size exclusion chromatography
25. PIB- Poly isobutylenes
26. OCP - Olefin copolymers
27. TE- Thickening efficiency
28. PS- Polystyrene
29. OEM- Original equipment manufacturer

SUMMARY OF THE WORK

PART - I

Synthesis, Characterization and Viscosity Studies of Homo and Copolymer of Methyl methacrylate and Evaluation of their Pour Point Properties in Different Lubricating Oils (Base Stocks)

This Part is divided into three chapters, Chapter I, Chapter II and Chapter III

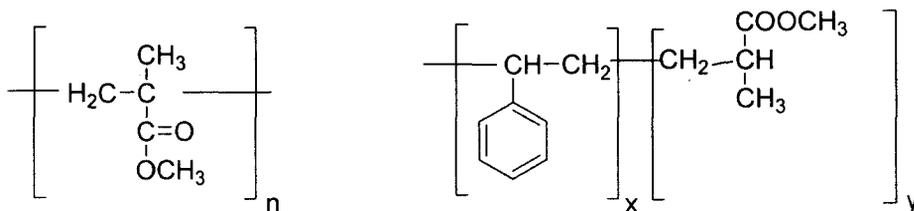
Chapter I A brief review of the present investigation

Chapter II This chapter is divided into two sections, Section A and Section B

Section A comprises the Synthesis and Characterization of Homopolymer of Methyl methacrylate (MMA) and its Copolymers with Styrene and Evaluation of their Pour Point Depressant Properties in Lubricating (Lube) Oils.

Homopolymer of methyl methacrylate (MMA) and its copolymer using different compositions of styrene were synthesized and characterized. The viscosity measurements of the synthesized homopolymer as well as the copolymer in toluene solution at 313 K were performed. Different equations were used to calculate intrinsic viscosity, viscometric constant values and molecular weight of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight (M_v) obtained by the two methods (single point determination and graphical extrapolation) were compared in order to verify the validity of the single point determination for the polymers. Viscometric properties derived included the determination of specific viscosity (it determines the contribution of solute to the viscosity of the solution), the reduced viscosity (that provides the measurements of the polymer capacity of increasing the solution viscosity) and intrinsic viscosity. Structure of poly(Methyl methacrylate)

(structure I) and copolymer of Methyl methacrylate with styrene (structure II) is given below.



Structure I

Structure II

Section B comprises the Studies on the Viscometric Properties of MMA – Styrene Copolymers in Three Different Solvents in Comparison to the Respective Homopolymers.

Homopolymer of Methyl methacrylate (PMMA) and styrene (PS) and their copolymers were synthesized and characterized. The viscometric measurements of the synthesized homopolymers as well as the copolymers were performed in three different solvents. Different equations were used to calculate intrinsic viscosity and viscometric constant values of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight obtained by the two methods (single point determination and graphical extrapolation) were compared. Measurements of viscometric properties included the determination of specific viscosity (it determines the contribution of solute to the viscosity of the solution), the reduced viscosity (that provides the measurements of the polymer capacity of increasing the solution viscosity) and intrinsic viscosity.

Chapter III Consists of experimental and References

PART II

Studies on Synthesis, Characterization, Pour Point Depressant and Viscosity Index Improver Properties of Homo and Copolymer of Acrylates with Styrene

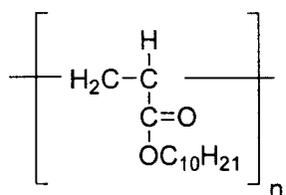
This Part is divided into three chapters, Chapter I, Chapter II and Chapter III

Chapter I A brief review of the present investigation

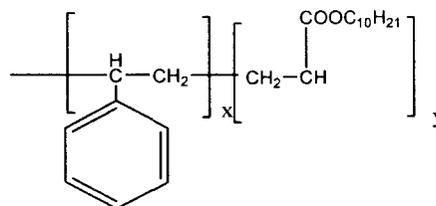
Chapter II This chapter is divided into three sections, Section A, Section B and Section C

Section A comprises the Synthesis of Poly(acrylates) and their Copolymer with Styrene and Evaluation of their Performance as Pour Point Depressant for Lubricating Oil

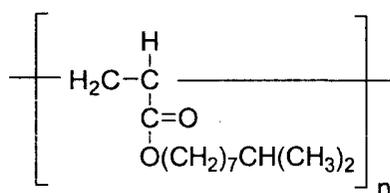
The potential for use of homopolymer of decyl acrylate, isodecyl acrylate, dodecyl acrylate and their copolymers with styrene as pour point depressant (PPD) additives in lubricating compositions has been investigated. The polymers (homo and copolymers) were prepared by free radical polymerization in toluene solvent, using benzoyl peroxide (BZP) as initiator and employing different levels of styrene (wt %) in the monomer mixture and were characterized employing TGA, FT-IR and FT-NMR techniques. Since the performance of such kind of additives in the field condition is very much dependent on the structure and morphology of the polymer dissolved in solvents, viscometric studies of the dilute solution of the polymers in toluene have also been employed. The resulting copolymers were evaluated for potential use as pour point depressant in lubricant compositions through ASTM method. The results indicated a good improvement in the performance of some of the experimental copolymers as compared to reference sample of poly(decylacrylate). Structure of poly(decyl acrylate) (Structure I), Copolymer of decyl acrylate with styrene (Structure II), poly(dodecyl acrylate) (Structure III), Copolymer of dodecyl acrylate with styrene (Structure IV) are given below-



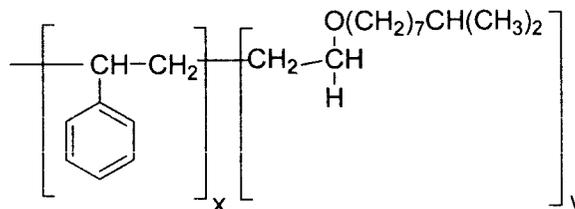
Structure I



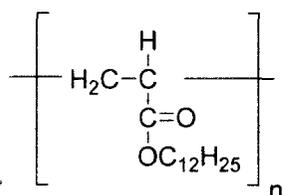
Structure II



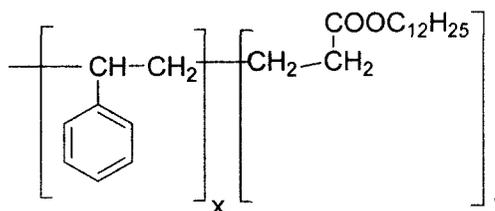
Structure III



Structure IV



Structure V



Structure VI

Section B comprises the Evaluation of Poly(acrylates) and their Copolymer as Viscosity Modifiers

Some long chain polyacrylate additives, such as poly(decyl acrylate), poly(dodecyl acrylate), poly(isodecyl acrylate) and their copolymers with styrene were synthesized and characterized. The enhancement of viscosity index (VI) of mineral base oils (lubricating oils) by the addition of prepared polymer as viscosity index improvers (VII) has been studied. Irrespective of the polymers (homo and copolymer) and nature of the base oils, VI values increases with the increase in additive concentration in the base oils studied.

VI values of the homopolymers indicated that better performance is obtained with the acrylate having greater chain length of the alcohols in the acrylate monomer. Again, branching in the carbon chain of the alcohol, deteriorates the performance of the acrylate when used as a VI improver in the lube oil. Thus the chain length and its arrangements in the polymer of a viscosity modifier play a significant role when added in the lube oil to act as a VI improver.

Section C comprises the Comparison of Viscometric Parameters of the Homo and Copolymer of Poly(decyl acrylate) in Lubricating Oil

Viscometric measurements of the synthesized homopolymer as well as that of the copolymer were performed in the base oils at 40⁰C. Different equations were used to calculate intrinsic viscosity and viscometric constant values and molecular weight of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight obtained by the two methods (single point determination and graphical extrapolation) were compared. Measurements of viscometric properties included the determination of specific viscosity (it determines the contribution of solute to the viscosity of the solution), the reduced viscosity (that provides the measurements of the polymer capacity of increasing the solution viscosity) and intrinsic viscosity.

Chapter III Consists of experimental and References

PART III

Synthesis Characterization and Viscosity Studies of Biodegradable Additives as a Potential Pour Point Depressant and Viscosity Modifier

Chapter I Short review on biodegradable lube oil additives

Chapter II

This chapter is divided into two - section A and section B

Section A comprises the Synthesis, Characterization, Viscosity Studies and Performance Evaluation of Polymer of Sunflower Oil and its Copolymers in Lubricating (Lube) Oil

Additives based on polymers of alkyl methacrylate used in lubricant composition improve the viscometric and rheological properties of the lubricant and provides fuel economy. They also looked upon to provide additional performance characteristics such as improved low temperature fluidity, dispersancy and thickening property. However, the recent demand for eco-friend technology guided us to incorporate the sunflower chemistry into the acrylate skeleton through the process of copolymerization in anticipation of getting an ideal blend of performance as well as eco -friend chemistry. The present investigation comprises the homo and copolymerization of sunflower oil with different mass fraction of methyl methacrylate (MMA), decyl acrylate (DA) and styrene, characterizations and their evaluations as a pour point depressant in base oils.

Section B comprises the Evaluation of Synthesized Biodegradable Polymers as Viscosity Modifier for Lube Oil

Polymer of sunflower oil, poly(methyl methacrylate), poly(decyl acrylate) and copolymer of sunflower oil with methyl methacrylate and also with decyl acrylate were synthesized and characterized. The enhancement of viscosity index (VI) of mineral base oils by the addition of prepared polymer as viscosity index improvers (VII) has been studied. VI of blended base oils made by the addition of these polymers is found to pass through maximum. It was observed that the occurrence of maximum depends on the mineral base oil used and the type and concentration of VI improvers.

Chapter III Consists of experimental and References

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PART – I

**SYNTHESIS, CHARACTERIZATION AND VISCOSITY STUDIES OF HOMO AND
COPOLYMER OF METHYL METHACRYLATE AND EVALUATION
OF THEIR POUR POINT PROPERTIES IN DIFFERENT
LUBRICATING OILS (BASE STOCKS)**

CHAPTER-I

1.1 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

1.1.1 Introduction

Lubricating oil (lube oil), commonly known as base oil or base stock, is the basic building block of a lubricant. They are complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with molecular weights ranging from medium to high values, which produce oils with desirable viscosities, densities and distillation curves.

The quality of base oils is determined by their olefinic, nitrogenated and sulfured compound contents. This is determined by the refining process which undergoes in its cleaning and removing of impurities. In order to meet composition specifications, these oils are submitted to the hydro treatment (HDT) process before addition of other compounds for commercial production. This process is characterized by the use of operational conditions of low or medium severity so that aromatic distribution is not seriously affected and sulfur compounds are not completely removed.

Wax-bearing lubricating oils are known to set to a semi-plastic mass on cooling below the temperature of the crystallization point of the wax contained in the lubricating oil. At this temperature paraffinic wax forms network of wax crystals and prevents the oil on flowing. The point at which the oil stops flowing is known as pour point of the lube oil which may be defined as the temperature at which the oil sample is no longer considered to flow when subjected to the standardized schedule of quiescent cooling prescribed by ASTM D97-47. The wax networks will also lead to an increase in oil viscosity. The increase in viscosity is generally temporary as a normal internal combustion engine can generate sufficient shear to disrupt the wax networks and allow the oil to flow. However, it should be emphasized that while the physical turning or cranking of the engine is usually unimpeded, the temporary disruption in the oil flow can lead to an increase in bearing wear. Studies have indicated that the amount of wax needed to prevent flow or gel for oil is quite small. Approximately 2% precipitated wax will gel middle distillates, and a similar amount is needed for lubricating oils. This problem presents a substantial disadvantage in the use of lubricating oils by the

petroleum industry. Dewaxing of oil improves the pour point, but this is an expensive procedure. Usually, the procedure is to dewax oil to a certain temperature and then add pour point depressants to improve the low temperature properties. However, at the lower temperature, the same amount of wax will still separate.

The pour point depressants do not make the wax more soluble in oil; they function rather by disrupting or preventing the formation of the waxy network. As little as 0.2 wt. % of a good pour point depressant can lower the pour point of the paraffinic oil or lubricating composition by 30-35⁰C.

Many different types of pour point depressants have been used in the prior art [1]. Previously used pour point depressants are predominantly oligomers having molecular weights of 1,000 to 10,000, or polymers which have molecular weights greater than 10,000. The earlier pour point depressants were either alkylated aromatic polymers or comb polymers. Comb polymers characteristically have long alkyl chains attached to the backbone of the polymer, with the alkyl groups being of different carbon chain lengths. The mechanism of action for pour point depressants has been the subject of much interest. Early indications were that alkylated aromatic compounds function as pour point depressants by coating the surface of the wax crystals and preventing further growth. More recently, however, it appears that the pour point depressants are either absorbed into the face of the wax crystal if the pour point depressant is an alkyl aromatic or co-crystallize with the wax crystal if it is comb polymer. Thus, crystal growth is not prohibited; it is simply directed or channeled along different routes. Light microscopy suggests that wax crystals are typically thin plates or blades, and when a pour point depressant is added to the system, those crystals are smaller and more branched, and thus the pour point depressant may disrupt or redirect crystal growth from different directions into a single direction, and bulkier crystals will be formed. These crystals then can form networks only at much lower temperatures which results in a lower pour point.

The observation of the previous researchers in concord with the present line of investigation is being presented, in a selective manner, in the following paragraphs.

The first formal reports of the action of pour point depressant (PPD) was made by Zimmer, Davis and Frolich [2] following the invention of paraflow by Davis [3]. Ruehrwein [4] reported a certain specificity of action for n-alkyl poly(methacrylate) in the series dodecyl, tetradecyl, hexadecyl and octadecyl. They reported that the longer alkyl polymers are effective in depressing the pour point of the high pour oils while the shorter alkyl polymers are effective on the lower temperature pour oils. Later on, with the development of engine and transmission technologies several types of polymeric products have been prepared and treated as pour point depressant for lube oil and similar oils. Some of them [5-8] are listed below.

- 1) Copolymer of styrene-maleic anhydride ester containing 20-22 carbons.
- 2) Copolymer of maleic anhydride and vinylmethyl ether esterified with alcohol of different chain lengths.
- 3) Mixed alkyl esters made by reacting two or more certain monohydric alcohols with inter-polymer which contain units derived from α , β unsaturated dicarboxylic acids or their derivatives and vinyl aromatic monomers having up to 12 carbon chains .
- 4) Copolymer of alkyl acrylates and 4-vinyl pyridine
- 5) Poly(alkyl acrylates) having C-20 to C-24 alkyl chain.
- 6) Alkyl naphthalenes.

In a recent paper Azim et al [9] have reported the synthesis of some polymeric additive based on styrene- maleic anhydride copolymer as multifunctional [Viscosity Modifier (VM), Pour Point Depressant (PPD), Detergent-dispersant] additives for lube oil.

Copolymers of maleic anhydride and vinyl acetate (VA) with different esters of acrylic acid were found to act as a PPD and VM. It was found that the efficiency of the prepared compounds as PPD increases with decreasing the concentration of the prepared polymers, increasing the chain length of alkyl groups and increases with decreasing the molecular weight. [10]. I.M. El- Gamel [11] has reported the synthesis of methacrylate - C-18 α -olefin copolymer as a potential PPD for waxy residue fuel oil and concluded that polymeric structure with long side chain of average 21 carbons have the potential to decrease the pour point of the oil. In a recent paper [12] Rasha has reported a novel PPD based on maleic anhydride -acrylates terpolymers.

N.S.Ahmed et al [13] has reported the synthesis of multifunctional lubricating oil additives based on polyalkyl polyamines which has PPD properties in lube oil, they claimed.

Commercially a line of poly(methacrylate) based pour point depressants are in use now a days such as, 'Acryloid' from the Rohm and Haas Company, 'TLA' followed by a numerical suffix or 'TC' followed by a numerical suffix from Texaco. There has also been a substantial patent activity concerned with pour point depressants which comprise poly(methacrylate) compositions. Thus U. S. Patent no. 3,607,749 and 4,203,854 disclosed poly(methacrylate) as viscosity index improvers, but without any data as to their low temperature performance.

U.S. Patent no. 3,598,736 disclosed the addition of small amounts of oil soluble copolymers of polymethacrylates (wherein the alkyl side chain contains from 10 to 20 carbon atoms with average of between 13.8 and 14.8 carbon atoms) to lubricating oils to reduce the pour point. Patent No. 3,679,644 (U.S) also reported the similar work.

U.S. Patent no. 4,073,738 has claimed the use of alkyl acrylate or alkyl methacrylate, wherein the alkyl group side chain can have from 8 to 30 carbon atoms and preferably from 8 to 22 carbon atoms, as a pour point depressant in lube oil.

U. S. Patent No. 4,088,589 disclosed a combination of pour point depressants of which one can be an oil soluble polymer of an alkyl acrylate or methacrylate which contains a side chain comprising 10 to 18 carbon atoms in the alkyl group.

U. S. Patent No. 2,655,479 of Munday et al has directed to polyester pour depressants and is particularly concerned with average side chain length of acrylate polymer pour depressants. They have claimed that homopolymers are not good pour point depressants but that copolymers are generally good pour point depressants. U. S. Patent 3,598,737 has disclosed lubricant compositions which contain copolymers of acrylate esters which are said to improve various characteristics including pour point. This patent states that the average number of carbon atoms should be at least 12.5 to 14.3.

U. S. Patent No. 3,897,353 disclosed oil compositions comprising lubricating oil and a pour point depressant which can be an alkyl methacrylate. These acrylates may be made from monomers wherein the alkyl portion of the ester or the side chain has from 12 to 18 carbon atoms and includes mixtures. However, the polymers of this patent are made from nitrogen- containing monomers.

From the above literature work the author has found some discrete work on the methacrylate chemistry functioning as a pour point depressant when added to lube oil and no systematic study in this direction has so far been carried out. Thus it was felt necessary to undertake a systematic study towards the synthesis and characterization of homo and copolymer of methyl methacrylate and evaluation of their pour point properties in different base stocks. Viscometric studies were also included in the investigation with the anticipation that it may put some light towards the morphological features of the additives in a solvent.

CHAPTER II

This chapter is divided into two sections, Section A and Section B

Section A comprises the Synthesis and Characterization of Homopolymer of Methyl methacrylate (MMA) and its Copolymers with Styrene and Evaluation of their Pour Point Depressant Properties in Lubricating (Lube) Oils.

Section B comprises the Studies on the Viscometric Properties of MMA – Styrene Copolymers in Three Different Solvents in Comparison to the Respective Homopolymers.

2.1 SECTION A: Synthesis and Characterization of Homopolymer of Methyl methacrylate (MMA) and its Copolymers with Styrene and Evaluation of their Pour Point Depressant Properties in Lubricating (Lube) Oils

2.1.1 Introduction

Polymers of alkyl methacrylate used as additives in lubricant composition for improving the viscometric and rheological properties of the lubricant [14-17]. They also looked upon to provide additional performance characteristic such as improved low temperature fluidity and dispersancy. Although poly alkyl methacrylates (PAMAs) are preferred type of additives in certain application, they often contribute to enhance formation of deposits in the engine due to thermal instability of these additives under high temperature conditions. Approach to overcome this shortcoming is always associated with a risk of affecting certain beneficial properties associated with normal poly(alkyl methacrylates), such as pour point depressant (PPD) and good shear stability. Therefore, the recent research on methacrylate additives has been concerned on copolymer of methacrylates with various stabilizing monomer.

It is well known that inclusion of styrene in the composition of an additive increases the resistance of the copolymer compounded oil to the action of heat. Since homopolymers of styrene are insoluble in lube oil they are introduced in the composition of oil soluble polymer by copolymerization which may be useful PPD / VM (Viscosity modifier) for petroleum and synthetic oil.

In this section the results of our investigation towards the synthesis, characterization and viscometric measurement of MMA - styrene copolymer in comparison to homopolymer of MMA will be discussed. Four copolymers from these two monomers were prepared by varying the styrene mass fractions in the monomer mixture from 2.5 % to 10 % (w/w) and employing free radical polymerization technique using benzoyl peroxide (BZP) as initiator in toluene solvent. Polymerization was carried out following the procedure as reported earlier [16]. Homopolymer of MMA was also prepared under identical condition.

Physical characterization of the copolymers was carried out employing gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), IR and NMR techniques. However, since performance of such kind of additives in field condition is very

much dependent on the structure and morphology of the polymer in desired solvent [14], viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution are concerned. Since report regarding such information is scanty [19, 20] and almost nil for polymers used as lube oil additives – present research also include viscometric study of the copolymers as well as the homopolymer in toluene.

Viscometry is the simplest technique used to study the macromolecules in solution and determine their molecular weight. According to Mark Houwink – Sukurda relation (eq 1), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = K M^a \quad (1)$$

where $[\eta]$, the intrinsic viscosity, can be calculate by using (eq 2 to eq 7), parameter ‘K’ and ‘a’ depends on the type of polymer, solvent, and temperature.

Because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from another technique, generally in determination of molecular mass of samples with the available literature value of the constants used in the particular equation. A number of mathematical relations are available in literature for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation [19-22]. The most commonly used equations are:

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

$$\text{Kraemer (K)} \quad \ln \eta_r / C = [\eta]_k - k_k [\eta]_k^2 C \quad (3)$$

$$\text{Martin (M)} \quad \ln \left(\eta_{sp}/C \right) = \ln [\eta]_m + k_m [\eta]_m C \quad (4)$$

$$\text{Schulz-Blaschke (SB)} \quad \eta_{sp}/C = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad (5)$$

Where, C is mass concentration in gm/cc.

$\eta_r = t/t_0$, relative viscosity or viscosity ratio (where t is time flow of solution and t_0 is time flow of pure solvent).

$\eta_{sp} = \eta_r - 1$, specific viscosity

$[\eta]_h =$ intrinsic viscosity, respective to Huggins equation.

$[\eta]_k =$ intrinsic viscosity, respective to Kraemer equation ;

$[\eta]_m =$ intrinsic viscosity , respective to Martin equation,

$[\eta]_{sb} =$ intrinsic viscosity or limiting number, respective to Schulz – Blaschke equation; k_h , k_k , k_m and k_{sb} are Huggins, Kraemer, Martin and Schulz- Blaschke coefficients, respectively.

Some relations have been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analysed in short period of time, practically in industrial laboratories. Most useful of them [19-23] are Solomon- Ciute (SC, eq 6) and Deb –Chanterjee (DC, eq 7) relations.

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2} / C \quad (6)$$

$$[\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp})^{1/3} / C \quad (7)$$

The use of these equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$ [22].

The behavior of the polymeric additives toward a specific solvent / base stock plays a significant role in their action as a performance additive in their end application. Since, viscometry provides very important data about the interaction of additive in base fluid and hence conformation of polymeric system [18] in the base stock, the process of polymerization in the presence of a suitable solvent has been attracting considerable interest [24, 25].

Since the behavior of polymers especially the copolymers in solution is a complex phenomenon, a comparison involving the values of their intrinsic viscosity obtained by graphic extrapolation and by a single point determination should be interesting.

In these works viscometric parameters (intrinsic viscosity and the value of constants) of toluene solution for sample of poly(methyl methacrylate) and copolymer of that consisting

of different percentage (w/w) of styrene was obtained by graphic extrapolation and single point determination. The viscosity average molecular weight determined by using different equations, was compared. The validity of single point determination method for these types of polymers, in the investigated condition, was also discussed.

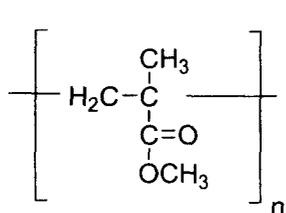
2.1.2 Results and discussion

Spectroscopic analysis

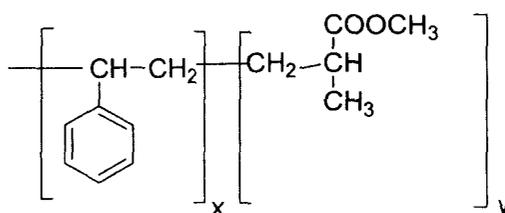
IR spectra of the homopolymer (Fig. 1a) showed a peak at 1732 cm^{-1} due to the presence of ester carbonyl group stretching vibration. The broad peak ranging from $(1260\text{ to }1000)\text{ cm}^{-1}$ appeared owing to the ester C-O stretching vibration along with a broad band from $950\text{ to }650\text{ cm}^{-1}$ (C-H bending) and from $3100\text{ to }2900\text{ cm}^{-1}$ due to presence of stretching vibrations.

The existence of copolymer was confirmed by IR (Figure 1b) and NMR (Figure 1c) analysis. Carbonyl stretching vibration at 1732 cm^{-1} of the homopolymer shifted to 1720 cm^{-1} in the copolymer. Peaks at 760 cm^{-1} and 697 cm^{-1} were attributed to the C-H bond of the phenyl group of styrene. In its ^1H NMR spectra the copolymer indicated the presence of phenyl group at 7.2 ppm and the $-\text{OCH}_2$ group from the acrylate at 3.9 ppm.

The extent of incorporation of styrene in the polymer chain [Table 1] was determined through a comparison of area of $-\text{OCH}_2$ group at 3.9 ppm in the area of signal due to phenyl protons at 7.2 ppm based on earlier reports [26] as well as on the basis of our earlier paper [16], which was further verified through an analysis of FT-IR spectral data following a method as also discussed in our earlier paper [16]. From above discussion structure of homopolymer and copolymer may be presented by structure I and structure II respectively.



Structure I



Structure II

Thermogravimetric analysis (TGA)

Table 2 presents a comparison between the values of molecular mass obtained by GPC and the TGA data for homo and copolymers. The molecular weight increases with increase in the concentration of styrene in the monomer composition. The TGA data shows that the copolymers are better in thermal stability than the homopolymer.

Viscometric analysis

Viscometric data were obtained using the seven equations mentioned. A linear relation for the plot of $\log\eta_{sp}$ vs $\log C[\eta]$ obtained for all samples (Fig. 2) indicated that measurements were performed in Newtonian flow region [27, 28].

Using the graphic extrapolation method respective intrinsic viscosities and constants were evaluated. In single point determinations, SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent system [19-23]. The same is used here also.

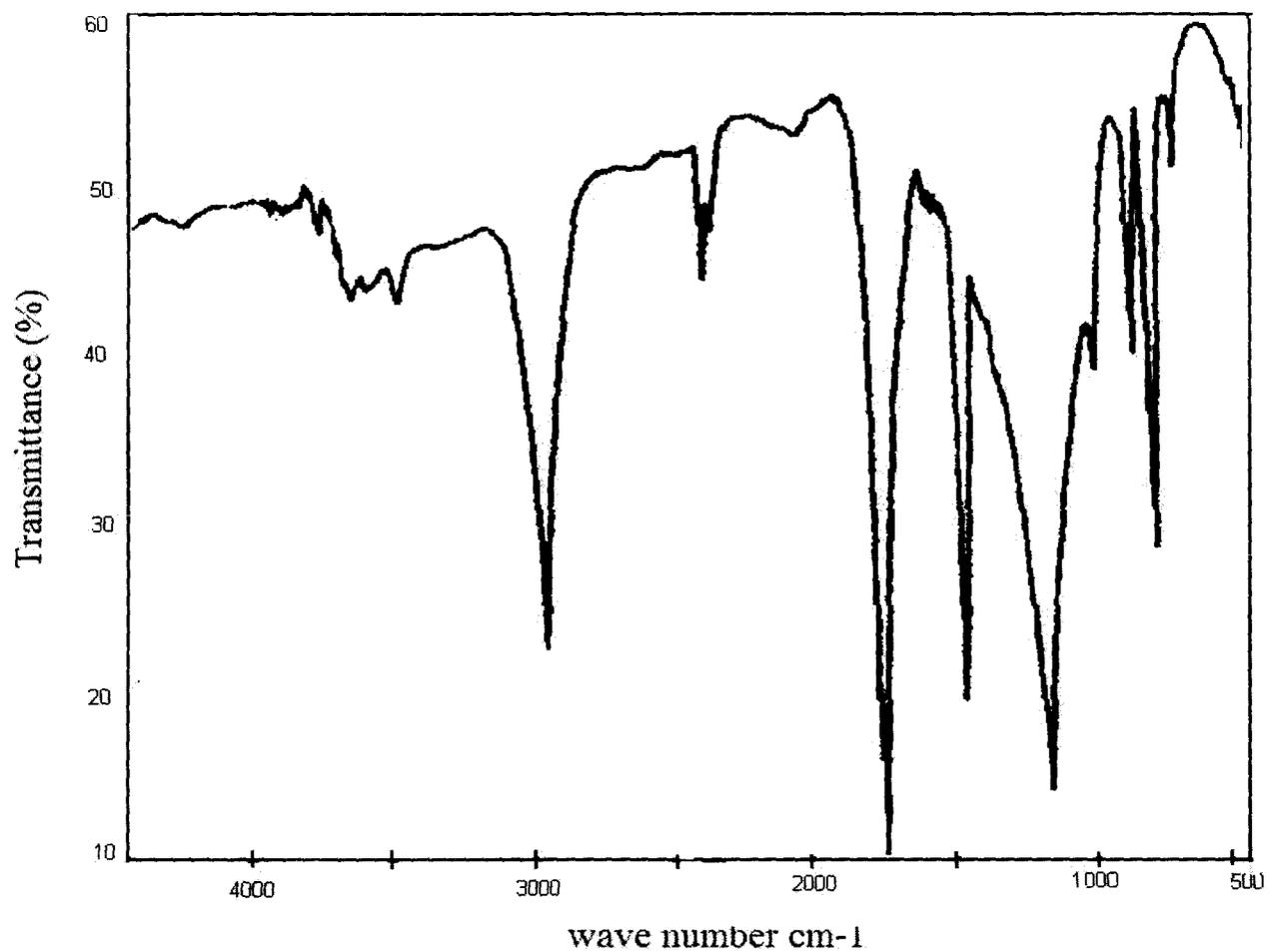


Fig. 1a FT-IR spectrum of poly(methyl methacrylate)

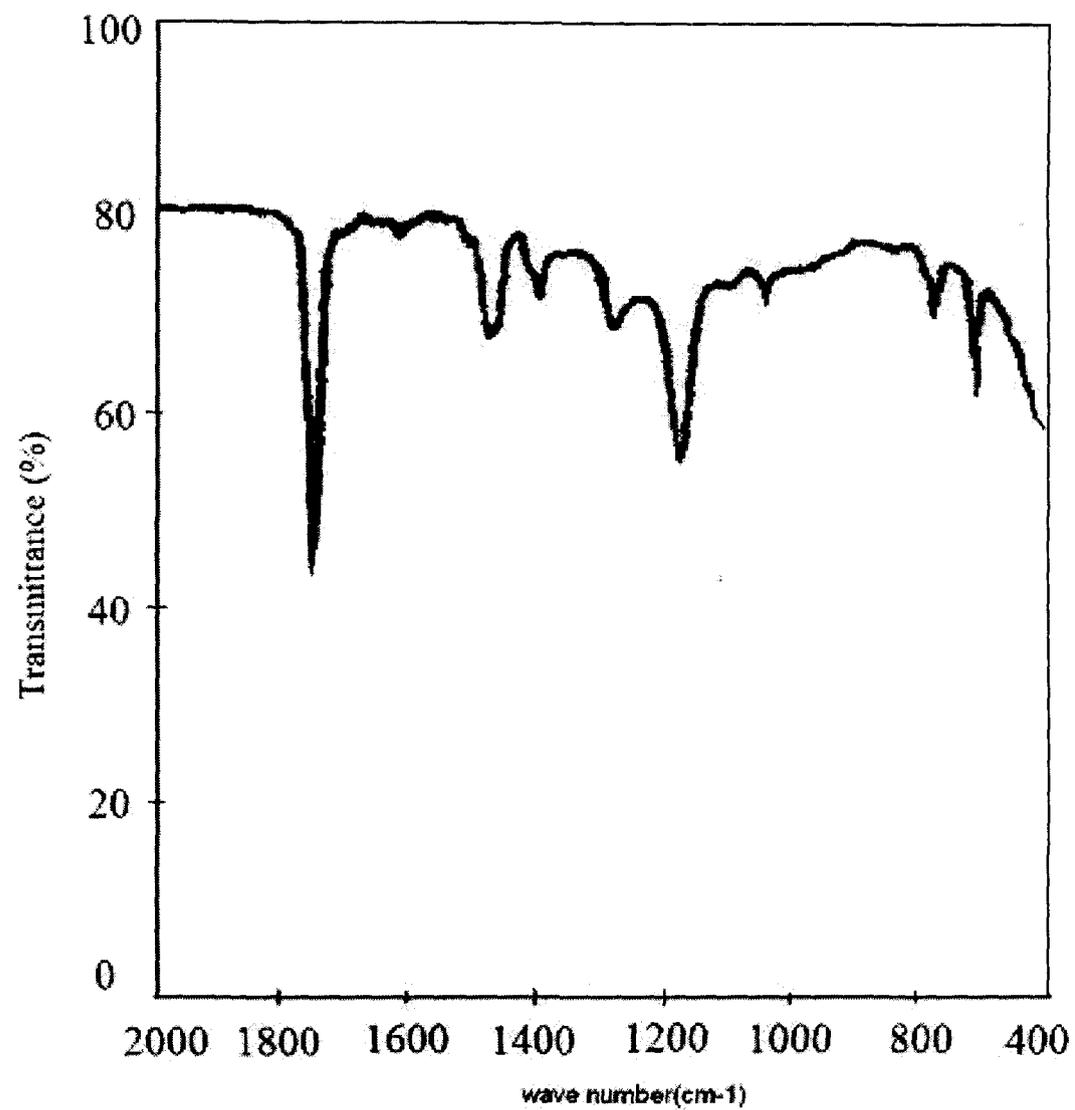


Fig. 1b FT-IR spectrum of copolymer of Methyl methacrylate + styrene

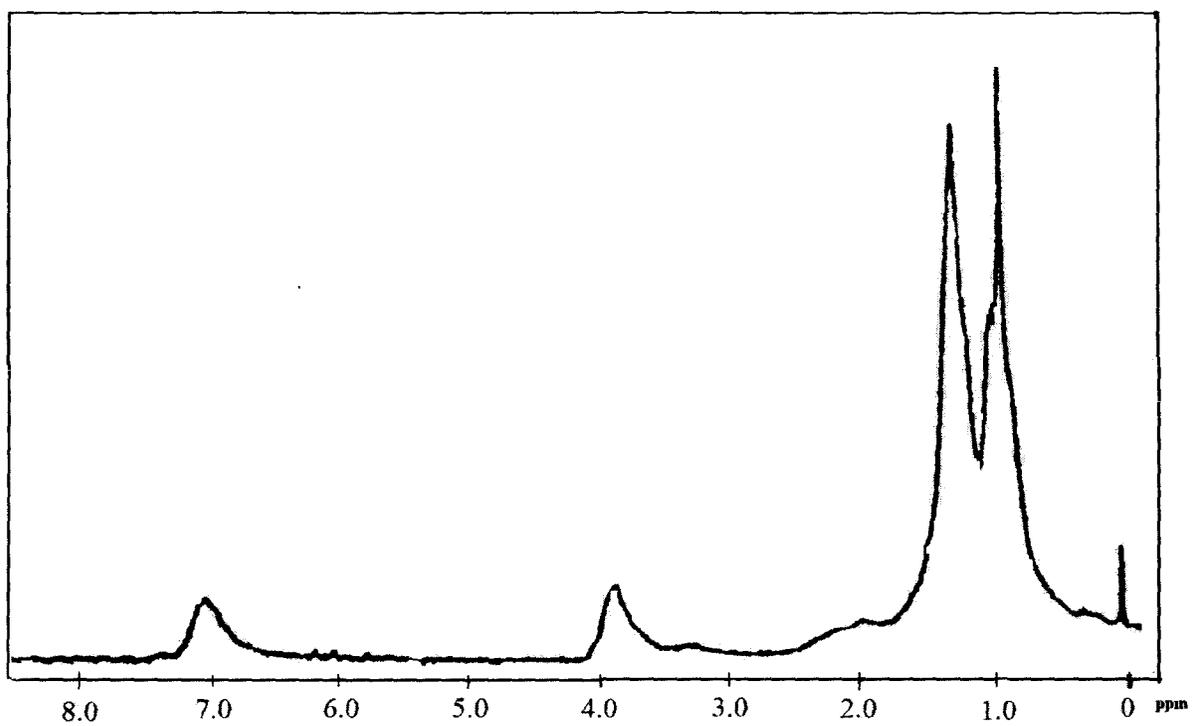


Fig. 1c NMR spectrum of copolymer of Methyl methacrylate + styrene

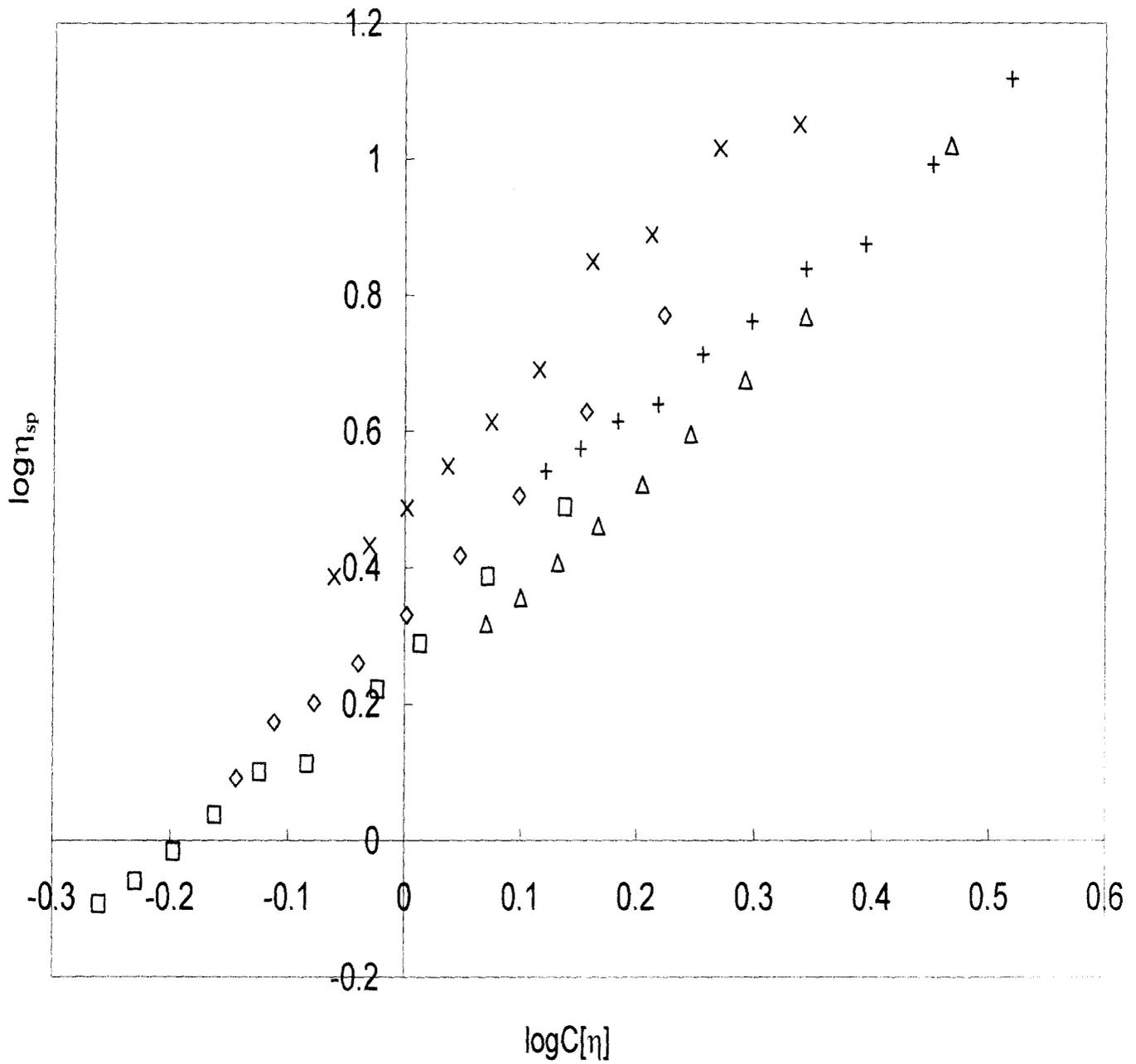


Fig. 2 Plot of $\log C[\eta]$ vs $\log \eta_{sp}$: ◇, Poly-1; □, Poly-2; △, Poly-3; x, Poly-4, +, Poly-5

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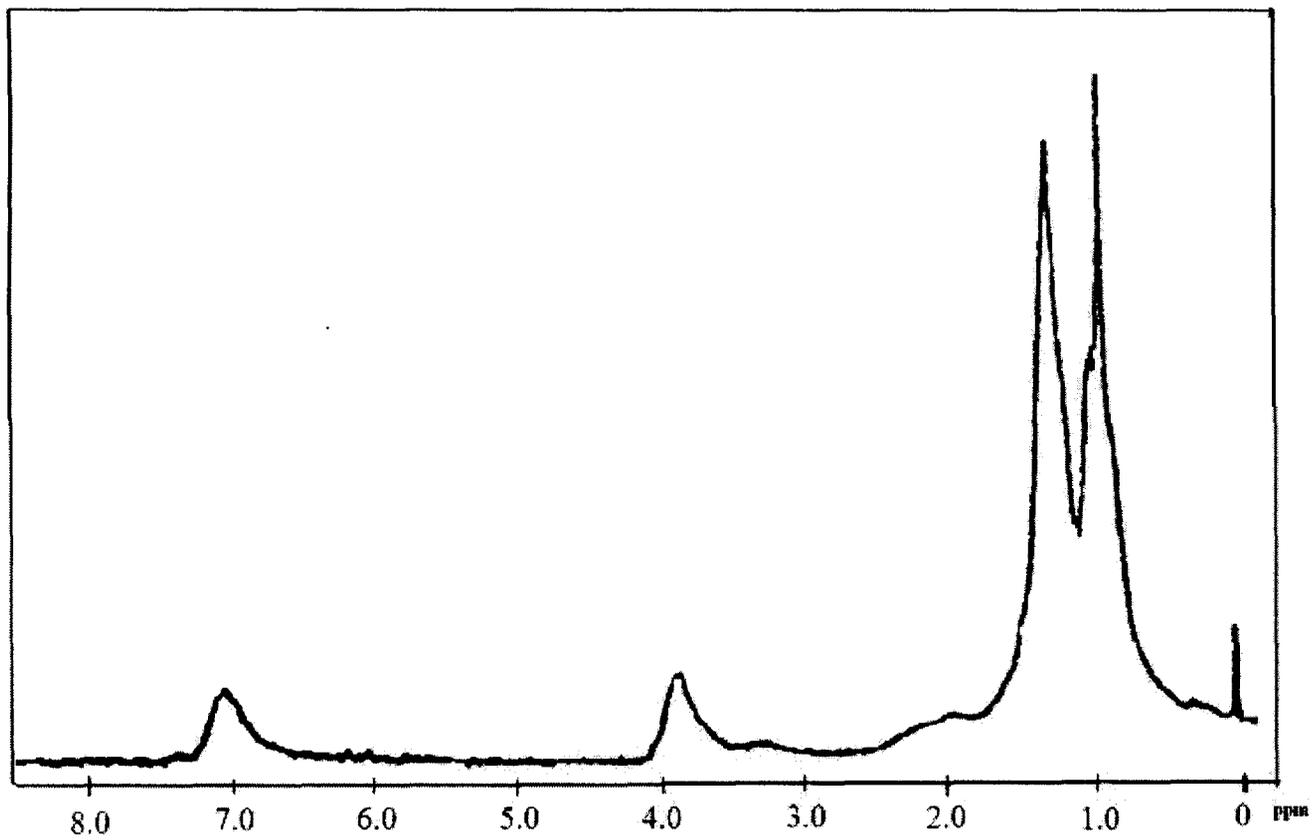


Fig. 1c NMR spectrum of copolymer of Methyl methacrylate + styrene

Table 4 presents intrinsic viscosity values, calculated from respective relative viscosity values (Table 3) related to all equations for the studied sample. Taking into account the data for homo and all copolymer samples, it can be noticed that, except one or two cases values are consistent. Comparison among the copolymers indicated that there is a gradual increase of $[\eta]$ values with the increase of styrene content in the copolymer. This indicates more extended conformation of the polymer chain compared to PMMA itself. Again the change observed for poly-3 to poly-5 is not very significant i.e., the increase of styrene concentration beyond 5 % (w/w) does not contribute much towards the $[\eta]$ value of the synthesized polymer. This may be because of the loss of flexibility of the polymer chain as the proportions of styrene increases in the copolymer. The same observation is also found in case of poly-2, in which the flexibility of poly(methacrylate) chain may be restricted in presence of styrene, the hydrodynamic volume exceeds that of PMMA which may reach a limiting value when the concentration of styrene is raised to 5 % in the feed. Therefore a sharp increment of $[\eta]$ is observed at 5 % styrene content [29, 30].

Although different intrinsic viscosity values may be found by graphic extrapolation of Huggins, Kreamer, Martin and SB equation (eq 2 to 5), but in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. For the homopolymer and copolymer, $[\eta]$ value obtained by Huggins and Kramer equation were identical.

Both homopolymer and copolymers in toluene medium indicating poor solvation (Table 5) as is evident from the respective viscometric constant values, and thus points towards the formation of micelles or spherical structures as discussed earlier [18]. This conclusion is further supported by positive values of Kraemer coefficient of the all the systems analyzed. However, it is interesting to notice that for all the polymers in toluene, k_{sb} values were close to 0.28. Thus it can be concluded that the relation $k_h + k_k \neq 0.5$ did not put any restriction for the application of SB equation.

The relation $k_k + k_h = 0.5$ was not found for the samples analyzed (Table 5), but found similar as reported elsewhere [28]. Maximum deviation for the homopolymer of MMA may be attributed to the comparatively poor solubility of the polymer in toluene.

By comparing $[\eta]$ values of PMMA and the copolymers determined through graphic extrapolation using Kraemer, Martin and SB equations with the values determined by Huggins equation in graphic extrapolation, it can be noticed that the range (-15.43 to 26.31 %, Table 6) was narrow when compared to the values obtained through a single point using SB, SC and DC equation (10.43 to 41.40 %). Again, the percentage differences ($\Delta \% = (100[\eta]/[\eta]_h) - 100$) in case of homopolymer are always higher (except one in each case) than the copolymer both in graphic extrapolation and single point determination compared to the same (Table 6).

This may be because of the fact that, the homopolymer, PMMA, with lowest molecular mass (M_n 45000 $\text{g}\cdot\text{mole}^{-1}$) in toluene which is not a good solvent seemed to produce higher differences, both in graphic extrapolation and in one point determination.

A close observation of the intrinsic viscosity values (Table 6) indicated that, for the copolymer system analyzed, the SB equation which is widely applied in industry quality control laboratories should be the most suitable for the application in one point determination. This table also indicated that for PMMA the graphical extrapolation method seemed to be more suitable in toluene rather than the single point determination and Martin equation produced the lowest deviation value among the four when compared to those obtained from the Huggins equation.

Table 7 presents a comparison between the value of molecular weight obtained by GPC (size exclusion chromatography, SEC) and viscometric methods for homopolymer and copolymers analyzed. The general trend in all the cases (except Poly -2) is a gradual increase in molecular weight with increase of styrene concentration. However, as expected, a difference was observed in the values of molecular weight obtained by GPC and viscometry. This is probably due to the differences in analysis conditions, like solvents, temperature, techniques and standards employed [31].

By comparing viscosity molecular weight with number average molecular weight obtained by GPC, it can be seen that graphical extrapolation values are more close to that of the SEC values rather than the single point determination values. The percentual difference ($\Delta \% = (100[M/M_h] - 100)$) obtained for viscometric molecular weight values showed in Table 8. These values were calculated taking M_v determined by Huggins equation as a reference. Martin equation showed the smallest $\Delta \%$ differences.

Plot of M_v and $[\eta]$ obtained by both Huggins and Kraemer equations, the most commonly employed relation in viscometry, showed a linear relationship (Fig. 3a). However, the plots involving M_v and $[\eta]$ vs the respective constant, k , showed a similar relation but not linear (Fig. 3b and 3c). Thus, the nature and extent of interactions involving the solvent and polymers (homo and copolymers), used as additives for lubricating oil, at different concentrations cannot be predicted by these two equations. But the intrinsic viscosity values may be correlated with the viscosity average (M_v) molecular weight.

Performance of the homo and copolymers as PPD

Properties of base oils were tabulated in Table 9 and pour point of the different levels of additive doped lube oils were tested and tabulated in Table 10. It indicated that the prepared copolymer samples are more efficient as pour point depressant than the homo polymer and the efficiency increases with the increase in concentration of additive up to a certain limit.

2.1.3 Conclusion

Viscometric parameters determined by graphic extrapolation and by single point determination points towards the more compatibility of the copolymers with the solvent in comparison to the homopolymer. Thus, introduction of styrene enhances the solubility, the thermal stability and thus may also enhance the performance of the polymer as well, when used in the field application as a performance additive (like VM or PPD). The study also indicated that the performance evaluation of this kind of additive might be done in a very simple way (viscometric method) when the other equipments are not available.

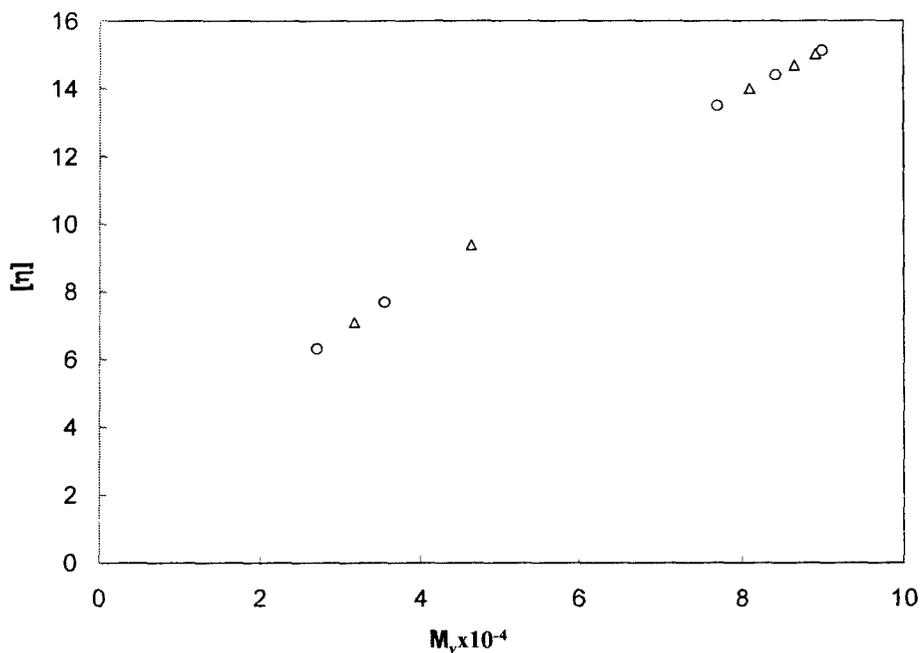


Fig. 3a Plot of viscometric molecular weight ($M_v \times 10^{-4}$) vs intrinsic viscosity ($[\eta]$):
 ○, Huggins value ; Δ , Kraemers value.

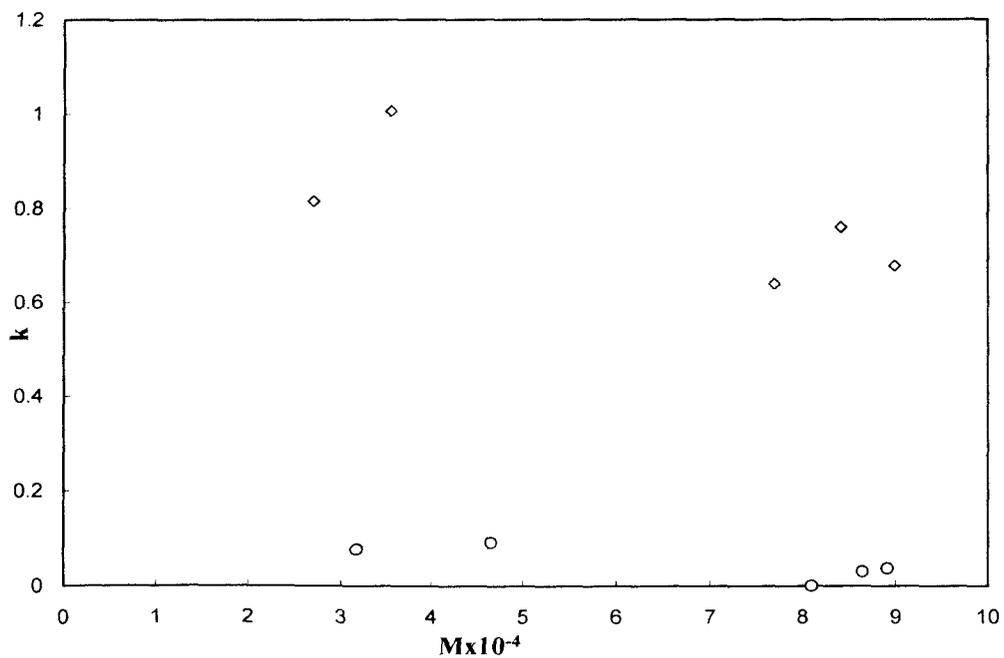


Fig. 3b Plot of viscometric molecular weight ($M \times 10^{-4}$) vs viscometric constant (k):
 \diamond , Huggins value; \circ , Kraemers value

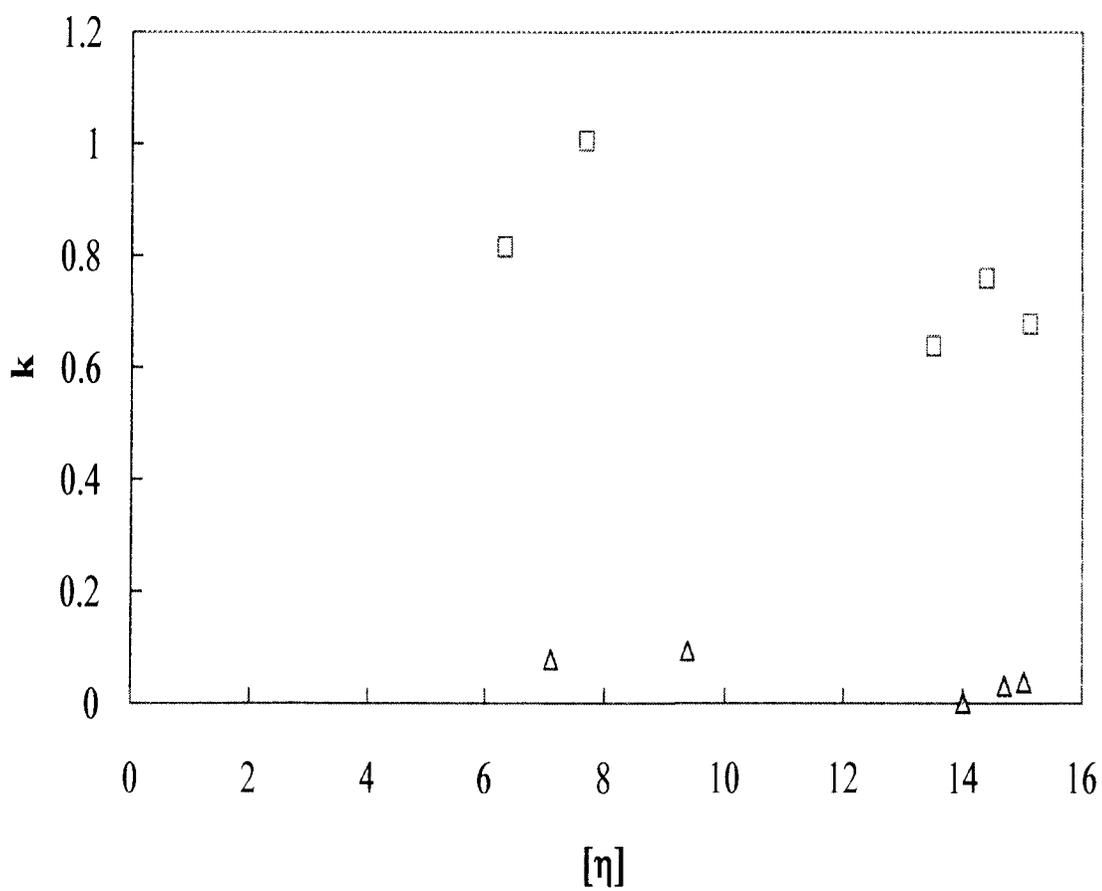


Fig. 3c Plot of intrinsic viscosity ($[\eta]$) vs viscometric constant (k) : \square , Huggins value; Δ , Kraemers value

Table 1 Composition of the monomers in the copolymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. Poly-1 is homopolymer of methyl methacrylate (MMA); Poly-2 to Poly-5 is the copolymer of MMA + different mass fractions of styrene.

Polymer sample	Mass fraction in the feed		Mass fraction of styrene in co polymer by PMR method	Mass fraction of styrene in co polymer by FT-IR
	MMA	Styrene		
Poly-1	1	-	-	-
Poly-2	0.975	0.025	0.01	0.015
Poly-3	0.95	0.05	0.02	0.023
Poly-4	0.925	0.075	0.035	0.037
Poly-5	0.90	0.10	0.04	0.045

Table 2 Molecular mass obtained by gel permeation chromatography and thermal gravimetric analysis data for homo and co polymers. Mn is number average molecular weight and Mw is weight average molecular weight. a- percent weight loss.

Polymer sample	Mn x 10 ⁻⁴	Mw x 10 ⁻⁴	TGA data	
			Decom. Temp./°C	PWL ^a
Poly-1	4.5	16	230/280	26/77
Poly-2	7.3	18	260/340	22/78
Poly-3	8.5	19	295/356	29/71
Poly-4	12	22	310/360	41/62
Poly-5	14.5	25	320/375	48/52

Table 3 Relative viscosity ($\eta_r = t/t_0$ where t_0 is time flow of pure solvent and t is time flow of solution) values at concentration 0.2175 g·cm⁻³ for all prepared homo and co polymer samples in toluene at 313 K using Ubbelohde OB viscometer having viscometer constant values are $K' = 0.00268 \text{ cm}^2 \text{ sec}^{-2}$ $L = -19.83 \text{ cm}^2$ and volume of the bulb is 3 cm³ and length of the capillary 11.3 cm.

Polymer sample	Relative viscosity ($\eta_r = t/t_0$)
Poly-1	6.890
Poly-2	4.086
Poly-3	10.464
Poly-4	13.547
Poly-5	14.122

Table 4 Intrinsic viscosity values for all prepared homo and co polymer samples calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination ($k_{sb}= 0.28$), c- single point determination. H, K, M, SB, SC and DC refer Huggin, Kraemer, Martin, Schulz- Blaschke, Solomon- Ciute and Deb –Chanterjee respectively.

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$	$[\eta]_{sc}^c$	$[\eta]_{dc}^c$
Poly-1	7.69	9.38	7.75	9.71	9.83	9.95	10.72
Poly-2	6.32	7.1	6.89	7.36	7.52	7.51	7.94
Poly-3	13.5	14	14.78	15.61	15.39	15.81	17.68
Poly-4	14.4	14.69	12.18	15.91	16.53	17.94	20.35
Poly-5	15.12	15.02	16.88	18.2	16.694	18.17	21.41

Table 5 Viscometric constants obtained for all prepared homo and co polymer samples. k_h , k_k , k_m and k_{sb} Huggins , Kraemer , Martin and Schulz- Blaschke coefficients, respectively

samples	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
Poly-1	1.006	0.093	0.740	0.294	1.099
Poly-2	0.816	0.078	0.476	0.311	0.894
Poly -3	0.639	0.0006	0.377	0.247	0.640
Poly -4	0.76	0.031	0.760	0.305	0.791
Poly -5	0.678	0.038	0.356	0.227	0.716

Table 6 Percentual differences ($\Delta \% = (100[\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values, Huggins equation taken as a reference. a- data from extrapolation; b – data from single point determination

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
Poly 1	21.97	0.78	26.31	27.88	29.39	39.36
Poly-2	12.34	9.003	16.45	19.01	18.87	25.69
Poly-3	3.70	9.48	15.55	14.01	17.11	30.96
Poly-4	2.01	-15.43	10.48	14.79	24.58	41.41
Poly-5	-0.66	11.64	20.37	10.41	20.15	41.60

Table 7 Determination of molecular weight by Mark- Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$

Sample	$M_h^a \times 10^{-4}$	$M_k^a \times 10^{-4}$	$M_m^a \times 10^{-4}$	$M_{sb}^a \times 10^{-4}$	$M_{sb}^b \times 10^{-4}$	$M_{sc}^b \times 10^{-4}$	$M_{dc}^b \times 10^{-4}$
Poly-1	3.54	4.65	3.58	4.88	4.97	5.05	5.59
Poly-2	2.70	3.17	3.04	3.33	3.43	3.43	3.70
Poly-3	7.69	8.09	8.71	9.99	9.22	9.56	11.16
Poly-4	8.41	8.64	6.67	9.65	10.17	11.38	13.54
Poly-5	8.99	8.91	10.47	11.62	10.31	11.58	14.54

a- data from extrapolation; b- data from single point determination

Table 8 Percentual differences obtained for viscometric molecular weight values ($\Delta \% = (100[M/M_h] - 100)$), Huggins equation taken as a reference. a- data from extrapolation; b- data from single point determination.

Sample	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
Poly-1	31.52	1.07	38.02	40.38	42.67	58.06
Poly-2	17.40	12.64	23.38	27.10	26.90	37.00
Poly-3	50.14	13.30	29.80	19.80	24.34	45.12
Poly-4	2.78	-20.60	14.74	20.95	35.40	61.08
Poly-5	-0.91	16.40	29.10	14.60	28.80	61.00

Table 9 Base oil properties

Base oil properties	Base oil					
	B1		B2		B3	
	A	B	A	B	A	B
Density ($\text{g}\cdot\text{cm}^{-3}$) at 40°C	0.85	0.89	0.90	0.93	0.98	0.97
Viscosity at 40°C in cSt	7.47	8.01	20.25	21.00	112.05	112.80
Viscosity at 100°C in cSt	3.52	3.81	5.54	5.79	10.82	11.33
Cloud point, $^\circ\text{C}$	-8	-8	-10	-10	-14	-12
Pour point, $^\circ\text{C}$	-3	-3	-6	-6	-9	-9

Table 10 Pour Point of additive doped Base oils

Base oil	PPD Sample	Pour Point (⁰ C) of base oils containing different %(W/W) of PPD					
		0.025		0.05		0.10	
		A	B	A	B	A	B
B1	Poly-1	-9	-9	-9	-9	-9	-9
	Poly-2	-12	-12	-15	-15	-15	-15
	Poly-3	-12	-15	-18	-18	-18	-18
	Poly-4	-15	-15	-15	-18	-21	-21
	Poly-5	-12	-12	-18	-18	-18	-21
B2	Poly-1	-9	-9	-12	-9	-12	-12
	Poly-2	-15	-15	-15	-15	-15	-15
	Poly-3	-18	-18	-18	-18	-18	-18
	Poly-4	-18	-21	-18	-18	-21	-18
	Poly-5	-21	-24	-21	-18	-24	-21
B3	Poly-1	-12	-12	-15	-12	-15	-12
	Poly-2	-18	-15	-18	-15	-15	-18
	Poly-3	-18	-18	-21	-18	-18	-21
	Poly-4	-21	-18	-24	-24	-21	-21
	Poly-5	-21	-21	-24	-24	-24	-24

2.2 SECTION B: Studies on the Viscometric Properties of MMA – Styrene Copolymers in three Different Solvents in Comparison to the Respective Homopolymers.

2.2.1 Introduction

Performance of the additive blended lube oils in the field condition is very much dependent on the structure and morphology of the polymers in the blends [18]. Thus, it is anticipated that viscometric studies of the polymers in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation of the polymer in dilute solutions are concerned. Therefore, the study may be very useful for evaluating the performance of polymer blended oil as an additive for lube oil, where the structure and morphology plays a significant role. Despite this, such information regarding lube oil additives is not yet emphasized.

Polymer samples may present the same molecular mass but may also be linear or branched showing different sizes and shapes. The conformation of the chain in solution and, consequently, the volume it occupies in the solvent medium, is completely dependent on the type of solvent and the temperature of the measurement. The better the solvent the higher extended conformation the chain will assume [14]. Thus the viscometric study, which is a function of molecular size and not the molecular mass, of the polymer solutions in different solvents may yield very useful parameters required for the choice of end application of the polymers.

2.2.2 Results and Discussion

Viscometric data were acquired using the seven equations mentioned. Linear relationship for the plot of $\log \eta_{sp}$ vs $\log C[\eta]$ (Fig 1a – 1c) indicated that the measurements were performed in Newtonian flow [27, 28].

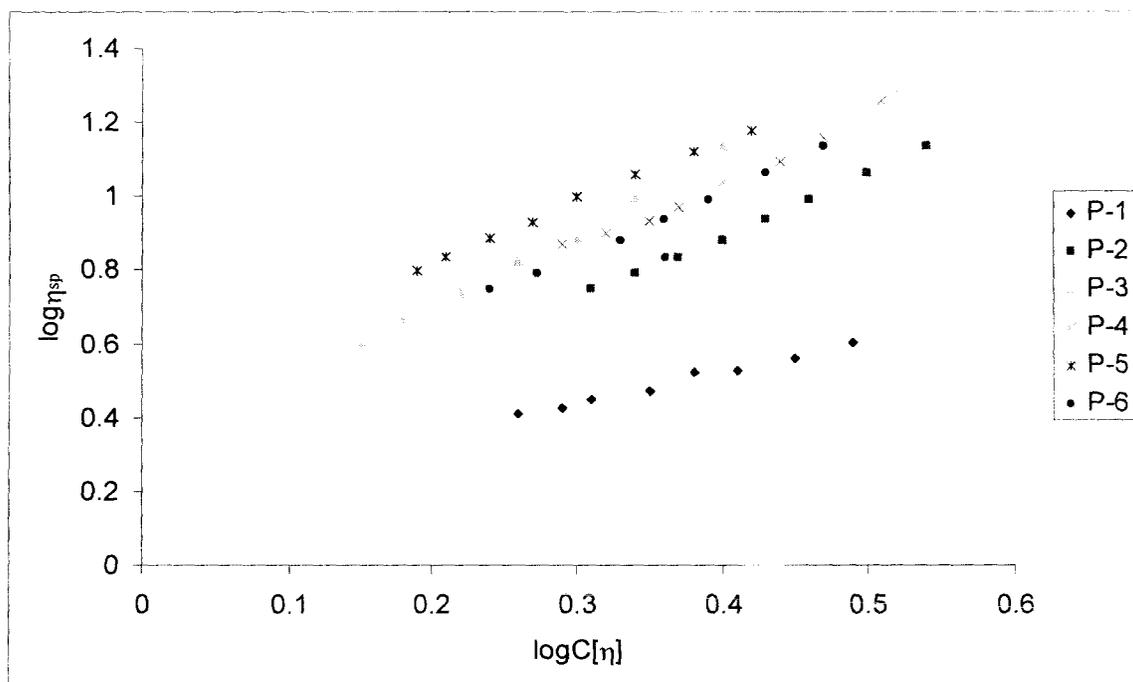


Fig 1a. Plot of $\log C[\eta]$ Vs $\log \eta_{sp}$ for all polymeric samples in chloroform solvent. Where P-1 poly (methyl methacrylate), P-2 polystyrene, P-3 to P-6 are the copolymer of methyl methacrylate + different mass fractions of styrene.

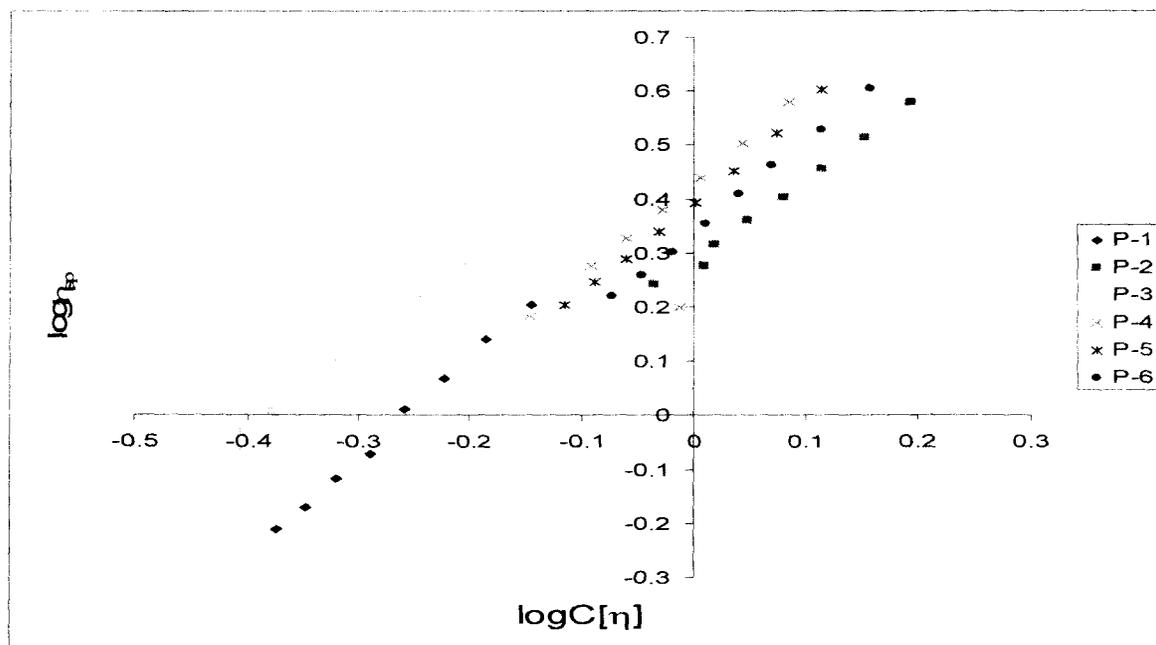


Fig 1b. Plot of $\log C[\eta]$ Vs $\log \eta_{sp}$ for all polymeric samples in toluene solvent. Where P-1 poly (methyl methacrylate), P-2 polystyrene, P-3 to P-6 are the copolymer of methyl methacrylate + different mass fractions of styrene.

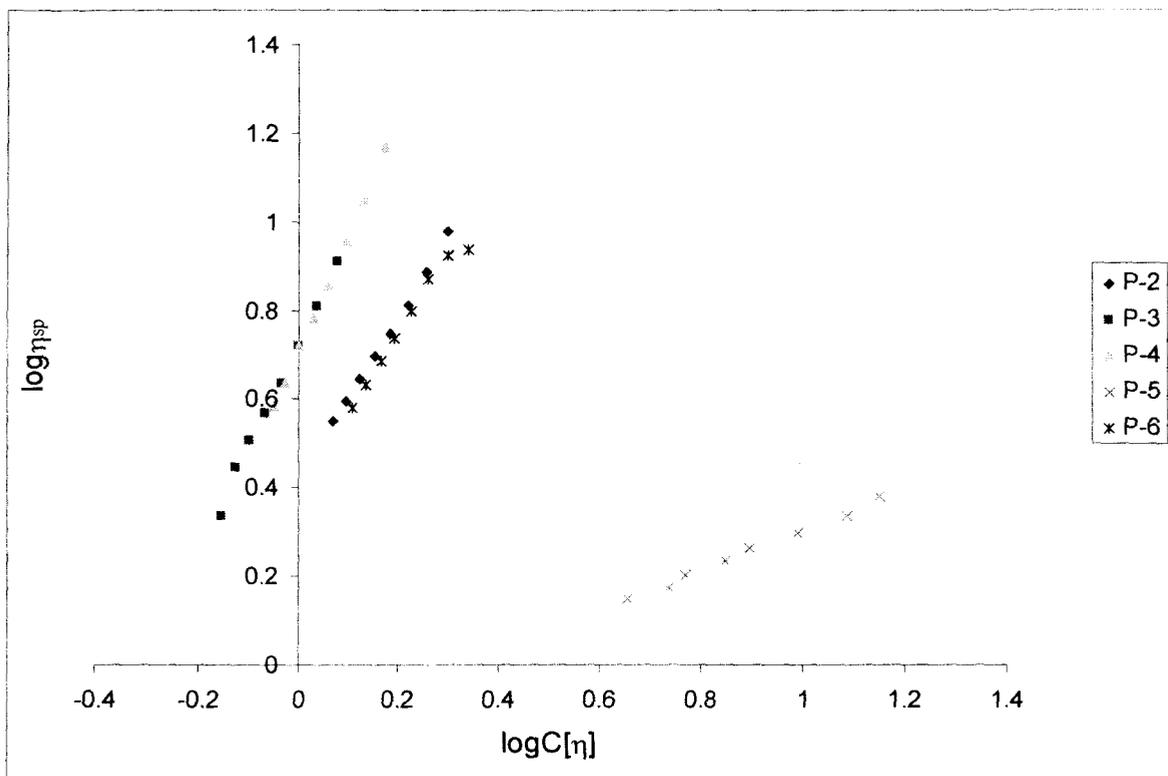


Fig 1c. Plot of $\log C[\eta]$ Vs $\log \eta_{sp}$ for all polymeric samples in carbon tetrachloride solvent. Where P-2 polystyrene, P-3 to P-6 are the copolymer of methyl methacrylate + different mass fractions of styrene.

Table 1A -1C presents intrinsic viscosity values related to all equations for the samples analyzed. Considering the different solvents employed (CHCl_3 , Toluene, CCl_4) and comparing $[\eta]$ for homo and copolymers, it is noticed that the higher values were obtained in chloroform followed by carbon tetrachloride and toluene. Thus considering all the polymers (homopolymer and copolymers) chloroform appeared to be more compatible to the polymer, leading to more extended conformations of the polymers in it. Carbon tetrachloride leads to the lowest values for the homo and copolymers, which varied in a small range in comparison to the other solvents, indicating similar contracted structures with a star like conformation [16]. Variation of $[\eta]$ obtained by graphic extrapolation method (eq. 2-5) was found to be less compared to those obtained by single point determination method (eq. 6-7) without any restriction of solvent.

As expected, the copolymer and also the homopolymers did not show a correlation or a constant variation as far as $[\eta]$ values, molecular weights and compositions are concerned [18]. It is also observed that $[\eta]$ values increase with the increase in styrene concentration except in one or two cases. $[\eta]$ values obtained by using DC equation are always higher irrespective of the nature of the solvent. PMMA was insoluble in CCl_4 .

Table 2A – 2C presents the viscometric constant calculated for homo and copolymers, in CHCl_3 . k_h and k_k fitted in the range of good solvents, whereas CCl_4 medium produced results indicating poor solvation and suggesting the formation of micellar spherical structure [18].

Although, k_{sb} values found for the samples were different from 0.28 the use of these values for the single point determination produced $[\eta]_{sb}$ values close to the ones obtained by extrapolation. It is also interesting to notice that for the best solvent, CHCl_3 , k_{sb} values for the copolymer were close to 0.28. It is also important to observe that the relation $k_h + k_k = 0.5$ was not found for the great majority of the sample analyzed. However, both $[\eta]_{sc}$ and $[\eta]_{dc}$ were similar to $[\eta]_h$, $[\eta]_k$, $[\eta]_m$ and $[\eta]_{sb}$, which were obtained by graphic extrapolation, with small percentage differences. So values different from 0.5 did not put any restriction for the application of SC equation.

Table 3A – 3C presents percentage differences ($\Delta \%$) calculated from intrinsic viscosity $[\eta]$ values obtained by K, M, SB, SC and DC equations, when compared with the values produced by Huggins (H) equation.

As expected different $[\eta]$ values were obtained by graphic extrapolation of H, K, M, and SB equations in all the three solvents analyzed. In CHCl_3 the percentage differences of $[\eta]$ values obtained for both the homo and copolymers when K, M and SB equations (graphic extrapolation) were compared to H equation, varied in the range from -23.07 to 14.38 and is less compared to the values (-12.53 to 92.89) obtained by using SB, SC and DC equations (single point determination method). In toluene the variations range from -20.00 to 66.96 and 23.45 to 66.96 respectively. In CCl_4 the percentage variation is much higher in both the cases. This suggests that the contracted structure of the homo and copolymers in CCl_4 solvent produces higher differences, both in graphic extrapolation and in one point determinations.

In comparison to graphic extrapolation method, the determination employing single point led to higher percentage differences in the values of intrinsic viscosities for all the polymers (homo and copolymers) in all the solvents analyzed, and SB equation seems to be better than the other two methods, SC and DC.

By comparing viscosity average molecular weight (M_v) Table 4A- 4C obtained in different solvents, with number average molecular weight obtained by SEC, it can be seen that M_v obtained in CHCl_3 found to be more close to the SEC values than the same obtained in other two solvents. This observation may be attributed to the comparatively poor solubility of the polymer in these solvents as is observed above in this study. It is also observed that in all the cases and irrespective of the solvents the single point determination values are more close to that of the SEC values rather than the graphical extrapolation values.

2.2.3 Conclusion

Viscometric parameters determined by graphic extrapolation and by single point determination points towards the more compatibility of the copolymers with the solvent in comparison to the homopolymer and best results are obtained when chloroform is used as solvent for the study. Introduction of styrene enhances the solubility, the thermal stability and thus may also enhance the performance of the polymer as well, when used in the field application as a performance additive (like VM or PPD). The study also indicated that viscometric analysis may be very useful for performance evaluation of this kind of additive when the other equipments are not available.

Table 1A. Intrinsic viscosity data in chloroform solvent

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$ (0.28)	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1	13.00	11.00	14.87	10.00	11.37	12.26	13.84
P-2	13.54	12.64	12.18	12.00	14.23	17.78	21.53
P-3	10.50	9.50	9.02	11.00	11.85	13.75	16.12
P-4	14.50	15.00	16.44	14.40	16.64	22.44	27.97
P-5	15.00	14.87	14.15	14.00	17.32	22.28	27.20
P-6	15.46	15.50	14.87	15.00	16.61	20.74	25.12

a- Graphic extrapolation method, b-single point determination method, P-1 homopolymer of MMA, P-2 homopolymer of styrene, P-3 copolymer of MMA and styrene(2.5%) , P-4 copolymer of MMA and styrene(5%), P-5 copolymer of and styrene (7.5%) , P-6 copolymer of MMA and styrene (10%)

Table 1B. Intrinsic viscosity data in toluene solvent

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$ (0.28)	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1	5.50	5.33	4.48	4.40	6.84	6.79	7.08
P-2	12.00	13.50	10.48	10.00	15.30	15.83	17.39
P-3	6.00	7.77	6.05	5.62	9.04	9.02	9.53
P-4	9.33	12.8	9.83	8.50	13.96	14.30	15.58
P-5	10.40	13.10	11.34	9.60	14.44	14.84	16.22
P-6	11.20	14.00	10.88	9.20	14.81	15.26	16.71

Table 1C. Intrinsic viscosity data in carbon tetrachloride solvent

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$ (0.28)	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1	-	-	-	-	-	-	-
P-2	10.00	13.00	12.18	10.00	15.19	17.22	19.96
P-3	5.00	6.40	4.95	7.00	10.31	11.04	12.42
P-4	6.25	8.00	5.85	5.70	13.17	15.14	17.69
P-5	10.00	13.00	7.39	10.00	14.17	16.84	16.25
P-6	11.00	12.80	11.02	10.50	15.75	18.08	21.11

Table 2A. Viscometric constant values in chloroform

Sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	0.29	0.08	0.14	0.37	0.37
P-2	0.82	0.01	0.58	0.36	0.83
P-3	0.83	0.05	0.97	0.32	0.89
P-4	1.20	8.99×10^{-3}	0.48	0.35	1.21
P-5	1.10	3.48×10^{-3}	0.65	0.38	1.10
P-6	0.86	0.04	0.54	0.33	0.89

Table 2B. Viscometric constant values in toluene

Sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	1.08	-0.42	1.69	1.33	0.66
P-2	0.97	0.02	0.96	0.73	0.99
P-3	1.90	0.07	1.33	1.15	1.97
P-4	1.59	0.05	0.72	0.88	1.64
P-5	1.27	0.05	0.70	0.79	1.32
P-6	1.09	0.08	0.08	0.81	1.17

Table 2C. Viscometric constant values in carbon tetrachloride

Sample	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	-	-	-	-	-
P-2	1.73	0.11	0.24	0.57	1.84
P-3	3.51	0.41	1.8	0.60	3.92
P-4	3.84	0.36	1.87	0.99	4.20
P-5	1.57	0.03	1.41	0.48	1.60
P-6	1.52	0.03	0.83	0.55	1.55

Table 3A. Percentual difference of intrinsic viscosity with respect to Huggins intrinsic viscosity (Using chloroform solvent)

Sample	K ^a	M ^a	SB ^a	SB ^b	SC ^b	DC ^b
P-1	-15.38	14.38	-23.07	-12.53	-5.69	6.46
P-2	-6.65	-10.04	-11.37	5.09	31.31	58.93
P-3	-9.52	-14.09	4.76	12.85	30.95	53.52
P-4	3.44	13.37	-0.69	14.75	54.75	92.89
P-5	-0.86	-5.66	-6.66	15.46	48.53	81.33
P-6	0.25	-3.81	-2.97	7.37	34.15	62.41

Table 3B. Percentual difference of intrinsic viscosity with respect to Huggins intrinsic viscosity (Using toluene solvent)

Sample	K ^a	M ^a	SB ^a	SB ^b	SC ^b	DC ^b
P-1	-3.09	-18.54	-20.00	24.36	23.45	28.72
P-2	12.50	-12.66	-16.66	27.55	28.16	44.91
P-3	29.50	0.75	-6.33	50.6	50.33	58.90
P-4	37.19	5.36	-8.89	49.66	53.27	66.96
P-5	25.92	9.04	-7.69	38.87	42.98	55.90
P-6	25.00	-2.87	-17.85	32.23	36.25	49.19

Table 3C. Percentual difference of intrinsic viscosity with respect to Huggins intrinsic viscosity (Using carbon tetrachloride solvent)

Sample	K ^a	M ^a	SB ^a	SB ^b	SC ^b	DC ^b
P-1	--	-	-	-	-	-
P-2	30.00	21.80	0.00	51.92	72.20	99.60
P-3	28.00	-1.00	40.00	106.20	120.80	148.40
P-4	28	-6.4	-8.8	110	142.24	183.1
P-5	30.00	-26.10	0.00	41.69	68.40	62.50
P-6	16.36	0.18	-4.50	43.52	64.36	91.90

Table 4 A. Determination of molecular weight by Mark - Houwinks equation $[\eta] = KM^a$
Where, K =0.00387 dl/g and a = 0.725 (Using chloroform solvent)

Sample	M _h ^a x 10 ⁻⁴	M _k ^a x 10 ⁻⁴	M _m ^a x 10 ⁻⁴	M _{sb} ^a x 10 ⁻⁴	M _{sb} ^b x 10 ⁻⁴	M _{sc} ^b x 10 ⁻⁴	M _{dc} ^b x 10 ⁻⁴
P-1	7.30	5.80	8.79	5.08	6.07	6.74	7.96
P-2	7.73	7.03	6.68	6.54	8.27	11.25	14.65
P-3	5.44	4.74	4.41	5.80	6.43	7.89	9.83
P-4	8.49	8.90	10.10	8.41	10.27	15.51	21.02
P-5	8.90	8.79	8.21	8.09	10.85	15.36	20.23
P-6	9.28	9.31	8.79	8.90	10.24	13.92	18.12

Table 4 B. Determination of molecular weight by Mark -Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387$ dl/g and $a = 0.725$ (Using toluene solvent)

Sample	$M_h^a \times 10^{-4}$	$M_k^a \times 10^{-4}$	$M_m^a \times 10^{-4}$	$M_{sb}^a \times 10^{-4}$	$M_{sb}^b \times 10^{-4}$	$M_{sc}^b \times 10^{-4}$	$M_{dc}^b \times 10^{-4}$
P-1	2.23	2.13	1.68	1.64	3.01	2.98	3.16
P-2	6.54	7.69	5.43	5.09	9.15	9.59	10.91
P-3	2.51	3.59	2.54	2.29	4.42	4.41	4.76
P-4	4.62	7.15	4.97	4.07	8.06	8.33	9.38
P-5	5.37	7.38	6.05	4.81	8.45	8.77	9.91
P-6	5.95	8.09	5.71	4.56	8.75	9.16	10.33

Table 4C. Determination of molecular weight by Mark- Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387$ dl/g and $a = 0.725$ (Using carbon tetrachloride Solvent)

Sample	$M_h^a \times 10^{-4}$	$M_k^a \times 10^{-4}$	$M_m^a \times 10^{-4}$	$M_{sb}^a \times 10^{-4}$	$M_{sb}^b \times 10^{-4}$	$M_{sc}^b \times 10^{-4}$	$M_{dc}^b \times 10^{-4}$
P-1							
P-2	5.09	7.30	6.68	5.09	9.06	10.77	13.20
P-3	1.95	2.75	1.92	3.11	5.30	5.83	6.86
P-4	2.66	3.74	2.43	2.34	7.44	9.01	11.18
P-5	5.09	7.30	3.35	5.09	8.23	10.44	9.94
P-6	5.80	7.15	5.81	5.44	9.52	11.52	14.26

CHAPTER III

3.1 Experimental

3.1.1 Materials used

Carbon tetrachloride, chloroform and styrene were purchased from Merck India Ltd., and were used as such. Methyl methacrylate was purchased from BDH, Benzoyl peroxide (BZP) from LOBA chemicals, India Ltd., Toluene from S.D fine chem. India Ltd., and was used after purification. Base oils were collected from Indian Oil Corporation Ltd., Dhakuria, Kolkata and Bharat Petroleum Corporation Ltd., Matigara, Darjeeling.

3.1.2 Purification of the materials

Methyl methacrylate (MMA) was shaken two to three times with 5% sodium hydroxide to eliminate hydroquinone inhibitor, dried over anhydrous CaCl_2 for 7-8 h and distilled. Benzoyl peroxide (BZP) was recrystallized from CHCl_3 -MeOH mixture. Toluene was purified following standard methodology.

3.1.3 Polymerization

The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask was placed desired mass of MMA and initiator (BZP) followed by the desired mass of styrene was added drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into 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. A homopolymer of MMA were similarly prepared and purified under the same conditions for use in reference experiments.

3.1.4 Spectroscopic Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells and the spectra were recorded at room temperature within the wave number range 400 to 4000 cm^{-1} . NMR spectra were recorded in Bruker Avance 300MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl_3 was used as solvent and TMS as reference material. Average molecular weights (M_w and M_n) were obtained by SEC (GPC) using THF as mobile phase in a Water GPC system at (303 ± 1) K. The retention times were calibrated against known monodisperse polystyrene standards [18].

3.1.5 Thermo gravimetric analysis (TGA)

The thermograms in air were obtained on a mettler TA – 3000 system, at a heating rate of 10 $\text{K}\cdot\text{min}^{-1}$.

3.1.6 Viscometric measurements

Viscometric measurements were carried out in different way. A) Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values are $K' = 0.00268 \text{ cm}^2 \text{ sce}^{-2}$, $L = -19.83 \text{ cm}^2$ and volume of the bulb is 3 cm^3 and length of the capillary 11.3 cm). Experimental determination was carried out by counting time flow at least nine different concentration of (0.2175 to 0.087) $\text{g}\cdot\text{cm}^{-3}$ of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and uncertainty was found to be nearly 0.17 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$ [32, 33] were employed.

B) Again viscometric properties were determined at 25 $^{\circ}\text{C}$ in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at least nine different concentration of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. For the viscosity –

average molecular weight determination, the constants $k = 0.00387 \text{ dl/g}$ and $a = 0.725$ [32, 33] were employed also.

3.1.7 Evaluation of prepared additive as pour point depressants in base oils

The prepared additives were evaluated as pour point depressant using base oils collected from two different sources A and B, (Table 10 Section A) through the pour point test according to the ASTM-D-97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentration. The experimental data were noted by taking an average of three experimental results under identical conditions.

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PART II

**STUDIES ON SYNTHESIS, CHARACTERIZATION, POUR POINT
DEPRESSANT AND VISCOSITY INDEX OF HOMO AND
COPOLYMER OF ACRYLATES WITH STYRENE**

CHAPTER I

1.1 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

Base fluids mineral oil generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. Additives are synthetic chemical substances that can improve lots of different parameters of lubricants. They can boost existing properties; suppress undesirable properties in the base fluids. They can assist each other (synergism) or they can lead to antagonistic effects. Some additives are multifunctional products that decrease the possibility of additives interfering with each other negatively. Additives are used to (a) reduce the oxidative or thermal degradation of an oil, (b) to lessen the deposition of harmful deposits on lubricated parts, (c) to minimize rust and corrosion, (d) to control frictional properties, and (e) to reduce wear. They are also employed to alter purely physical properties of oil such as viscosity / viscosity temperature relationship known as viscosity modifier (VM) or viscosity index improver (VII) and also to improve the low temperature flow properties of the lube oil that is pour point depressant (PPD).

Today, multifunctional additives play a major role in the technology of engine oils. Thus, research throughout the world is increasingly directed toward producing additives with more than one purpose (i.e., multifunctional additives) (Akhmedov, 1987; Eckert and Wortel, 1972; Ford and Wood, 1971; Kapur et al., 1995; Mohamed et al., 1994; Ranney, 1978; and Schwab and Heilweil, 1976) [1-7].

Numerous investigation and the accumulated experience in use of high molecular weight compounds as additive to produce oil with given properties are now opening of possibilities in the development of multifunctional polymeric additives that have not only PPD properties but also VM properties.

In accordance with the present invention, it will be very pertinent to include a brief introduction of PPD and VM additives used in lube oil formulation, in this chapter.

As a brief introduction of PPD has already been presented in chapter I of Part I, a short discussion only on VMs is presented here.

An ideal lubricant for most purposes would possess the same viscosity at all temperatures [8]. Although a few non-polymeric substances such as metallic soaps exhibit VI

improving properties [9] all commercially important VI improvers today are oil-soluble organic polymers. Suitable polymers exert a greater thickening effect on oil at higher temperatures than they do at lower temperatures [10]. The viscosity index is an indicator of the change in viscosity as the temperature is changed. Higher the VI, lesser the change in viscosity of an oil for a given temperature. Viscosity index improvers are used to limit the rate of change of viscosity with temperature. These improvers have little effect on oil viscosity at low temperatures. However, when heated the improvers enable the oil viscosity to increase within the limited range permitted by the type and concentration of the additive. This quality is most apparent in the application of multigrade motor oils. Viscosity index improvers are long chain, high molecular weight polymers that function by increasing the relative viscosity of oil more at high temperatures than they do at low temperatures. Generally this results from the polymer changing its physical configuration with increasing temperature of the mixture. It is postulated then in cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules and the oil produces a proportionally greater thickening effect. Although the oil polymer mixture still decreases in viscosity as the temperature increases, it does not decrease as much as the oil would alone [11].

Some of the polymers generally used commercially as VII, and known to possess certain inherent advantages and disadvantages in performance, are- i) Poly isobutylenes (PIBs), ii) Hydro-generated Styrene – isoprene copolymers, iii) Olefin copolymers (OCP); e.g. Ethylene- propylene copolymer, IV) Esters of styrene- maleic anhydride copolymers and v) Poly(alkyl methacrylates) (PMA).

Olefin copolymers (or OCP) used as viscosity index improvers conventionally comprise copolymers of ethylene, propylene and optionally, a diene. Small polymeric side chains do not exert a substantial viscosity modifying effect in oil. Polymerized propylene has one methyl branch for every two backbone carbon atoms. Ethylene polymer is substantially straight chained. Therefore, at a constant amount of polymer in oil (treat rate), an OCP having a higher ethylene content will display an increased high temperature thickening effect (thickening efficiency, or TE). However, polymer chains having long ethylene sequences have a more crystalline polymer structure. Crystalline polymers are less oil soluble than

amorphous polymers and as a result, the OCP can drop out of the oil, causing the plugging of engine filters (and the loss of the viscosity modifying effect). Further, OCPs having substantial crystalline segments have been found, again primarily at low temperatures, to interact with waxes in the oil, and other OCP chains, which results in uncontrollable increases in low temperature viscosity and, in extreme cases, the gelling of the lubricating oil. These problems have been found to manifest in Ziegler Natta polymerized OCPs containing greater than about 60 wt. % ethylene (herein after referred to as "high ethylene content OCPs").

Due to their molecular architecture, star polymers are known to provide improved shear stability compared to OCPs. VI improvers that are star polymers made by hydrogenation of anionically polymerized isoprene are commercially available. Anionic polymerization results in a relatively low molecular weight distribution (M_w/M_n). Hydrogenation results in alternating ethylene/propylene units having a composition comparable to a polymer derived from 40 wt. % ethylene and 60 wt. % propylene. These VI improvers provide excellent shear stability, good solubility and excellent cold temperature properties. However, improvements in the balance between the thickening efficiency and shear stability of star polymers remain possible.

U.S. Pat. No. 4,116,917 exemplifies certain star polymers comprising hydrogenated poly(butadiene/isoprene) tapered arms containing about 44.3 wt. % polymer derived from butadiene. Since butadiene initially reacts faster than isoprene when anionic polymerization is initiated with secondary butyllithium (the process described in the patent), a polybutadiene block is first formed. As the butadiene concentration is lowered through polymerization, isoprene begins to add to the living polymer so that, when the polymerization reaction is complete, the chain is made up of a polybutadiene block, a tapered segment containing both butadiene and isoprene addition product, and a polyisoprene block resulting in a living tapered polymer chains that, when coupled with divinylbenzene, produce a star polymer having a polybutadiene block positioned distal from the divinylbenzene-coupled core. The long ethylene sequences of these external hydrogenated polybutadiene blocks were found to cause the same low temperature performance problems associated with high ethylene content OCPs.

To provide an improvement in thickening efficiency, while maintaining low temperature performance, U.S. Pat. No. 5,460,739 suggests star polymers comprising triblock copolymer arms of hydrogenated polyisoprene/polybutadiene/polyisoprene. The hydrogenated polybutadiene block provides an increased ethylene content, which improves thickening efficiency. The patent suggests that, by placing the hydrogenated polybutadiene block more proximal to the nucleus, the adverse effect on low temperature properties could be minimized. Such polymers were found to provide improved low temperature properties relative to the tapered arm polymers of U.S. Pat. No. 4,116,917. However, when such polymers were provided with a hydrogenated polybutadiene block of a size sufficient to provide a credit in thickening efficiency, a debit in low temperature performance remained relative to the pure polyisoprene polymers.

Therefore, Among the OCPs, there remains a need for improved VI improvers that are capable of providing a good viscosity temperature relationship, without the associated reduction in solubility and cold temperature performance.

Although PMAs are preferred type of VII in certain applications, they often contribute to enhanced formation of deposits in the engine due to thermal instability of these additives under high temperature conditions. The usual approach to overcome this shortcoming is to incorporate a dispersancy property into the VII. Dispersant versions of PMA type VIIs are usually derived from a nitrogen-containing methacrylate monomer or by grafting the PMA polymer with a nitrogen compound. Although dispersant-PMAs function as better VIIs as compared to parent PMAs, there is a risk of affecting certain beneficial properties associated with normal PMAs such as pour point depressancy and good shear stability; particularly in the case of grafted PMAs.

Thus, within the category of PMA type VMs, considerable need and potential exists to develop polymers with improved performance.

In a recent communication AAA Abdel Azim [12] has reported that, polymeric additive based on octadecene- methacrylate copolymer has been prepared and evaluated as multifunctional additive (VI, PPD, Dispersancy- detergent). The octadecene – MA copolymer reacted with different long chain alcohols to produce different types of ester

which were than aminated with different types of amines. It was found that the efficiency of the prepared compounds as viscosity index increases with increase in the concentration of additive and increase in the alkyl chain length of that compound where as their efficiency as PPD increases with decreasing the concentration of prepared polymer.

In a similar work [13] has described a method to prepare a series of copolymer and terpolymers, derivative of alkyl acrylate and maleic anhydride. They investigated the influence of the structure of the copolymer and terpolymers, PPD properties were found to increase with increase in concentration in solution and they also gave better result when the alkyl chain length of the copolymer is similar to the composition of the n-paraffin in waxy oil.

Floeria et al [14] investigated the influence of chemical composition on the PPD properties of methacrylate copolymers as additive for lube oils, methacrylate- styrene copolymer and observed that the efficiency is related to the length of the alkyl side chain of the polymethacrylates and to the nature of the base oils.

U.S. Patent 5834408 described preparation and evaluation of acrylate copolymers as a PPD in lube oil compositions.

U.S. Patent 4867894 describes that copolymers of the methyl methacrylate having an average molecular weight from 50,000 to 500,000 showed pour point properties of petroleum oil.

U.S. Patent 4956111 describes the use of poly methacrylate polymer having an average chain length of alkyl group in the polymer ranging between 12.6 – 13.8 can reduce the pour point to 35⁰ C and is compatible with other additive e.g. VII and detergents.

U.S. Patent 4906702 discloses the olefin copolymer of unsaturated carboxylic acid ester as PPD for lube oil.

U.S. Patent 4088589 discloses a lubricating oil composition comprising a lubricating oil and VII amount of an oil soluble polymer composition consisting of a specific amount of copolymer of ethylene α - Olefin showed multifunctional properties eg. PPD, VII properties.

U.S. Patent 4073738 discloses acrylate and methacrylate based copolymers with conjugated dienes exhibit high stability to shear and may be useful in particular as a VII.

U.S. Patent 4668412 has claimed the synthesis of a dispersant VII and pour point depressant of a terpolymer of maleic anhydride and lauryl methacrylate and stearyl

methacrylate which has been formulated with dimethyl amino propyl amine and manich base of amino ethyl pyrazine, paraformaldehyde and 2, 6-ditertiarybutyl phenol.

U.S. Patent 4032459 discloses lubricating composition containing hydrogenated butadiene-isoprene copolymers with PPD, VII properties.

U.S. Patent 5955405 discloses a methacrylate copolymers comprising from 5 to 15 wt% butyl methacrylate, 70-90 wt% C-10 to C-15 alkyl methacrylate, from 5-10 wt% C16 – C30 alkyl methacrylate as having excellent low temperature properties in lubricating oils.

U.S. Patent 4886520 discloses an oil composition comprising mineral oils showed more enhance PPD and VII properties by the addition of a terpolymer comprising an alkyl ester of an unsaturated monocarboxylic acid, and olefinically unsaturated homo and heterocyclic nitrogen compound and then an allyl acrylate or methacrylate or a perflouro alkyl ethyl acrylate or methacrylate.

U.S. Patent 6458749 discloses polymerization of a mixed methacrylate made of C16 – C24 carbon containing alcohols when polymerized are especially effective by satisfying different aspects of low temperature fluidity properties for a broad range of base oils.

Thus from the above literature survey it is observed that in most of the cases the recent development in the additive chemistry has either an additive with an improved VM properties or with a better PPD performances. But reports regarding the development of a multifunctional additives comprising VM – PPD properties are still limited.

Thus considering the present need and the emphasis as given by the original equipment manufacturers (OEMs), it is felt to undertake the present investigation towards the development of an efficient multifunctional additive having VM as well as PPD properties for lube oils of varied compositions (different sources).

CHAPTER II

This chapter is divided into three sections, Section A, Section B and Section C

Section A comprises the Synthesis of Poly(acrylates) and their Copolymer with Styrene and Evaluation of their Performance as Pour Point Depressant for Lubricating Oil

Section B comprises the Evaluation of Poly(acrylates) and their Copolymer as Viscosity Modifiers

Section C comprises the Comparison of Viscometric Parameters of the Homo and Copolymer of Poly(decyl acrylate) in Lubricating Oil

2.1 SECTION A: Synthesis of Poly(acrylates) and their Copolymer with Styrene and Evaluation of their Performance as Pour Point Depressant for Lubricating Oil

2.1.1 Introduction

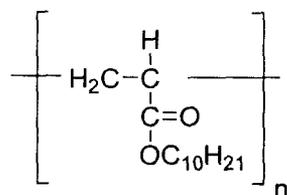
Pour point depressants are used to modify and control wax crystallization phenomena in paraffinic mineral oils. As temperature decreases, waxy components begin to form small, plate-like crystals. The plates eventually row together to form an interlocking network that effectively traps the remaining liquid. Flow ceases unless a force strong enough to break the relatively weak wax gel matrix structure is applied. Control of wax crystallization in lubricants is often described as pour point depressant (PPD). PPDs are used to maintain fluidity of lubricants under various cooling conditions, and their effectiveness depends on the lube oil composition and of course, on their chemistry and concentration [15].

Synthesis of poly(acrylates) (decyl, isodecyl and dodecyl) and their few copolymers with styrene, characterization of these polymers and their evaluation as pour point depressant comprises the subject matter of this chapter. The copolymers were prepared by varying the styrene concentration in the monomer mixture and employing free radical polymerization technique using benzoyl peroxide as initiator in toluene solvent. Characterization of the polymers (both homo and copolymer) was carried out employing IR, NMR and TGA techniques. Viscomertic characterization of these samples was carried out in toluene solvent.

2.1.2 Results and Discussion

Spectroscopic analysis

FT-IR spectrum of the poly(decyl acrylate) (Figure 1) exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1260 and at 1175 cm^{-1} can be explained owing to the C-O (ester bond) stretching vibration and the absorption bands at 975 , 750 and 711 cm^{-1} were due to the bending of C-H bond. The broad peak ranging from 2900 - 3100 cm^{-1} was due to the presence of stretching vibration. From this discussion and from ^1H NMR spectral data (Figure 2) structure of this polymer may be presented by structure I.

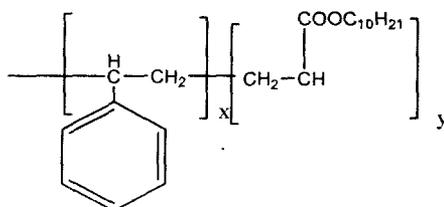


Structure I

The existence of the PDA- styrene copolymer was confirmed by FT-IR and NMR analysis. The copolymer in its IR spectrum (Figure 3) showed broad peak ranging from 1732 to 1720 cm^{-1} . This was attributed to the stretching vibration of the ester carbonyl group whereas the absorption bands at 758, 711, 695 and 662 cm^{-1} were due to C-H bond of the phenyl group of styrene.

In the ^1H NMR spectra (Figure 4) of one of the respective copolymers, a broad multiplet centered at 8.07 ppm indicated the presence of a phenyl group. A broad singlet at 4.06 ppm was due to the proton of the $-\text{OCH}_2$ group. The absence of singlet between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer.

The proton decoupled ^{13}C NMR spectrum (Figure 5) of the above sample of copolymer was in complete agreement with the original structure-II



Structure II

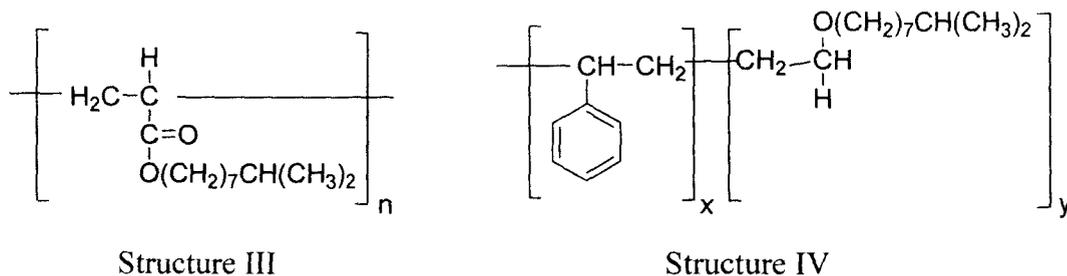
The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of $-\text{OCH}_2$ group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports [16, 17].

It was further verified through an analysis of FT-IR spectral data [6]. The intensity of C=O absorption in FT-IR spectra of present copolymers, as compared to the carbonyl absorption in a standard, were analyzed for quantitative determination of the content of acrylate component in the copolymer blends of known quantities of an ethylene-propylene

and poly(decyl acrylate) in which varied quantities of PDA were present. The comparative results obtained on comparisons are presented in Table 1.

FT-IR spectra (Figure 6) of homopolymer of isodecyl acrylate exhibited absorption at 1732 cm^{-1} for the ester carbonyl stretching vibration along with other peaks at 1456.2, 1379, 1260 and 1166.9 cm^{-1} , owing to the CO stretching vibration and absorption bands at 750 and 710 cm^{-1} were due to the bending of C-H bond. In its ^1H NMR spectra (Figure 7) homopolymer of isodecyl acrylate showed a broad singlet centred at 4.02 ppm due to the proton of $-\text{OCH}_2$ group, a broad singlet at 0.86 ppm was due to methyl's of isodecyl chain. The proton decoupled ^{13}C -NMR (Figure 8) of the above sample was in complete agreement with the homopolymer.

The existence of its copolymer with styrene was confirmed by FT-IR, ^1H -NMR and ^{13}C -NMR analysis. In its FT-IR spectra (Figure 9) of the copolymer showed a broad peak ranging from $1722\text{--}1732\text{ cm}^{-1}$ along with other peaks at 753.56, 712.15, 700.75, 667.98 cm^{-1} were due to C-H bond of the phenyl group of styrene. In the ^1H NMR spectra (Figure 10) of the copolymer, a broad multiplet ranging from 7.23 to 7.58 ppm indicated the presence of phenyl group of styrene. Broad singlet at 4.06 ppm was due to the proton of $-\text{OCH}_2$ group. Methyls of the isodecyl chain appeared between 0.81 to 0.86 ppm at the absence of singlets between 5 and 6 ppm indicated the absence of any vinylic proton in the copolymer. The existence of copolymer was further confirmed by the presence of aromatic carbon ranging between 124 to 141 ppm in the ^{13}C -NMR spectrum (Figure 11) of the polymer. The carbonyl carbon appears at 174.47 ppm along with other carbons. From the above discussions probable structure of poly(isodecyl acrylate) and its copolymer with styrene was assigned as structure III and structure IV respectively.

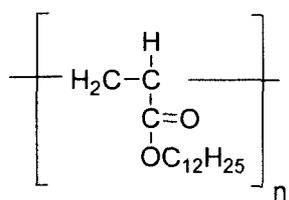


The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of signal of $-\text{OCH}_2$ group at 4.6 ppm and the area of signal of phenyl

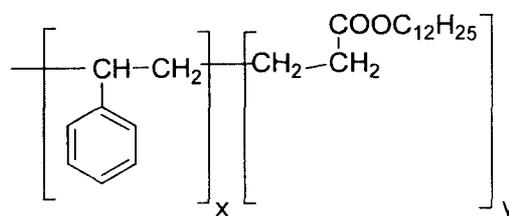
group at 7.41 ppm based on earlier reports [16, 17]. It was further confirmed through FT-IR spectral data. The intensity of carbonyl absorption in FT-IR spectra of the copolymer as compared to the same in a standard by analyzed for quantitative determination of the content of acrylate component in the copolymer (Table I).

FT-IR spectra (Figure 12) of the homopolymer of dodecyl acrylate exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration along with other peaks at 1456, 1260, 1164.9, 1112, 1028 and 711 cm^{-1} due to the bending of C-H bond. ^1H NMR spectra (Figure 13) of the homopolymer indicated the existence of $-\text{OCH}_2$ group at 4.02 ppm (broad singlet) along with the methyl protons ranging between 0.86 to 0.90 ppm together with methylene proton ranging between 1.3 to 1.6 ppm. The proton decoupled ^{13}C -NMR (Figure 14) of the above sample was in complete agreement with the homopolymer.

The existence of copolymer of dodecyl acrylate with styrene was confirmed by the analysis of FT-IR, ^1H NMR and ^{13}C -NMR spectra of the copolymer. FT-IR spectra (Figure 15) of the copolymer showed sharp peak at 1732 cm^{-1} for the ester carbonyl along with other peaks at 1028, 900, 760, 700 due to C-H bond of phenyl group of styrene. ^1H NMR spectra (Figure 16) of the copolymer showed broad singlet at 4.02 ppm due to $-\text{OCH}_2$ protons. A broad multiplet centered at 7.45 ppm was due to aromatic protons. The absence of singlet between 5 to 6 ppm indicated the absence of vinylic protons in the copolymer. ^{13}C -NMR spectrum (Figure 17) of the above sample showed the presence of ester carbonyl at 173 ppm with the aromatic carbon appeared in the range 125 to 134 ppm. The extent of incorporation of styrene in the polymer chain was also determined by the method as applied earlier and tabulated as Table I. The structure of poly(dodecyl acrylate) and its copolymer with styrene presented by structure V and structure VI.



Structure V



Structure VI

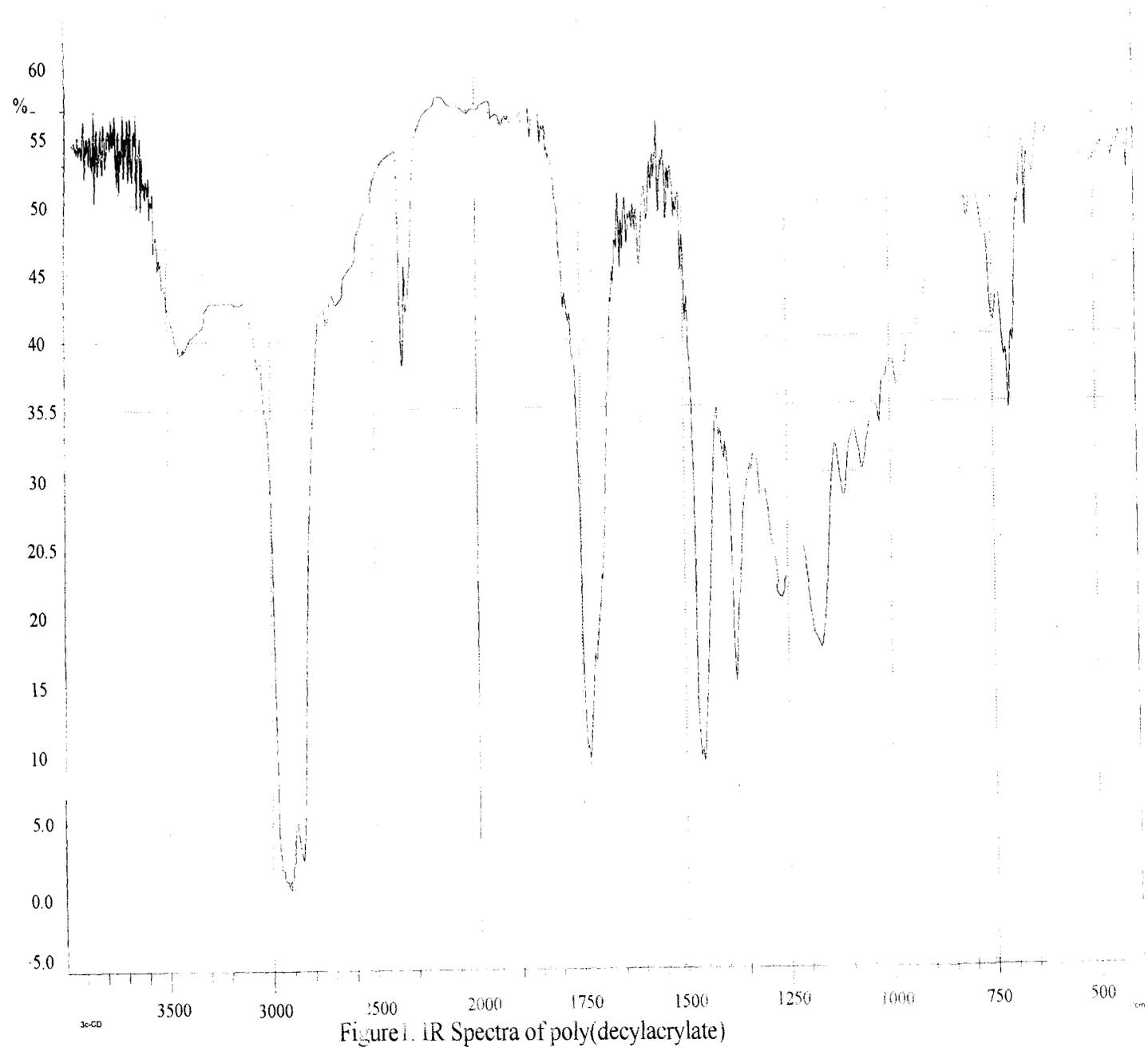
Thermal stability of the prepared compounds

Table 2 presents thermal stability data of all prepared sample. Introduction of styrene increases thermal stability of the acrylate polymer as was observed in our earlier studies [18].

Viscometric analysis

Viscometric data were obtained using the six equations mentioned in Part I, Chapter I. Huggins (H), Kraemer (K), Martin (M) and Schulz–Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz–Blascke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz–Blascke (SB) equation is commonly applied in single point determinations because it was found that $k_{sb} = 0.28$ for many polymer-solvent systems. In this work, this value was used.

Table 3 presents intrinsic viscosity $[\eta]$ values related to all equations (eq 2 to 7) for the samples analyzed. Taking into account the data for all the homo and copolymer samples, it can be noticed that, the variation of $[\eta]$ values among each set of homo and copolymers (i.e., P-1 to P-4, P-5 to P-8 and P-9 to P-12) are consistent. There is a gradual decrease in the $[\eta]$ values with the increase in styrene concentration in the feed of the copolymer of PDA-styrene (P1-P4). Again it is observed that there is a sudden drop of the $[\eta]$ value as it proceeds from homopolymer to copolymer followed by a gradual increase in the same value with the increase in the styrene concentration for PIDA – styrene system (P-5 to P-8) and PDDA-styrene system (P-9 to P-12).



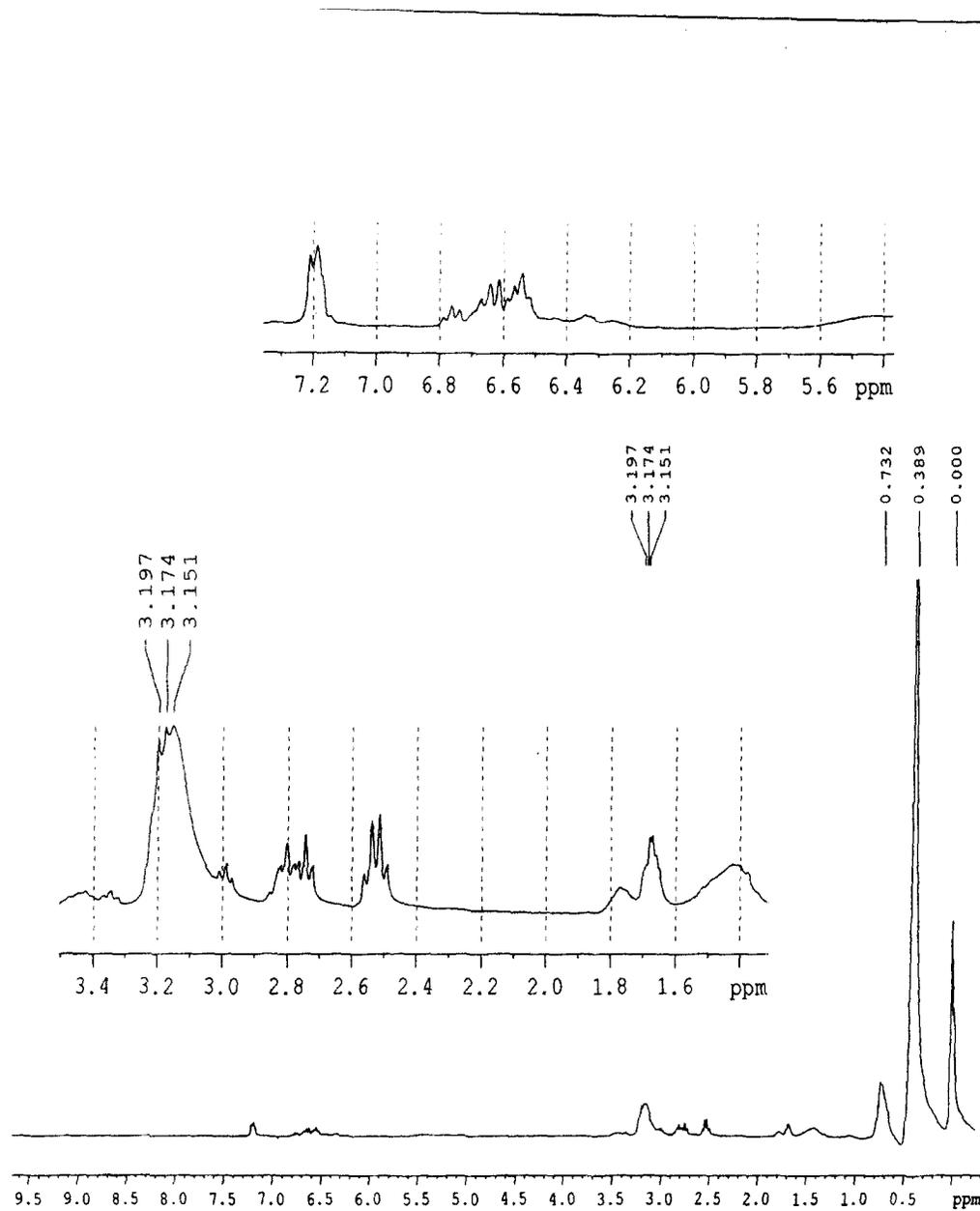


Figure 2. ¹H NMR of poly(decylacrylate)

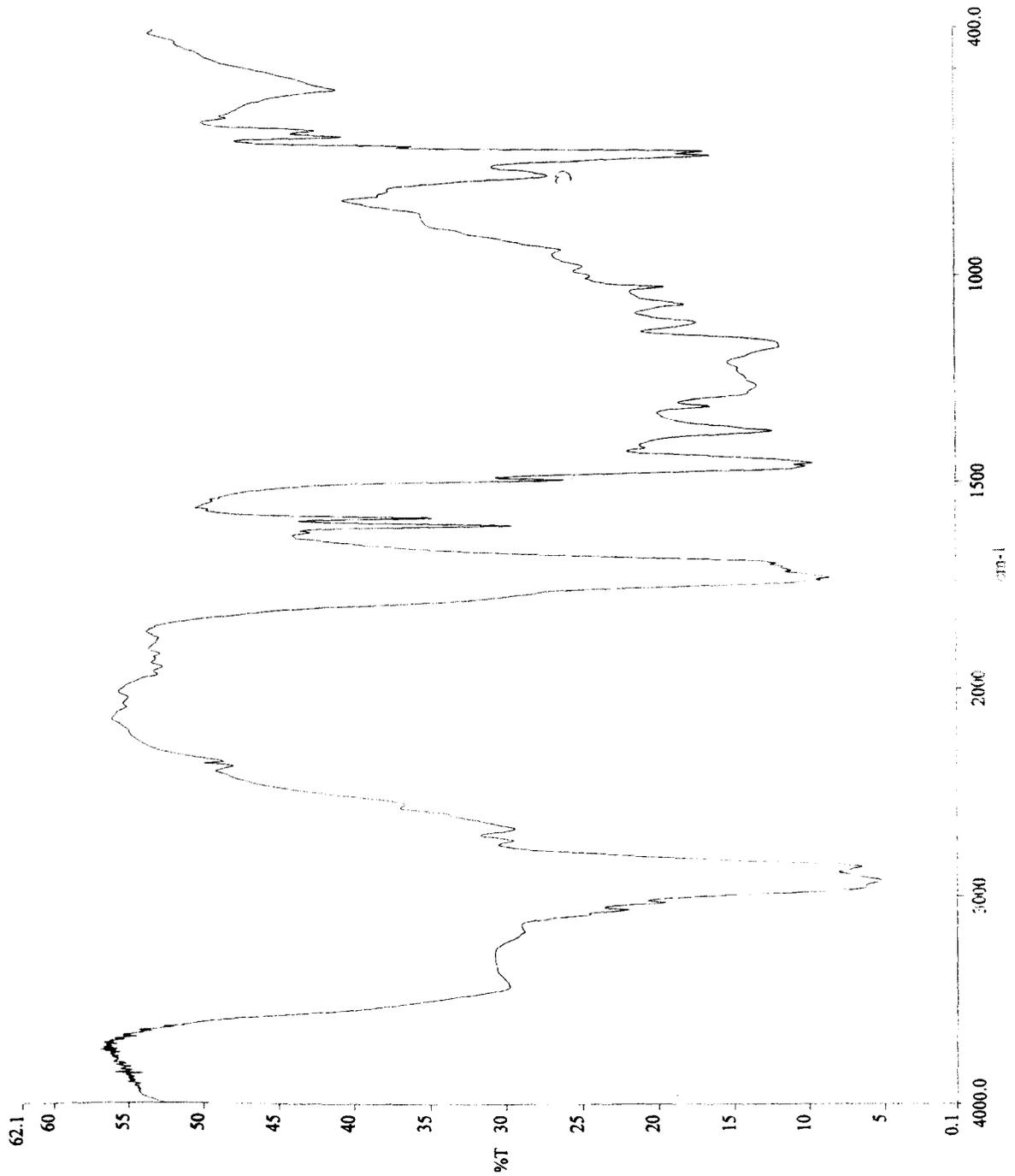
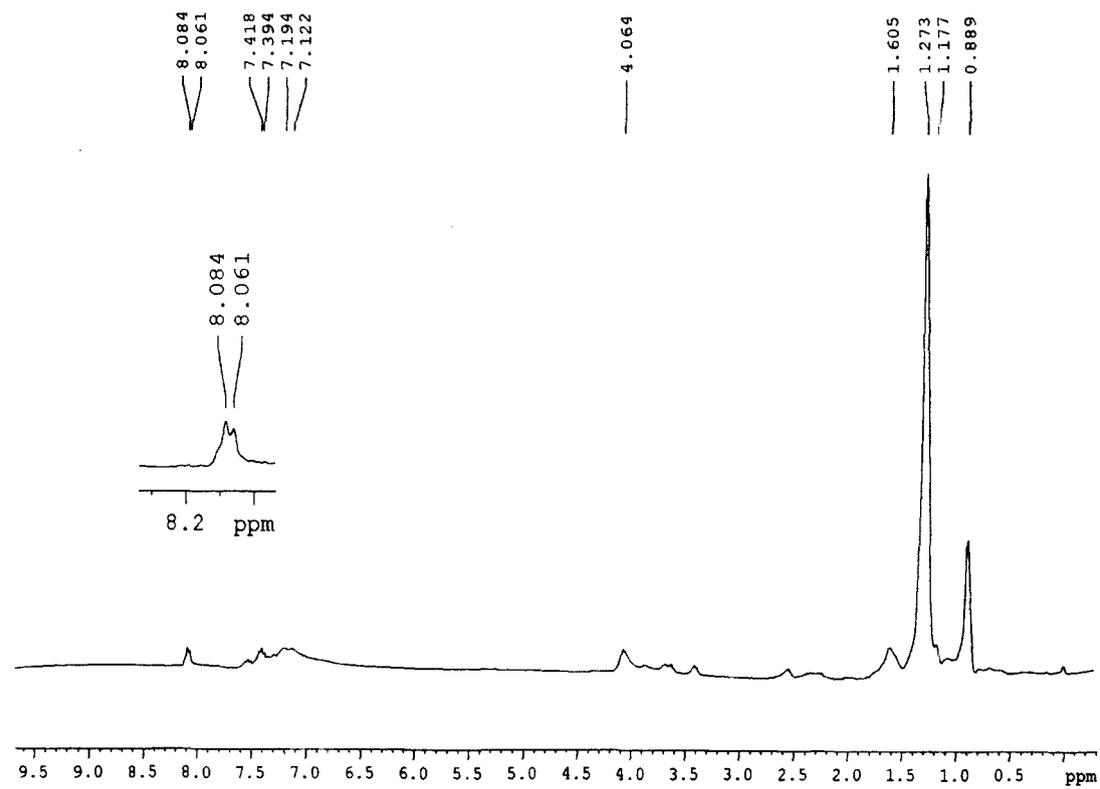
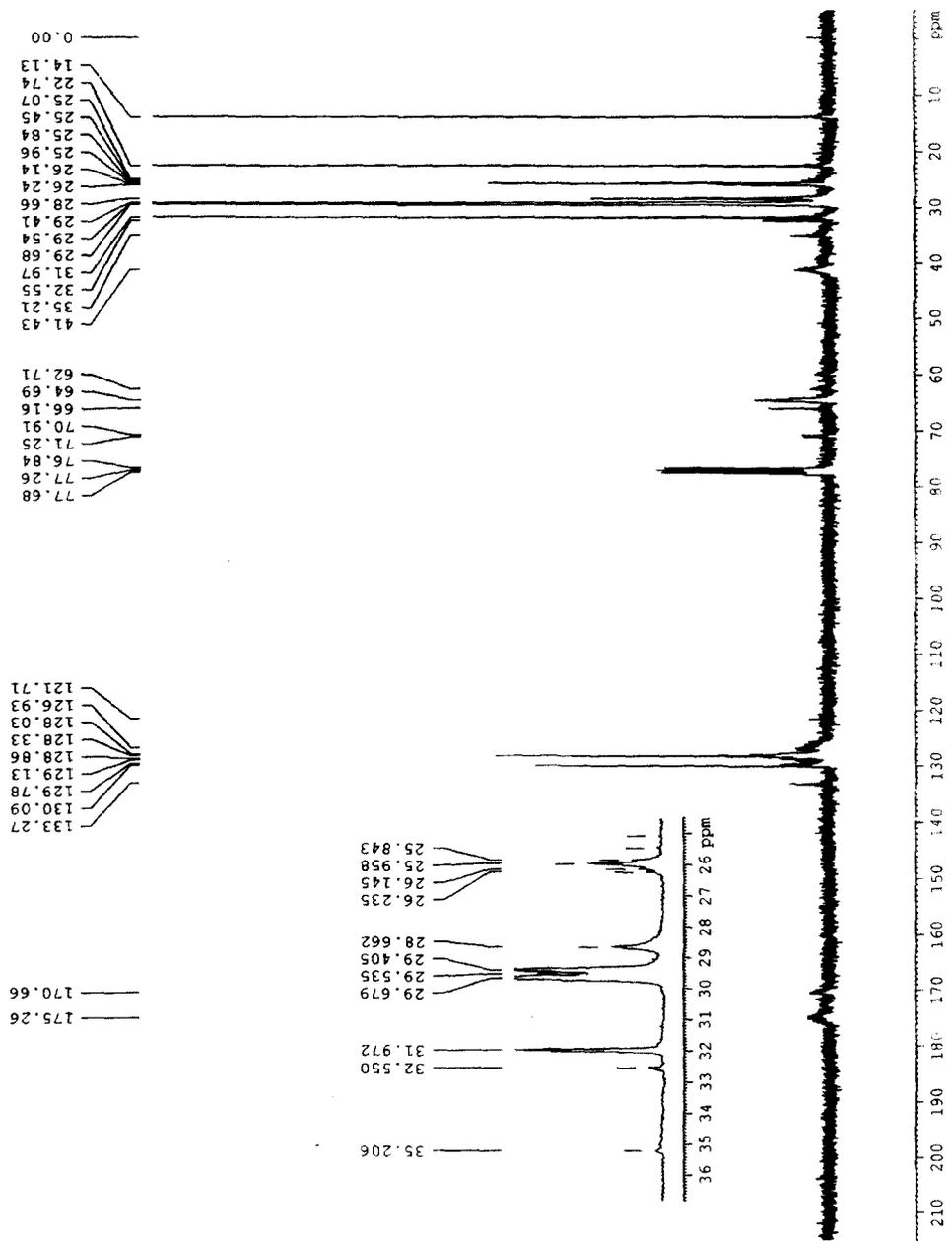


Figure 3. IR Spectrum of copolymer of butyl acrylate with styrene

Figure 4. ^1H NMR of copolymer of decylacrylate with styrene



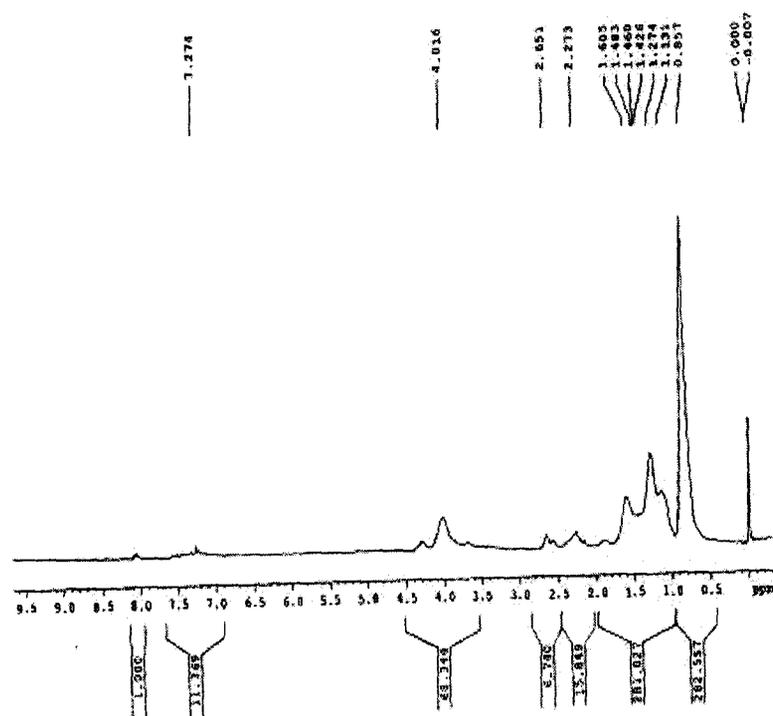


Figure 7. ^1H NMR Spectra of poly(isodecyl acrylate)

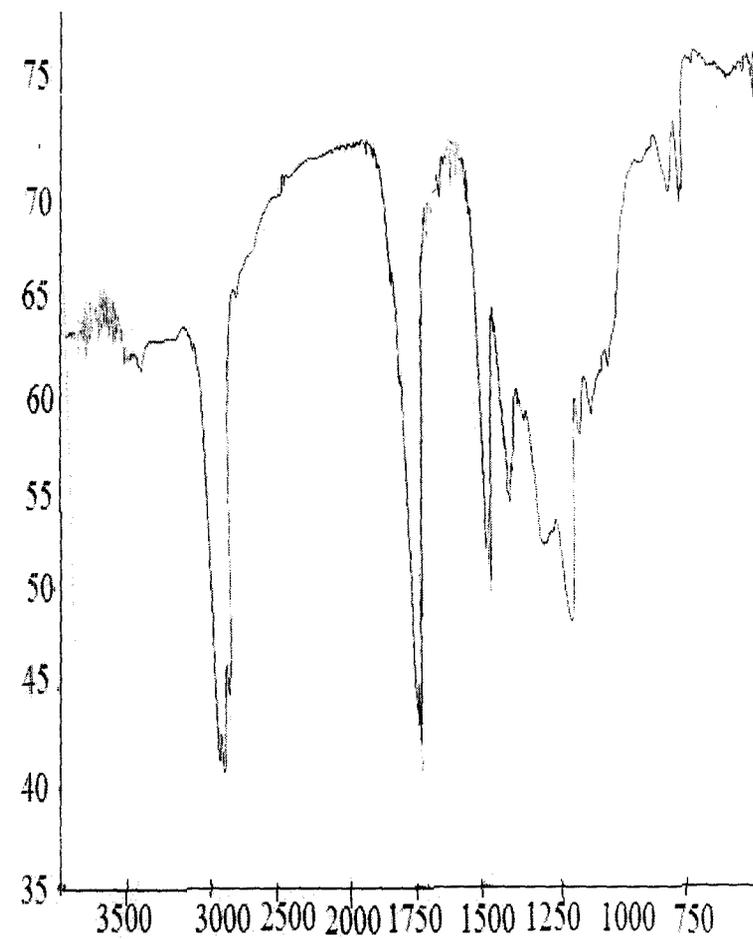
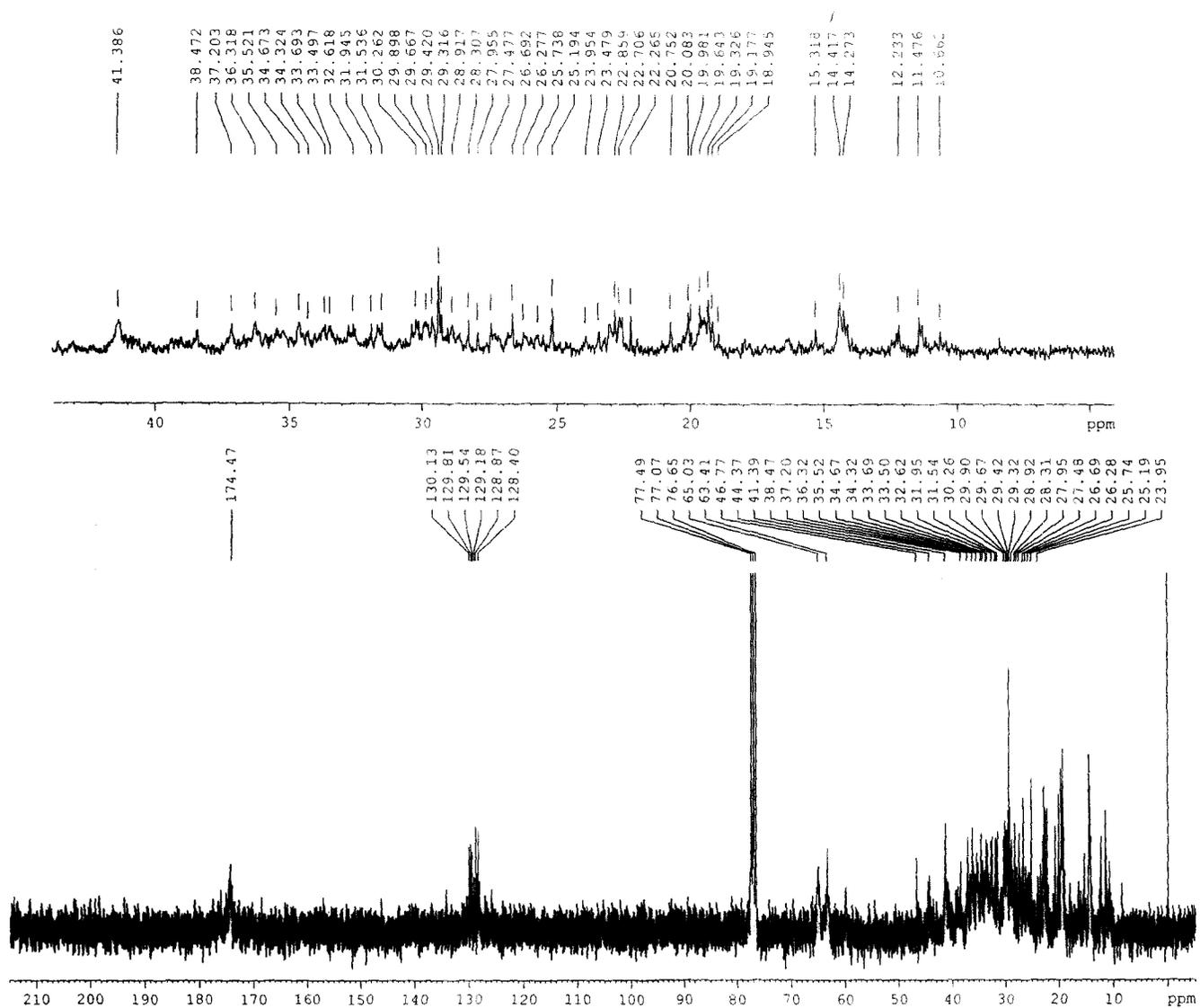


Figure 6. IR Spectra of poly(isodecyl acrylate) cm^{-1}



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 PROCNO 1

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 TD 65536
 SOLVENT CDC13
 NS 997
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 26008
 DW 27.800 usec
 DE 6.00 usec
 TE 0.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
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 P1 10.00 usec
 PL1 -1.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.00 dB
 PL12 15.72 dB
 PL13 16.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
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 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure 8. ^{13}C NMR spectra of poly(isodecylacrylate)

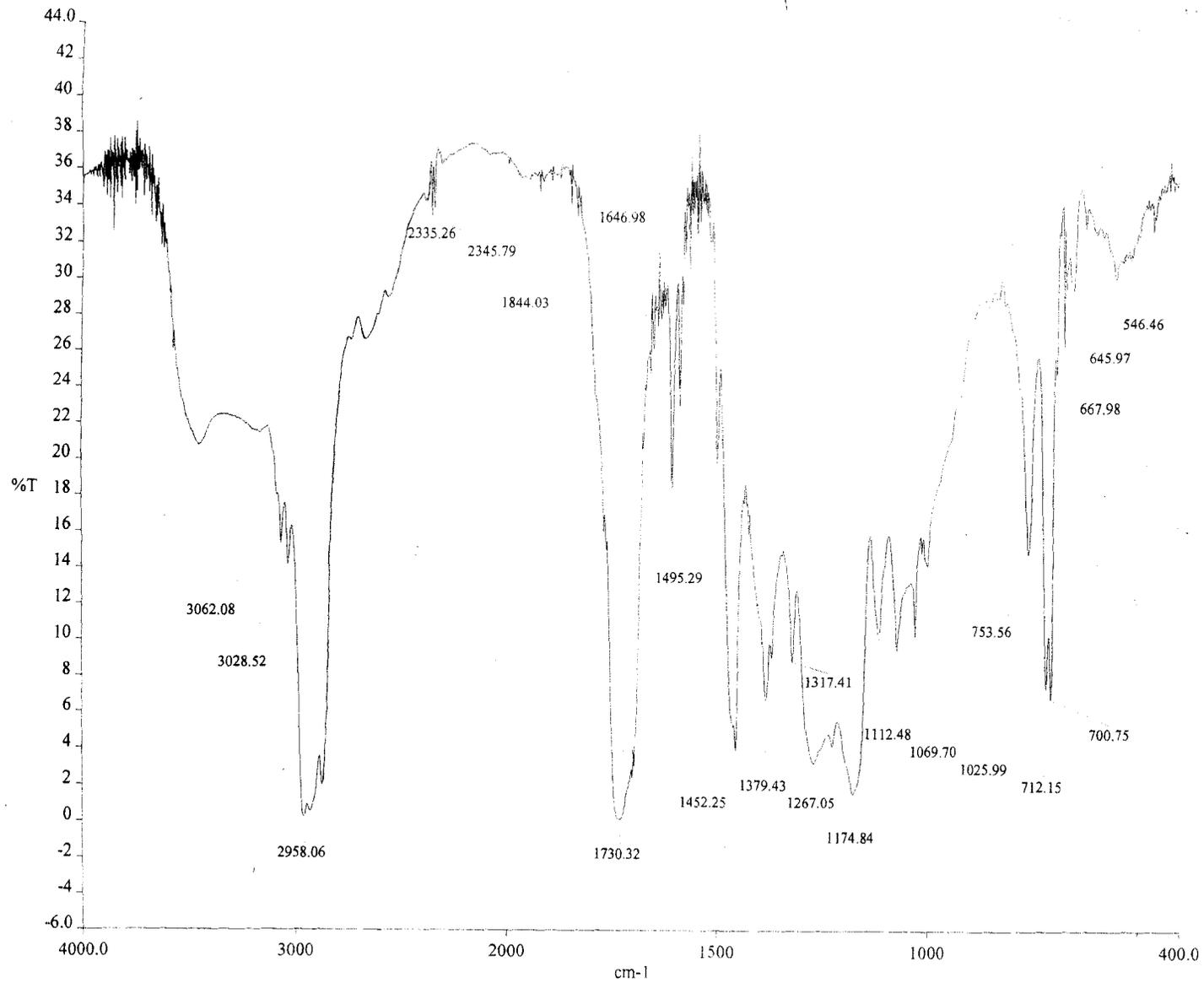


Figure 9. IR spectra of copolymer of isodecylacrylate + styrene

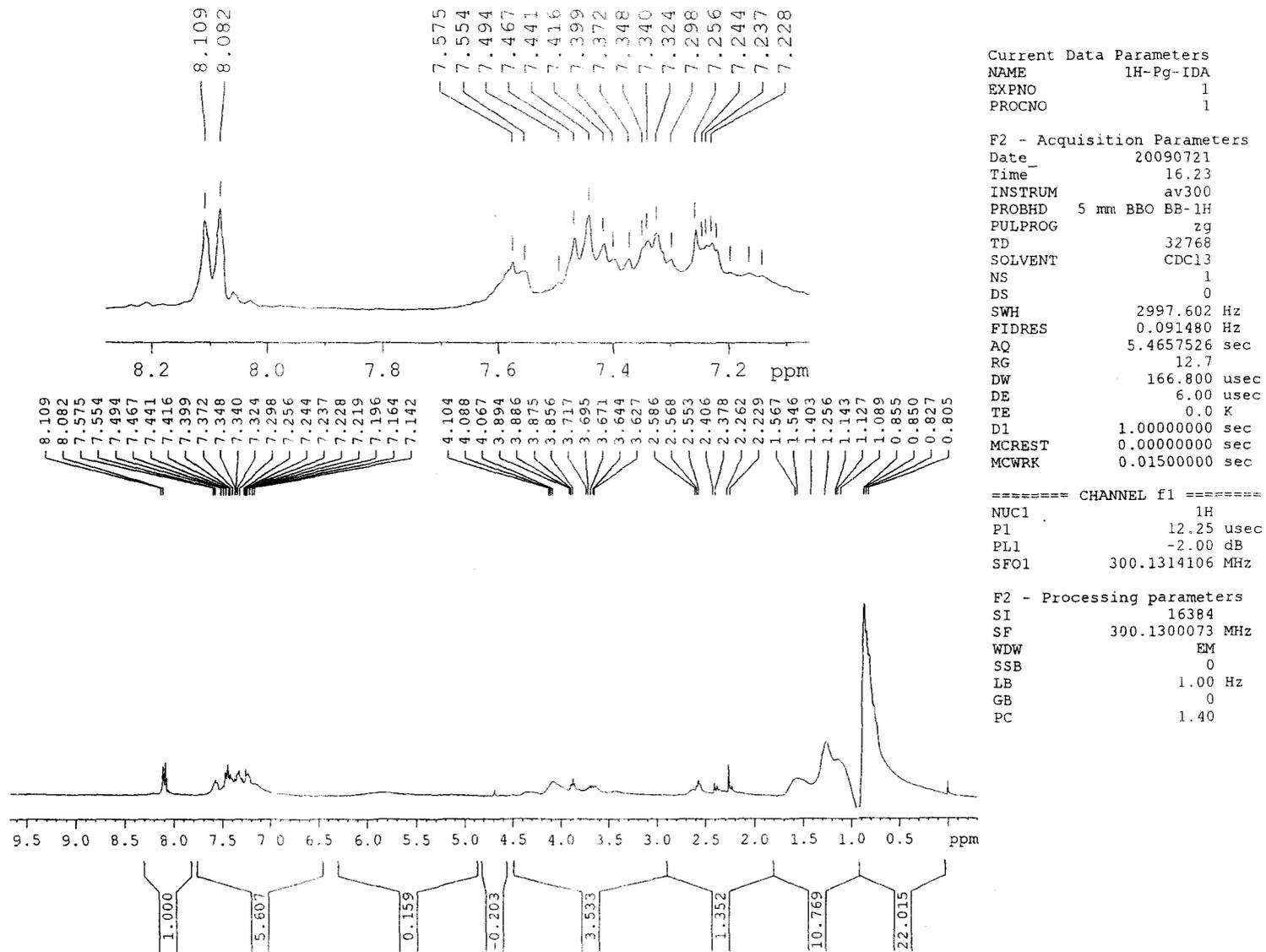
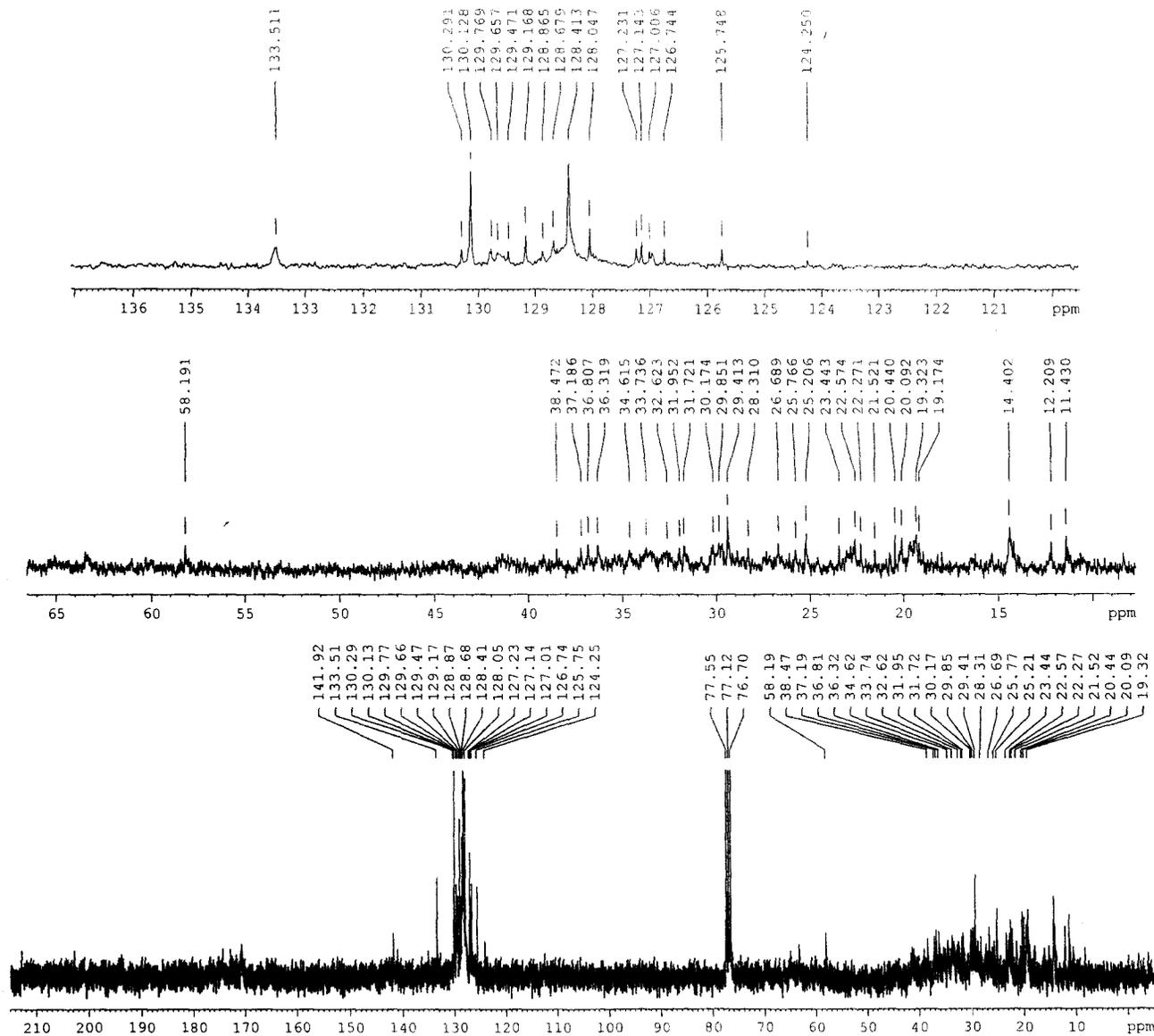


Figure 10. ^1H NMR spectra of copolymer of isodecylacrylate + styrene



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PROCNO 1

F2 - Acquisition Parameters

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FIDRES 0.274439 Hz
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RG 26008
DW 27.800 usec
DE 6.00 usec
TE 0.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

==== CHANNEL f1 =====
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P1 10.00 usec
PL1 -1.00 dB
SFO1 75.4752953 MHz

==== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 0.00 dB
PL12 15.72 dB
PL13 16.00 dB
SFO2 300.1312005 MHz

F2 - Processing parameters
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure 11. ^{13}C NMR spectra of copolymer of isodecylacrylate + styrene

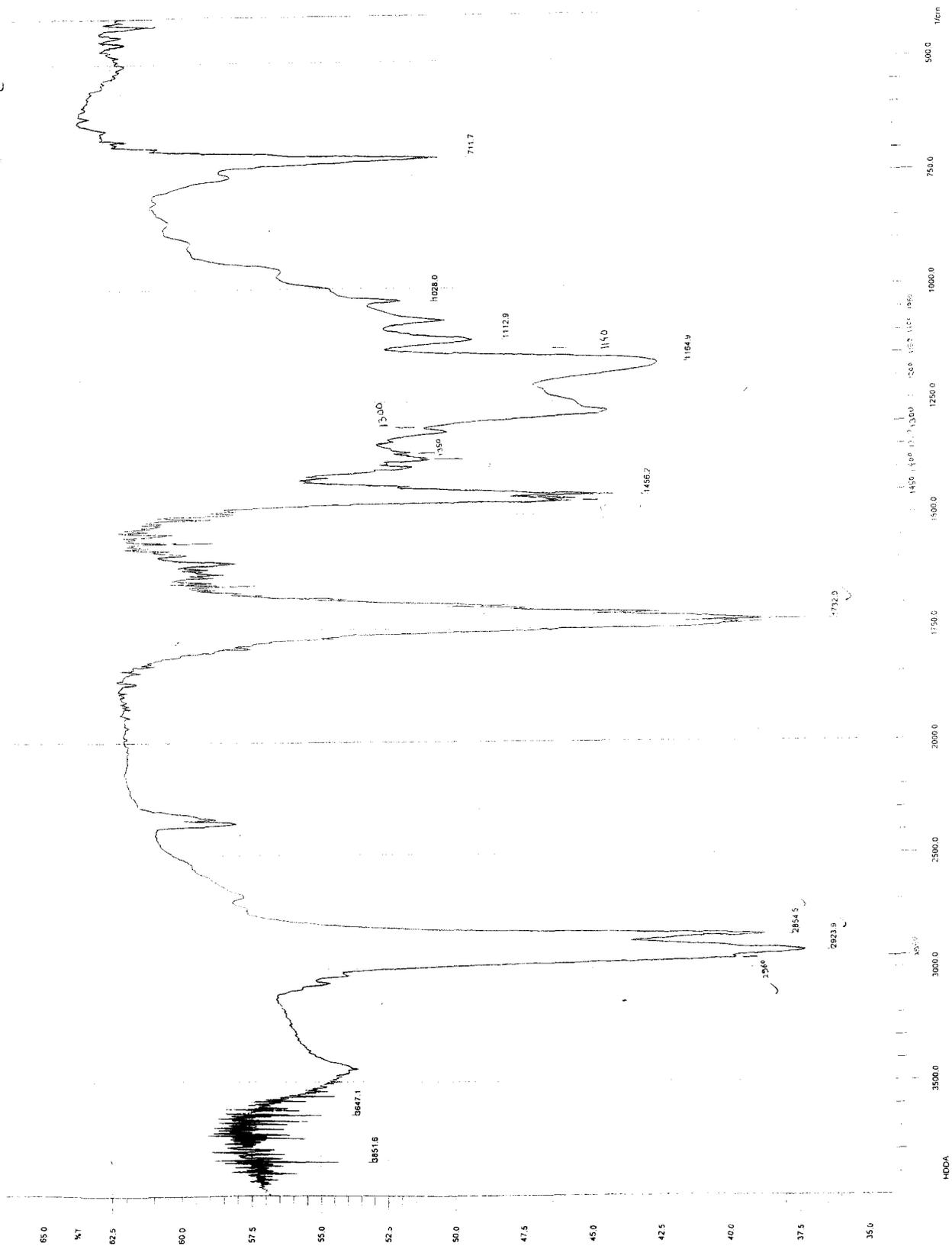


Figure 12. IR spectra of poly(dodecylacrylate)

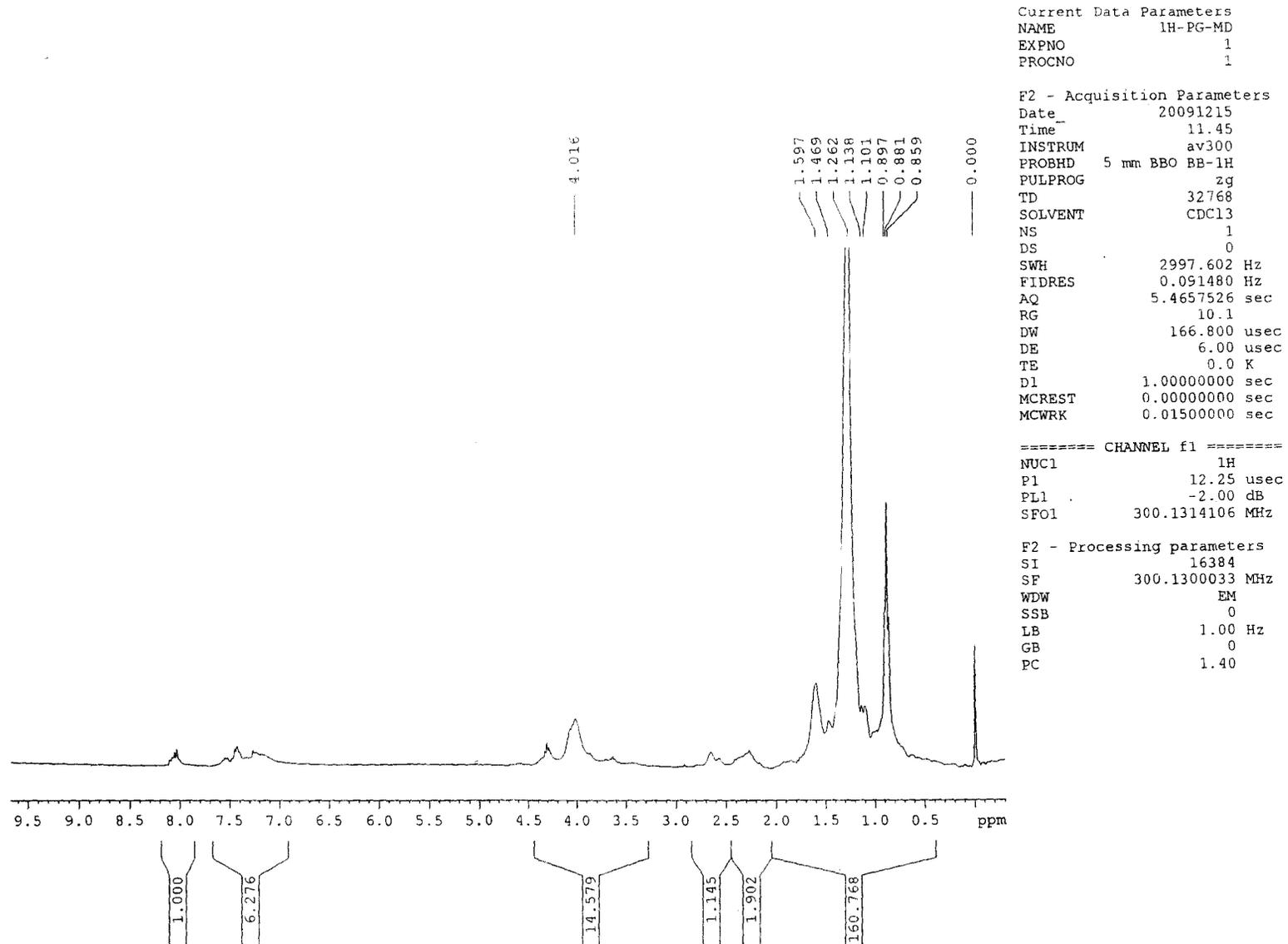


Figure 13. ^1H NMR spectra of poly(dodecylacrylate)

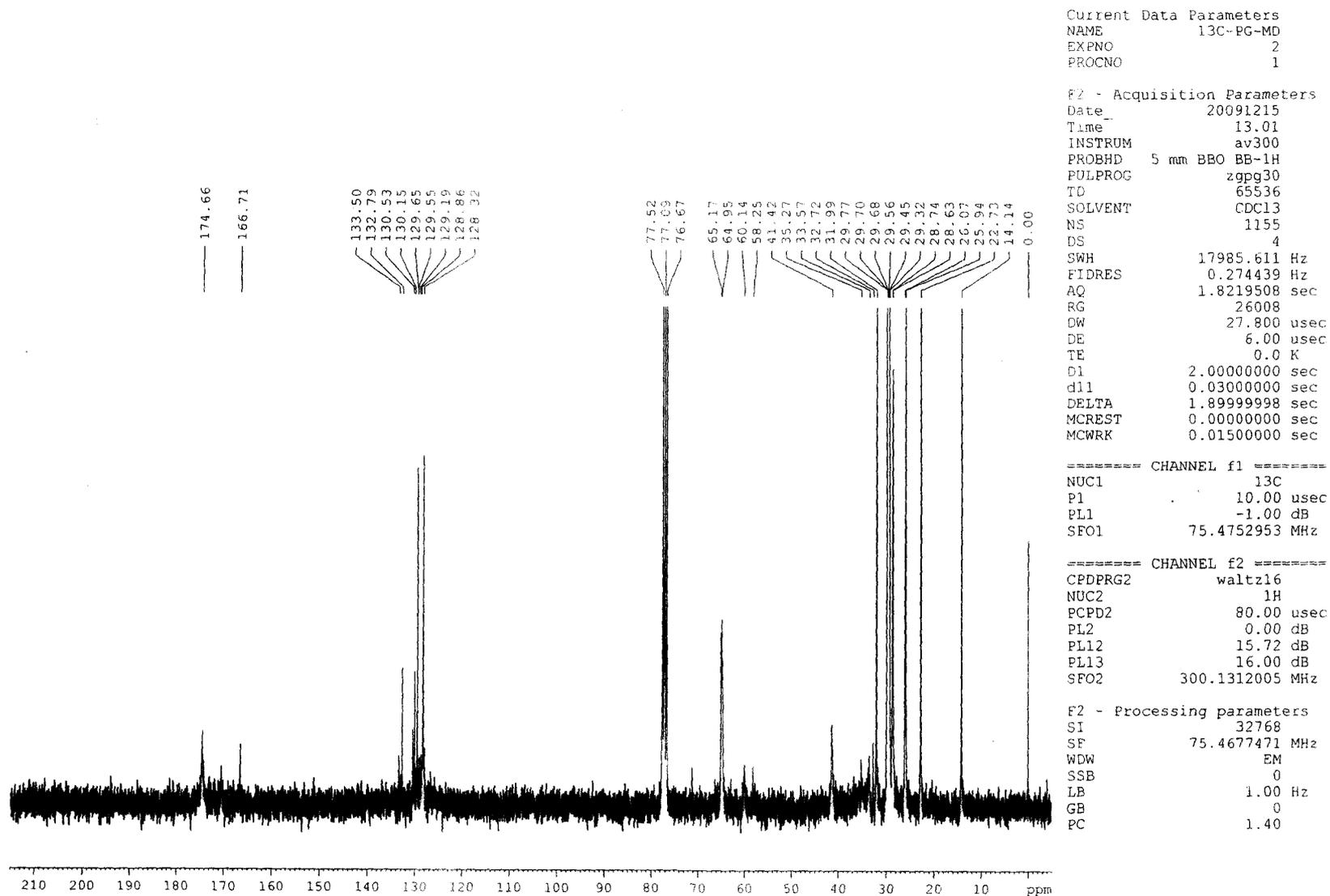


Figure 14. ^{13}C NMR spectra of poly(dodecylacrylate)

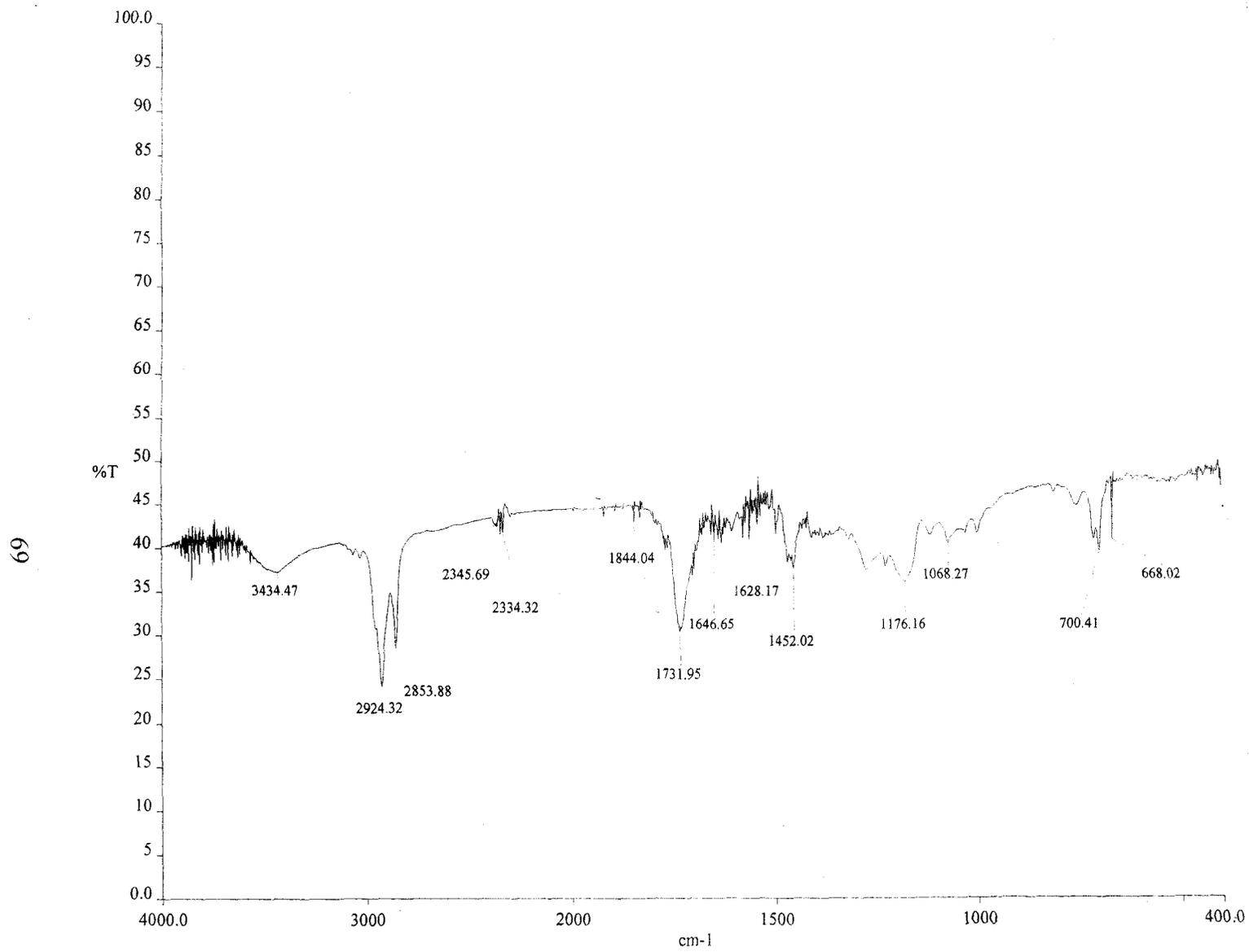


Figure 15. IR spectra of copolymer of dodecylacrylate + styrene

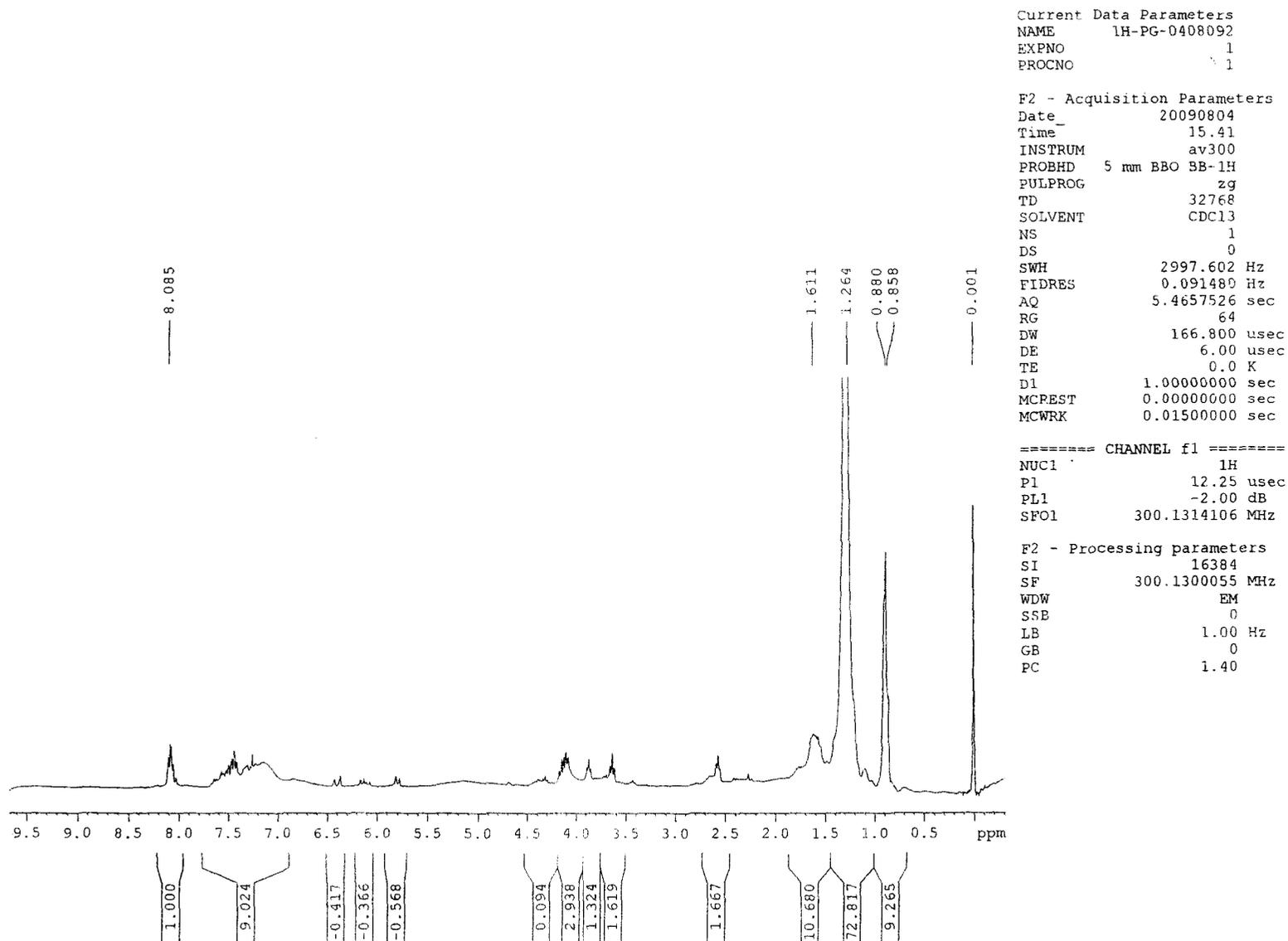
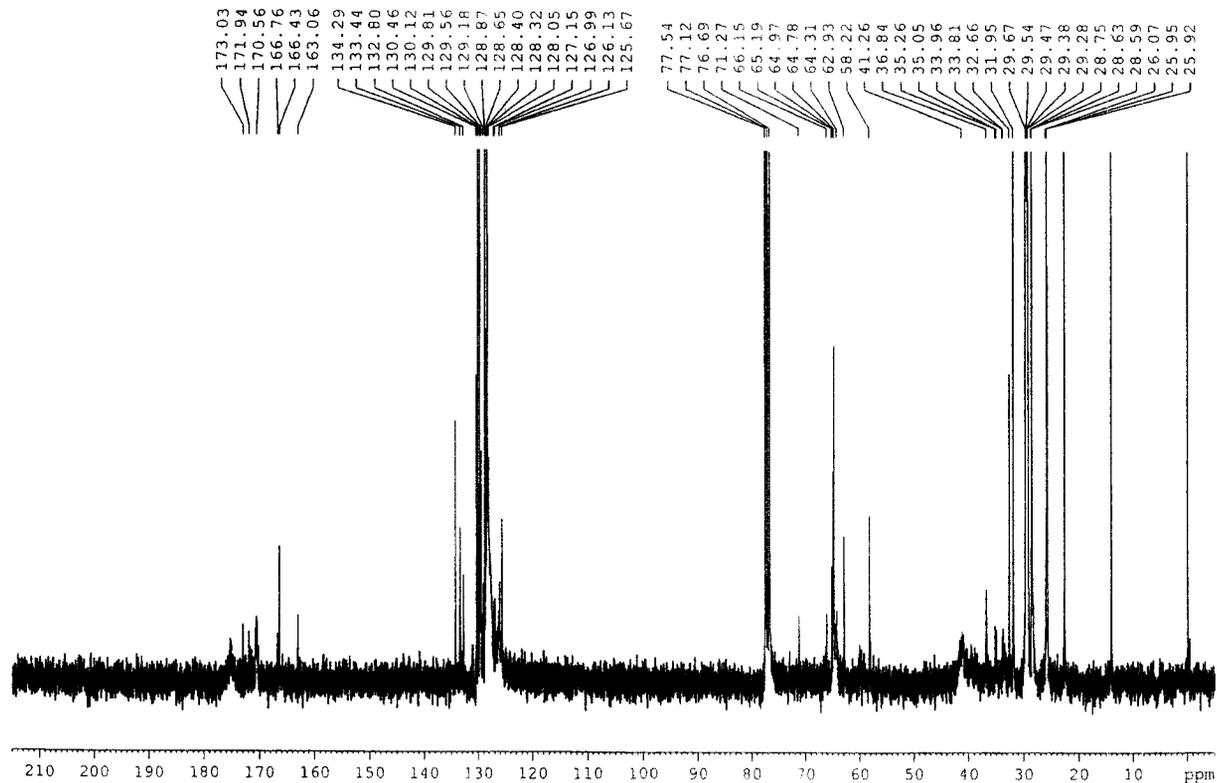


Figure 16. ^1H NMR spectra of copolymer of dodecylacrylate + styrene



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 PROCNO 1

F2 - Acquisition Parameters
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 SOLVENT CDC13
 NS 1322
 DS 4
 SWH 17985.611 Hz
 FIDRES 0.274439 Hz
 AQ 1.8219508 sec
 RG 26008
 DW 27.800 usec
 DE 6.00 usec
 TE 0.0 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 MCREST 0.00000000 sec
 MCWRK 0.01500000 sec

===== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -1.00 dB
 SFO1 75.4752953 MHz

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.00 dB
 PL12 15.72 dB
 PL13 16.00 dB
 SFO2 300.1312005 MHz

F2 - Processing parameters
 SI 32768
 SF 75.4677472 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

Figure 17. ^{13}C NMR spectra of copolymer of dodecylacrylate + styrene

Except copolymer of decyl acrylate (P-2 to P-4), comparison among the copolymers of PIDA- Styrene and PDDA- styrene indicated that although there is a sudden drop in the $[\eta]$ values at a 5% styrene concentration but beyond that a gradual increase of $[\eta]$ values with the increase of styrene content in the monomer composition is observed. This may be because of the flexibility of the respective homopolymer chain by the incorporation of styrene in the copolymer. However, beyond the concentration of 5% of styrene the hydrodynamic volume exceeds that of PIDA and PDDA and thus the gradual increase of $[\eta]$ values is observed [19, 20]. The abnormalities as are observed with PDA styrene system may be because of the fact that increase in styrene concentration in the feed of PDA- Sty composition does not have contribution towards the $[\eta]$ value of the copolymer. This may be because of the loss of flexibility of the polymer chain with incorporation of the styrene in PDA.

Although different intrinsic viscosity values may be found by graphic extrapolation of Huggins, Kraemer, Martin and SB equation (eq 2 to 5), but in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. Values obtained by single point determination method were higher than the values obtained by graphic extrapolation method as was observed earlier [19].

Both homopolymer and copolymers in toluene medium indicating poor solvations (Table 4) as is evident from the respective viscometric constant values, and thus points towards the formation of micelle or spherical structures as discussed earlier [19]. However, it is interesting to notice that for all the polymers in toluene, k_{sb} values were not close to 0.28 except few cases and $k_h + k_k$ values were not found to close to 0.5 in most of the cases. But negative value of Kraemers coefficient for all copolymeric sample did not put any restriction to explain better solubility of copolymer in toluene.

Table 5 presents the percentual differences ($\Delta \% = 100 ([\eta]/ [\eta]_h) - 100$) of intrinsic viscosity $[\eta]$ values of homopolymers and the copolymers determined through graphic extrapolation using Kraemer, Martin and SB equations with respect to Huggins equation. It can be noticed that the range was narrow when compared to the values obtained through a single point using SB, SC and DC equation. Again, the percentage differences in case of polymers of dodecyl acrylate are higher than those of polymers of isodecyl acrylate both in graphic extrapolation and single point determination method (except P-3 and P-7).

Table 6 presents the percentual difference ($\Delta \% = [100(M/M_h)] - 100$), obtained for viscometric molecular weight values. These values were calculated considering Huggins equation as a reference. Martin equation showed the smallest Δ differences except P-1.

Viscometric molecular weight (M_v) obtained by using Mark - Houwink equation, is presented in Table 7. As was reflected in the respective $[\eta]$ values, the homopolymer showed higher Viscometric Molecular weight (M_v) compared to the copolymers.

Performance of the polymeric samples as pour point depressant (PPD)

Pour point of the different levels of additive doped lube oils were tested and tabulated in Tables 8. It indicated that the prepared copolymer samples are more efficient as pour point depressant than the homopolymer and the efficiency increases with the increase in concentration of additive up to a certain limit.

The greater hydrodynamic volume of the copolymer may restrict the formation of wax deposition network in the base oil, which is responsible for their poor flow ability at a lower temperature [21].

This is further supported by the intrinsic viscosity $[\eta]$ and viscometric molecular weight (M_v) values obtained by viscometric analysis with the copolymer and homopolymer samples. Both the parameters showed lesser values in case of copolymer than that of the homopolymer. Since the structure and morphology of the polymer chain plays a significant role for an additive to act as an effective PPD [17], incorporation of aromatic ring in the acrylate chain may be responsible for this encouraging PPD performance of the copolymer. The greater hydrodynamic volume, not only made the polymer less compatible with the solvent (less $[\eta]$ values) but at the same time prevents the formation of wax crystal network, which is responsible for reducing flow ability of the base oils.

2.1.3 Conclusion

Incorporation of styrene in the acrylate back-bone raises the thermal stability of the copolymer and extent of styrene incorporation directly proportional to the thermal stability of the copolymer.

Intrinsic viscosity values of the copolymer are less than the corresponding homopolymer and the values obtained by single point determination method are higher than the values obtained by graphical extrapolation method.

Viscometric molecular weight of the copolymer is less than the homopolymer of acrylate.

Pour point depressant (PPD) performance of the copolymer is always better than the homopolymer in the entire base oils studied. Increase in styrene concentration in the copolymer (up to a certain limit) induces better PPD performance into the additive.

Table 1: Composition of the monomers in the copolymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. P-1 is homopolymer of decyl acrylate (DA); P-2 to P-4 is the copolymer of DA+ different mass fractions of styrene ; P-5 is homopolymer of isodecyl acrylate (IDA); P-6 to P-8 is the copolymer of IDA+ different mass fractions of styrene; P-9 is homopolymer of dodecyl acrylate (DDA); P-10 to P-12 is the copolymer of DDA+ different mass fractions of styrene ;

Sample No	% of weight in the feed		% of weight in copolymer	
	DA	Styrene	By PMR method	By FT-IR
P-1	1	-	-	-
P-2	0.975	0.025	0.01	0.015
P-3	0.95	0.05	0.02	0.023
P-4	0.925	0.075	0.035	0.037
P-5	1	-	-	-
P-6	0.975	0.025	0.01	0.015
P-7	0.95	0.05	0.02	0.023
P-8	0.925	0.075	0.035	0.037
P-9	1	-	-	-
P-10	0.975	0.025	0.01	0.015
P-11	0.95	0.05	0.02	0.023
P-12	0.925	0.075	0.035	0.037

Table 2: Thermal Gravimetric Analysis Data of all prepared samples

Sample	Decomp.Temp.	PWL
P-1	250/340	23/86
P-2	300/400	45/84
P-3	320/430	60/85
P-4	320/440	62/85
P-5	180/300	15/86
P-6	200/340	25/80
P-7	230/400	29/90
P-8	240/410	32/92
P-9	230/330	32/91
P-10	230/340	30/70
P-11	230/380	15/60
P-12	240/400	15/60

Table 3: Intrinsic viscosity values of all prepared samples calculated by using different equation (eq 2 to eq 7) a- extrapolation of graph, b- single point determination

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1	4.335	5.004	4.180	5.368	6.490	6.697	7.340
P-2	2.677	3.538	3.375	3.760	4.106	4.105	4.350
P-3	2.445	3.248	3.087	3.430	3.768	3.758	3.963
P-4	2.401	3.225	3.001	3.38	3.634	3.619	3.8
P-5	3.774	3.845	3.881	3.945	4.02	3.983	4.119
P-6	2.737	2.876	2.846	2.930	3.074	3.046	3.110
P-7	2.877	3.167	3.099	3.229	3.505	3.474	3.573
P-8	3.004	3.287	3.222	3.378	3.561	3.529	3.623
P-9	4.059	4.361	4.336	4.512	4.637	4.599	4.773
P-10	2.621	2.752	2.724	2.772	2.882	2.857	2.933
P-11	3.211	3.522	3.452	3.626	3.784	3.750	3.876
P-12	3.424	3.859	3.766	4.016	4.128	4.091	4.230

Table 4. Viscometric constants obtained for all prepared homo and copolymer samples. k_h , k_k , k_m and k_{sb} Huggins, Kraemer, Martin and Schulz- Blaschke coefficients respectively

Sample	k_h	k_k	k_m	k_{sb}	k_h+k_k
P-1	1.572	-0.134	2.079	0.462	1.438
P-2	1.167	-0.045	2.078	0.371	1.122
P-3	2.183	-0.084	-4.084	0.452	2.099
P-4	2.085	-0.076	-3.085	0.450	2.009
P-5	0.475	0.107	0.359	0.294	0.582
P-6	0.850	-0.044	0.604	0.462	0.806
P-7	1.140	-0.089	0.694	0.501	1.051
P-8	1.103	-0.084	0.683	0.480	1.019
P-9	0.76	0.044	0.478	0.347	0.804
P-10	0.802	-0.017	0.572	0.465	0.785
P-11	1.057	-0.057	0.649	0.453	1.000
P-12	1.194	-0.065	0.670	0.441	1.129

Table 5. Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values, Huggins equation taken as a reference. a- data from extrapolation; b – data from single point determination

Sample	K ^a	M ^a	SB ^a	SB ^b	SC ^b	DC ^b
P-1	15.432	-3.575	23.829	49.711	54.486	69.319
P-2	32.162	26.074	40.455	53.380	53.343	62.495
P-3	32.842	26.257	40.286	54.110	53.370	62.085
P-4	34.319	34.989	40.774	51.135	50.728	58.267
P-5	1.881	2.835	4.531	6.518	5.538	9.141
P-6	5.079	3.982	7.052	12.313	11.290	13.628
P-7	10.080	7.716	12.235	21.828	20.751	24.192
P-8	9.421	7.257	12.450	18.542	17.477	20.606
P-9	7.440	6.824	11.160	14.240	13.304	17.591
P-10	5.074	3.930	5.761	9.958	9.004	11.904
P-11	9.685	7.505	12.924	17.845	16.786	20.710
P-12	12.704	9.988	17.290	20.561	19.480	23.540

Table 6. Determination of molecular weight by Mark - Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl.g}^{-1}$ and $a = 0.725$

Sample	M _h ^a	M _k ^a	M _m ^a	M _{sb} ^a	M _{sb} ^b	M _{sc} ^b	M _{dc} ^b
P-1	16051	19563	15264	21554	28004	29244	33186
P-2	8255	12128	11364	13190	14893	14888	16127
P-3	7285	10778	10048	11623	13229	13180	14182
P-4	7105	10673	9664	11387	12584	12513	13384
P-5	13,270	13,616	13,792	14,107	14,478	14,295	14,972
P-6	8,520	9,122	8,991	9,359	10,000	9,874	10,162
P-7	9,127	10,419	10,112	10,702	11,984	11,838	12,306
P-8	9,687	10,968	10,670	11,389	12,249	12,097	12,544
P-9	14,672	16,199	16,071	16,977	17,630	17,431	18,347
P-10	8,026	8,593	8,464	8,671	9,149	9,039	9,373
P-11	10,620	12,064	11,734	12,558	13,319	13,154	13,768
P-12	11,603	13,684	13,232	14,458	15,017	14,473	15,531

Table 7. Percentual differences obtained for viscometric molecular weight values ($\Delta \% = [100(M/M_h)] - 100$)

Sample	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	21.880	-4.903	34.284	74.468	82.194	106.75
P-2	46.917	37.662	59.782	80.411	80.351	95.360
P-3	47.948	37.927	59.547	81.592	80.114	94.674
P-4	50.218	36.016	60.267	77.114	76.115	88.374
P-5	2.607	3.934	6.307	9.103	7.724	12.826
P-6	7.066	5.528	9.847	17.371	15.892	19.272
P-7	14.156	10.792	17.256	31.303	29.703	34.831
P-8	13.224	10.148	17.570	26.448	24.879	29.493
P-9	10.408	9.535	15.710	20.161	18.805	25.048
P-10	7.065	5.457	8.036	13.992	12.621	16.783
P-11	13.597	10.490	18.249	25.414	23.861	29.642
P-12	17.935	14.039	24.606	29.423	24.735	33.853

Table 8. Pour point of additive doped base oils

Sample	Base oils		Pour point of Base oil	Pour point of additive doped Base oil		
				2.5%	5%	10%
P-1	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-12
	BO2	S1	-6	-9	-9	-12
		S2	-6	-9	-9	-12
P-2	BO1	S1	-3	-12	-15	-15
		S2	-3	-12	-15	-15
	BO2	S1	-6	-15	-21	-24
		S2	-6	-15	-24	-21
P-3	BO1	S1	-3	-12	-21	-21
		S2	-3	-15	-21	-24
	BO2	S1	-6	-12	-21	-21
		S2	-6	-15	-21	-24
P-4	BO1	S1	-3	-15	-24	-24
		S2	-3	-15	-21	-24
	BO2	S1	-6	-15	-24	-24
		S2	-6	-15	-21	-24

P-5	BO1	S1	-3	-6	-6	-9
		S2	-3	-6	-9	-9
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-12
P-6	BO1	S1	-3	-9	-9	-6
		S2	-3	-9	-9	-12
	BO2	S1	-6	-12	-12	-9
		S2	-6	-9	-12	-12
P-7	BO1	S1	-3	-9	-12	-15
		S2	-3	-9	-15	-18
	BO2	S1	-6	-12	-15	-21
		S2	-6	-15	-15	-15
P-8	BO1	S1	-3	-12	-15	-15
		S2	-3	-15	-12	-12
	BO2	S1	-6	-15	-15	-18
		S2	-6	-15	-18	-24
P-9	BO1	S1	-3	-6	-12	-15
		S2	-3	-9	-12	-15
	BO2	S1	-6	-12	-12	-12
		S2	-6	-12	-15	-18
P-10	BO1	S1	-3	-9	-15	-18
		S2	-3	-12	-15	-21
	BO2	S1	-6	-12	-15	-15
		S2	-6	-15	-18	-21
P-11	BO1	S1	-3	-9	-12	-18
		S2	-3	-12	-12	-15
	BO2	S1	-6	-15	-15	-18
		S2	-6	-12	-15	-21
P-12	BO1	S1	-3	-9	-12	-15
		S2	-3	-12	-15	-18
	BO2	S1	-6	-12	-15	-18
		S2	-6	-12	-18	-21

2.2 SECTION B: Evaluation of Poly(acrylates) and their Copolymer as Viscosity Modifiers

2.2.1 Introduction

The development of modern engine and transmission technologies would be impossible without lubricant additives. From its conception in the early 1900s, the lubricant additive industry has worked in partnership with the oil and the automotive industries to enhance durability and performance of engine and drive line systems through lubricant design [22]. Additives are synthetic chemicals that can improve or add performances of lubricants. Some additives impart new and useful properties to the lubricant; some enhance properties already present, while some act to reduce the rate at which undesirable changes take place in the product during its service life. One of the important types of additive is viscosity index improvers commonly known as viscosity modifier [23].

The viscosity index is an indicator of the change in viscosity as the temperature is changed. The higher the viscosity index (VI), the lesser the viscosity of an oil changes for a given temperature change. Viscosity index improvers are used to limit the rate of change of viscosity with temperature. These improvers have little effect on oil viscosity at low temperatures. However, when heated the improvers enable the oil viscosity to increase within the limited range permitted by the type and concentration of the additive. This quality is most apparent in the application of multigrade motor oils.

Viscosity index improvers function by increasing the relative viscosity of oil more at high temperatures than at low temperatures [3-5]. Generally this results from the polymer changing its physical configuration with increasing temperature of the mixture. It is believed that the polymer molecule in solution exists as a random coil, which is swollen by the lube oil solvent. The volume of this molecule determines the viscosity increase. In cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules, having greater volume and the oil produces a proportionally greater thickening effect which in turn raises the VI of the oil.

An ideal lubricant for most purposes would possess the same viscosity at all temperatures [8]. Viscosity index improvers (VII) are added to lubricating oils to make them conform more closely to the ideal lubricant. Although a few non-polymeric substances such as metallic soaps exhibit VI improving properties [9], all commercially important VI improvers today are oil-soluble organic polymers. Suitable polymers exert a greater thickening effect (percent increase in viscosity of the base oil for unit weight of polymer) on oil at higher temperatures than they do at lower temperatures [10] and thus improve the VI of lube oil.

Considering the above discussion and the past literature reports (as elaborated in Chapter I of this Part), present investigation comprises the synthesis, characterization and evaluation of poly(decyl acrylate), poly(dodecyl acrylate), poly(isodecyl acrylate) and their copolymer with styrene as a potential viscosity index improver (VII) for lube oil.

2.2.2 Result and Discussion

The prepared polymers were tested for their effectiveness as viscosity index improvers for base oil (BO1 and BO2) according to ASTM D-2270. In this respect, the kinematic viscosity of the oil doped with different concentrations of the tested additives was determined at 313 K and 373 K. The concentrations were ranging from 1% to 6% (w/w), which is used to study the effect of the additives concentration on VI of lube oils.

It is clear from the VI data tabulated in Table 2 to Table 13 and also from Figure 1 and Figure 2, as evaluated in present investigation indicated that irrespective of the polymer (homo and copolymer) and nature of the base oil VI values increases with the increase in additive concentration in the base oils studied. A critical observation of the VI values of the homopolymers indicated that better performance is obtained with the acrylate having greater chain length of the alcohols in the acrylate monomer. It is also observed that branching in the carbon chain of the alcohol deteriorates its performance when used as a VII in the lube oil. Thus, the chain length and its arrangements play a significant role when added in the lube oil to act as a VII.

As the temperature is raised, the lube oil viscosity decreases; meanwhile the polymer molecule expands due to the increase in the solvation power and the increased size of the micelle. This increase in micelle size counterbalances the reduction of the viscosity of the

lube oil and, hence, decreases the changes of viscosity with temperature of the mixture [24-26]. The increase in concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution and thus exerting greater thickening effect and so as to VII.

2.2.3 Conclusion

Irrespective of the polymers (homo and copolymer) and nature of the base oils, VI values increases with the increase in additive concentration in the base oils studied.

VI values of the homopolymers indicated that better performance is obtained with the acrylate having greater chain length of the alcohols in the acrylate monomer. Again, branching in the carbon chain of the alcohol, deteriorates the performance of the acrylate when used as a VI improver in the lube oil. Thus, the chain length and its arrangements in the polymer of a viscosity modifier play a significant role when added in the lube oil to act as a VI improver.

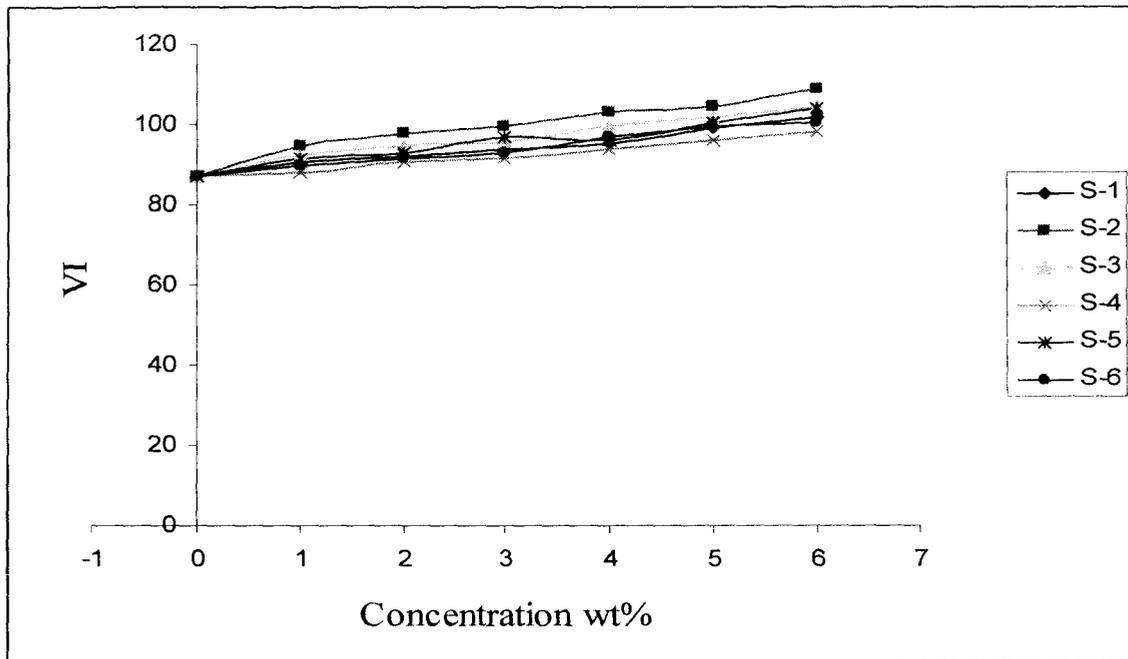


Figure 1. Plot of Viscosity Index (VI) vs polymer concentration in BO1 base oil, where S-1 poly(decyl acrylate), S-2 poly(isodecyl acrylate), S-3 poly(dodecyl acrylate).

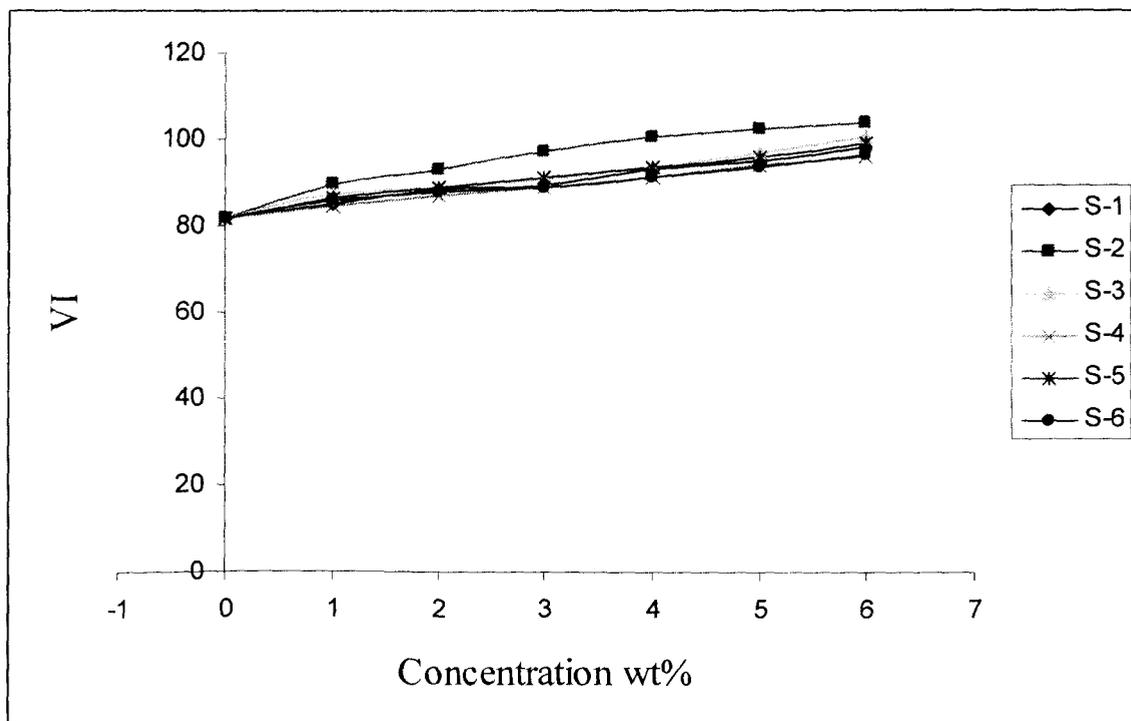


Figure 2. Plot of Viscosity Index (VI) vs polymer concentration in BO2 base oil, where S-1 poly(decyl acrylate), S-2 poly(isodecyl acrylate), S-3 poly(dodecyl acrylate).

Table 1. Base oil properties

Base oil properties	Base oils	
	BO1	BO2
Viscosity at 40 ⁰ C in cSt	7.202	23.609
Viscosity at 100 ⁰ C in cSt	1.872	3.951
Cloud point, ⁰ C	-8	-10
Pour point, ⁰ C	-3	-6

Table 2. VI values for poly(decyl acrylate) (S-1) in BO1 oil

Solution Conc. Wt %	Kinematic Viscosity at 40 ⁰ C	Kinematic Viscosity at100 ⁰ C	VI
0	7.202	1.872	87.00
1	7.262	1.891	90.48
2	7.298	1.901	91.93
3	7.345	1.914	93.66
4	7.403	1.928	95.08
5	7.440	1.946	98.98
6	7.479	1.962	101.95

Table 3. VI values for poly(decyl acrylate) (S-1) in BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40 ⁰ C	Kinematic Viscosity at100 ⁰ C	VI
0	23.609	3.951	81.68
1	23.982	4.032	85.09
2	24.070	4.080	88.41
3	24.125	4.099	89.30

4	24.232	4.157	92.80
5	24.303	4.189	94.80
6	24.393	4.248	98.15

Table 4. VI values for poly(isodecyl acrylate) (S-2) in BO1 oil

Solution Conc. Wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.302	1.903	92.51
2	7.340	1.915	94.52
3	7.382	1.925	95.36
4	7.424	1.945	99.52
5	7.460	1.959	101.95
6	7.502	1.975	104.58

Table 5. VI values for poly(isodecyl acrylate)(S-2) in BO2 oil

Solution Conc. wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1%	24.026	4.060	87.21
2%	24.083	4.087	88.71
3%	24.156	4.116	90.48
4%	24.248	4.164	93.38
5%	24.335	4.223	96.77
6%	24.402	4.284	100.34

Table 6. VI values for poly(dodecylacrylate)(S-3) in BO1 oil

Solution Conc. Wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.357	1.918	94.52
2	7.422	1.938	97.60
3	7.474	1.953	99.52
4	7.546	1.977	103.00
5	7.603	1.993	104.58
6	7.682	2.022	108.68

Table 7. VI values for poly(dodecyl acrylate)(S-3) in BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
	24.070	4.097	89.59
2	24.147	4.149	93.09
3	24.236	4.217	97.32
4	24.311	4.270	100.34
5	24.371	4.310	102.48
6	24.419	4.338	103.80

Table 8. VI values for copolymer of DA+ styrene (S-4) BO1 oil

Solution Conc. Wt%	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.246	1.882	88.11
2	7.310	1.900	90.77
3	7.385	1.914	91.35
4	7.451	1.932	93.66
5	7.529	1.952	95.93
6	7.610	1.972	98.15

Table 9. VI values for copolymer of DA+ styrene (S-4) BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.899	4.017	84.78
2	23.986	4.054	86.91
3	24.092	4.092	89.00
4	24.159	4.125	91.06
5	24.267	4.174	93.95
6	24.357	4.214	95.93

Table 10. VI values for copolymer of IDA+ styrene (S-5) in BO1 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.284	1.893	89.89
2	7.334	1.905	91.35
3	7.410	1.923	93.09
4	7.498	1.949	96.77
5	7.606	1.976	99.52
6	7.673	1.991	100.61

Table 11. VI values for copolymer of IDA+ styrene (S-5) BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.949	4.040	86.00
2	24.020	4.067	87.81
3	24.084	4.088	89.00
4	24.158	4.124	91.06
5	24.234	4.166	93.66
6	24.342	4.214	96.21

Table 12. VI values for copolymer of DDA+ styrene(S-6) BO1 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	7.202	1.872	87.00
1	7.339	1.906	91.35
2	7.422	1.925	93.09
3	7.510	1.951	96.77
4	7.608	1.965	95.93
5	7.684	1.992	100.34
6	7.738	2.014	104.06

Table 13. VI values for copolymer of DDA + styrene (S-6) in BO2 oil

Solution Conc. Wt %	Kinematic Viscosity at 40°C	Kinematic Viscosity at 100°C	VI
0	23.609	3.951	81.68
1	23.987	4.050	86.61
2	24.080	4.087	88.71
3	24.171	4.128	91.35
4	24.250	4.165	93.38
5	24.364	4.215	95.93
6	24.478	4.275	99.25

2.3 SECTION C: Comparison of Viscometric Parameters of the Homo and Copolymer of Poly(decyl acrylate) in Lubricating Oil

2.3.1 Introduction

Lubricating oil (also known as 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 medium to high values, very low volatility and with high viscosity index. The proportions of different hydrocarbon components determine the characteristics of the base oils.

Properties of such base oils can be improved by the incorporation of suitable performance polymer, generally called additives.

They added to impart specific property to the oil. Some of them impart new and useful properties to the lubricant, and others enhance properties already present [27, 28]. These additives are more active than the base oils. However, some of their properties are very often controlled by the chemical compositions of the base oils whereas some properties are controlled by the structure of the chemical additives designed for that purpose. Thus a comparative study in terms of chemistry of the additive and composition of the base oil is very much pertinent to be included in our investigation.

Recent research [29] towards the understanding of additives performance in base oils indicated that the performance of additives when used in lubricating oil and applied in field conditions are very much dependent on the structure and morphology of the polymer dissolved in it. Therefore, viscometric studies [a brief introduction is given in Part 1, Chapter 1, sec A] with these additives in base oils may give valuable information as far as the base stock employed and morphological feature of the polymer in a dilute solution in the base oils is concerned [30].

Therefore, the study, which is most probably the first report of such an investigation, may be very useful for predicting the performance of the additive in base oils of different compositions.

In the present case we have undertaken poly(decyl acrylate) as the additive and base stocks of two different compositions for the present investigation.

2.3.2 Results and discussion

Viscometric data were obtained using the seven equations as mentioned in Chapter I of Part I. A linear relation for the plot of $\log \eta_{sp}$ vs $\log C[\eta]$ obtained for all samples [Figure 1a & 1b] indicated that measurements were performed in Newtonian flow [31,32]. Huggins (H), Kraemer (K), Martin (M) and Schulz–Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz–Blaschke (SB) equation is commonly applied in single point determinations because it was found that $k_{sb} = 0.28$ for many polymer-solvent systems [33-36]. In this work, this value was used.

Table 1-2 presents intrinsic viscosity $[\eta]$ values of polymer solution in base oils BO1 and BO2 related to all equations for the samples analysed. Considering the oils (BO1 and BO2) and comparing the values of $[\eta]$ for homo and copolymers, it is noticed that the higher values were obtained in BO2 oil compared to BO1 oil. Thus considering all the polymers (homo and copolymers), oil BO2 appeared to be more compatible to the polymer and thus pointing towards providing more extended conformations of the polymers. This fact is further supported by the respective k_h+k_k values, which is well within 0.5 (Table 7). Lower values in BO1 oil in comparison to the BO2 oil, indicating contracted structures with star like conformation for the additives in this oil. Variation of $[\eta]$ obtained by graphic extrapolation method (equation 2-5) was found to be less compared to those obtained by single point determination method (equation 6-7) without any restriction to lubricating oil .

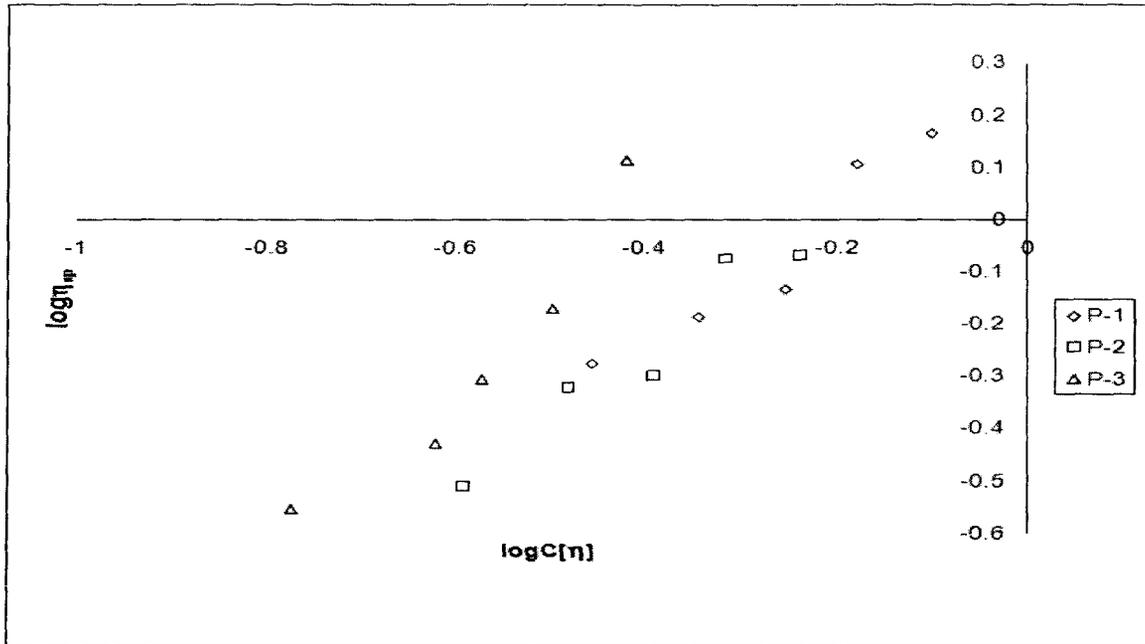


Figure 1a. Plot of $\log \eta_{sp}$ vs $\log C[\eta]$ for BO1.

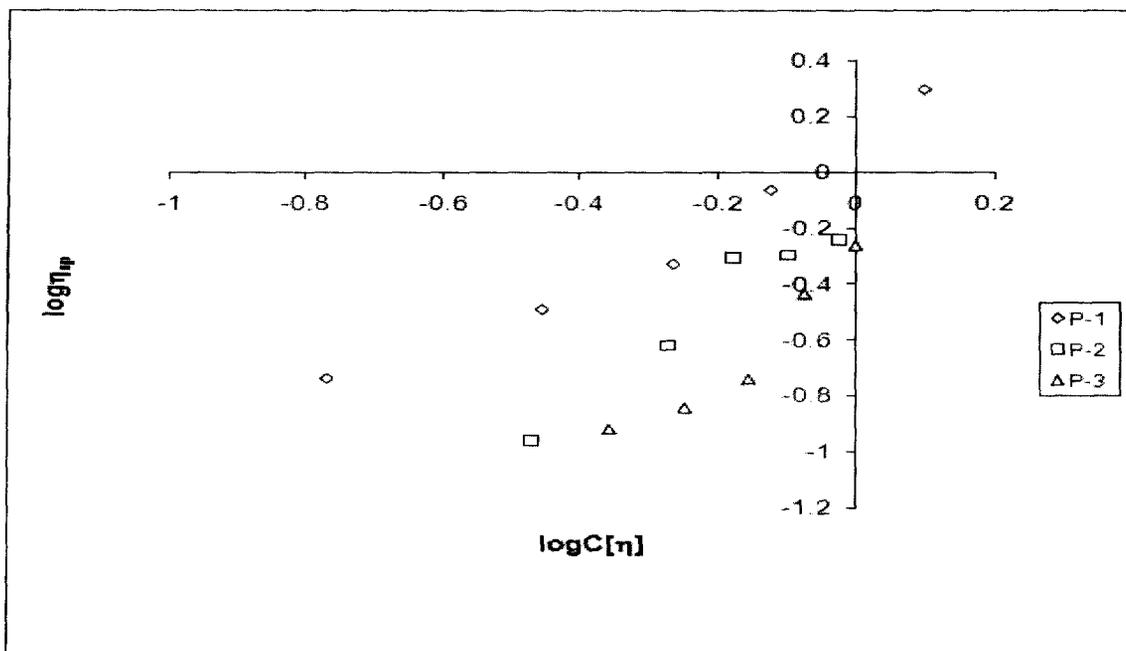


Figure 1b. Plot of $\log \eta_{sp}$ vs $\log C[\eta]$ for BO2.

It is also observed that $[\eta]$ values decrease with the incorporation of styrene, but increases with increases in styrene concentration in case of oil BO2 and decreases in oil BO1. Intrinsic viscosities $[\eta]$ values obtained by using DC equation are always higher irrespective of the nature of the base stock.

It is also observed that there is a drop in intrinsic viscosity values in case of copolymer when added to base oils, particularly in BO1 oil, in comparison to the homopolymer. However, it does not change much with increase in styrene concentration in BO2 oil. Although the change is similar in BO1 oil, but the drop in intrinsic viscosity values of the copolymer is more than what was observed in oil BO2 and the reduction in intrinsic viscosity values gradually increases with the increase in styrene concentration.

Table 3 & 4 presents values of viscometric constants calculated for homo and copolymers in BO1 and BO2 oil respectively, k_h and k_k fitted in the range of good solvents, whereas sample P-3 in BO1 oil indicating more incompatibility. Although k_{sb} values found different from 0.28 in case of BO1 oil, but it has a close tendency to acquire this value (except P-3) in case of oil BO2. It is also important to observe that the relation $k_h+k_k=0.5$ was not found for the great majority of samples analyzed. However, intrinsic viscosities obtained by using single point determination methods were similar to values obtained by using graphic extrapolation method with small percentage differences. So values different from 0.5 did not put any restriction for the application of SC and DC equation.

Table 5 - 6 presents the percentual differences of intrinsic viscosity values where Huggins value taken as references. In both the oils it is observed that that differences is smaller in graphic extrapolation method compared to single point determination method. It is also observed that the differences are smaller in oil BO2 compared to oil BO1.

Table 7 – 8 presents viscometric molecular weight of all the polymers (homo and copolymer). Homopolymer showed higher molecular weight than the copolymer. As expected the molecular weights are greater in oil BO2 compared to oil BO1. Again in oil BO1, a gradual decrease in viscometric molecular weight of the copolymer was observed with increase in styrene concentration although such a variation was not observed in oil BO2.

2.3.3 Conclusions

Viscometric analysis of the polymer may be carried out in lubricating oil to get more information about their morphological structure when added to the oil as a performance additive. Oil compatibility of the additive can be predicted easily through Viscometric analysis. Properties like intrinsic viscosity, viscosity average molecular weight of the polymeric additives are influenced by the compositions of the base oils. This work is probably the first report of viscometric studies of polymeric additives in base oils.

Table 1. Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method. P-1 poly(decyl acrylate), P-2 and P-3 are copolymer of decyl acrylate with different % ratio of styrene.

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{SB}$	$[\eta]^b_{SB}$	$[\eta]^b_{SC}$	$[\eta]^b_{DC}$
P-1	2.691	3.075	2.974	2.931	3.515	3.544	3.649
P-2	1.967	2.036	2.054	1.938	2.162	2.18	2.213
P-3	1.294	1.020	1.118	1.343	1.974	1.99	2.005

Table 2. Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method.

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{SB}$	$[\eta]^b_{SB}$	$[\eta]^b_{SC}$	$[\eta]^b_{DC}$
P-1	4.642	4.303	4.609	4.571	4.718	4.687	4.746
P-2	3.317	3.538	3.602	3.684	3.836	3.832	3.821
P-3	3.501	3.187	3.430	3.555	3.925	3.921	3.917

Table 3. Viscometric constant values in BO1 oil

Sample	k_h	k_k	k_m	k_{sb}	$k_h+k_k=0.5$
P-1	1.08	3.64×10^{-3}	0.692	0.74	1.083
P-2	0.80	-0.186	3.374	1.72	0.614
P-3	0.70	-5.103	0.513	0.524	-4.40

Table 4. Viscometric constant values in BO2 oil

Sample	k_h	k_k	k_m	k_{sb}	$k_h+k_k=0.5$
P-1	0.063	0.245	1.474	0.107	0.308
P-2	0.66	-0.376	-8.89×10^{-3}	0.77	0.284
P-3	0.535	-0.432	1.44	0.705	0.103

Table 5. Percentual differences ($\Delta \% = 100 \times [\eta]/[\eta]_h - 100$) of intrinsic viscosity values (In BO1 oil), Where Huggins value taken as a reference.

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
P-1	14.27	10.52	8.92	30.62	31.70	35.6
P-2	3.51	4.42	-1.47	9.91	10.83	12.51
P-3	-21.17	-13.6	3.79	52.55	53.79	54.95

Table 6. Percentual differences ($\Delta \% = 100 \times [\eta]/[\eta]_h - 100$) of intrinsic viscosity values (In BO2 oil), Where Huggins value taken as a reference.

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
P-1	-7.30	-0.71	-1.53	1.64	0.97	2.24
P-2	6.66	8.59	11.06	16.46	15.53	15.19
P-3	-8.97	-2.03	1.54	12.11	11.99	11.88

Table 7. Viscometric molecular weight of all prepared sample in BO1 oil by using Mark – Houwink equation $[\eta] = KM^a$, Where $K = 0.00387$ and $a = 0.725$.

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{DC}^b
P-1	8315	9995	9545	9355	12019	12156	12656
P-2	5396	5659	5729	5287	6148	6219	6349
P-3	3029	2181	2475	3188	5423	5484	5541

Table 8. Viscometric molecular weight of all prepared sample in BO2 oil by using Mark – Houwink equation $[\eta] = KM^a$, Where $K = 0.00387$ and $a = 0.725$.

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{DC}^b
P-1	17639	15887	17467	16951	18039	17876	18187
P-2	11095	12128	12432	12824	13559	13540	13486
P-3	11954	10500	11620	12208	13995	13975	13956

CHAPTER III

3.1 EXPERIMENTAL

3.1.1 Materials used

Acrylic acid, styrene and hydroquinone were purchased from Merck India Ltd, decyl alcohol, isodecyl alcohol and dodecyl alcohol were purchased from SRL, India and were used as such in the present study. Benzoyl peroxide (BZP) procured from LOBA chemicals, Toluene from S.D fine Chem., India Ltd., and were used after purification following the method as stated in Chapter III of Part I of this thesis. Base oils were collected from Indian Oil Corporation Ltd., Dhakuria, Kolkata and Bharat Petroleum Corporation Ltd., Matigara, Darjeeling.

3.1.2 Preparation of esters

Decyl acrylate was prepared by reacting acrylic acid with decyl alcohol (1.1:1 molar ratio). The reaction was carried out in a resin kettle in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid, and toluene as a solvent under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403 K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester, decyl acrylate. The same procedure is applied to prepare isodecyl acrylate and dodecyl acrylate.

3.1.3 Purification of prepared esters

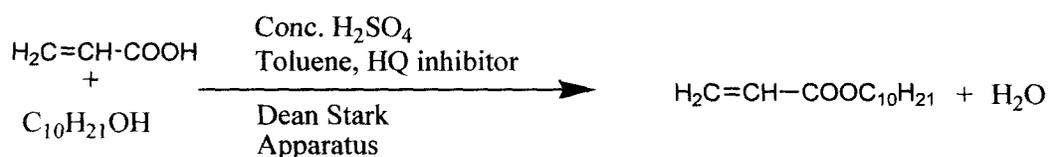
The prepared esters were purified according to the following procedure: a suitable amount of charcoal was added to the ester, allowed to reflux for 3 h, and then filtered off. The filtrate was washed with 0.5N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide, the ester was then left overnight on calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

3.1.4 Preparation of poly(acrylates) and their copolymers with styrene and their purification

The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask was placed desired mass of acrylate and initiator benzoyl peroxide (BZP) followed by the desired mass of styrene was added drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into 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. Homopolymers of acrylates were similarly prepared and purified for use in reference experiments.

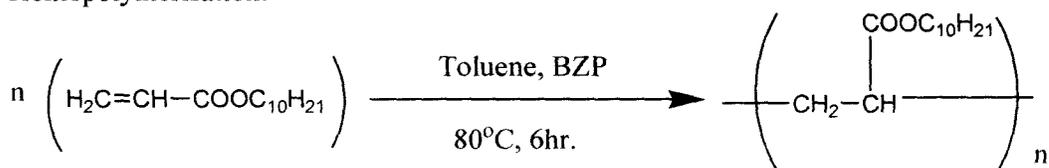
Scheme I

Esterification:



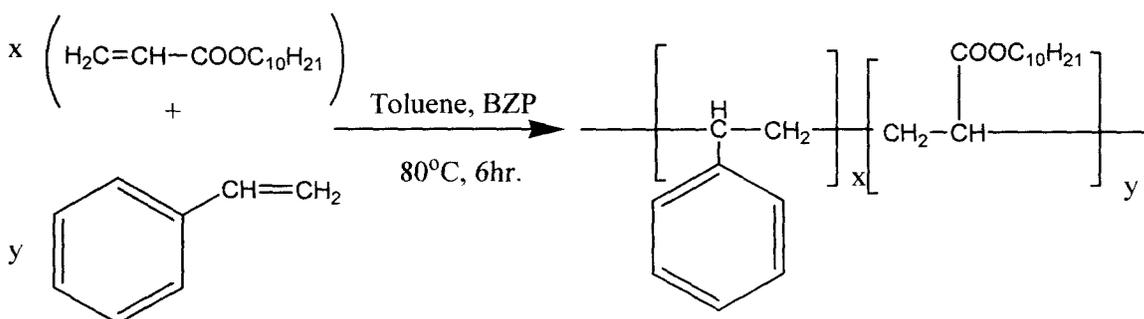
Scheme-II

Homopolymerisation:



Scheme-III

Copolymerisation:



3.1.5 Preparation of Polymer – base oil blend

Base oils of two different viscosity grades, (BO1 and BO2) were collected from two different refineries, A and B. In all the cases blending of the additives with the oils were carried out by taking required amount of polymer in the calculated amount of oil (w/w) and then heating the mixture at 333 K for 30 min with constant stirring.

3.1.6 Spectroscopic measurements

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

3.1.7 Viscometric measurements

Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values are $K' = 0.00268 \text{ cm}^2 \text{ sce}^{-2}$, $L = -19.83 \text{ cm}^2$ and volume of the bulb is 3 cm^3 and length of the capillary 11.3 cm). Experimental determination was carried out by counting time flow at least six different concentrations of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and uncertainty was found to be nearly 0.17 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$ [30, 37] were employed. The commonly used equations (eq1 to 7) employed to determine the viscometric parameters of the polymer are mentioned in Part I Chapter I.

3.1.8 Thermo gravimetric analysis (TGA)

The thermo grams in air were obtained on a mettler TA – 3000 system, at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$.

3.1.9 Evaluation of prepared additive as pour point depressants in base oils

The prepared additives were evaluated as pour point depressant using base oils collected from two different sources A and B, (Table 5) through the pour point test according to the ASTM-D-97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentration. The experimental data were noted by taking an average of three experimental results under identical conditions.

3.1.10 Evaluation of prepared additive as viscosity index improvers in base oils

The properties of base stock oils viscosities and viscosity index of these oils were calculated to ASTM D2270-87 method using viscosity index calculator. The kinematic viscosity of the oil contains the tested compound which was determined at 40⁰C and 100⁰C. Different concentrations between 1 wt % and 5 % were used to study the effect of concentration on VI of the lube oil.

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PART III

**SYNTHESIS CHARACTERIZATION AND VISCOSITY STUDIES OF
BIODEGRADABLE ADDITIVES AS A POTENTIAL POUR POINT DPRESSANT
AND VISCOSITY MODIFIER**

CHAPTER I

1.1 A SHORT REVIEW ON BIODEGRADABLE LUBE OIL ADDITIVES

1.1.1 Introduction

Widely used engine oil additive is mainly dithiophosphate, overbased calcium sulphonate, succinimides dispersants, polymer viscosity improvers and pour point depressants. Uses of this additive create a potential environmental hazardness emission and sludge obtained during purification [1]. To counterpart this, biodegradable base stocks were developed, but reports are still scanty regarding the biodegradability of the performance additives added to the base fluids used to formulate a finished product.

The use of vegetable oils and animal fats for lubrication purposes has been practiced for many years. With the discovery of petroleum and the availability of inexpensive oils, alternatives became unattractive and were left by the wayside. Attention was refocused on vegetable oils during wartime and oil shortage situations. During World War I and World War II, the use of vegetable oils for fuel, lubricants, greases and energy transfer increased rapidly. Also, the oil embargo of 1973 brought needed attention to alternatives for petroleum oils.

However, from the past two decades, a renewed interest in vegetable oil-based lubricants as environmental interest has increased. In Europe during the 1980s, various mandates and regulations were placed on petroleum products necessitating the use of biodegradable lubricants. During the 1990s, many American companies began developing biodegradable products. A prime example is when the Mobil Corporation introduced its Environmental Awareness Lubricants (EAL) line of hydraulic fluids. The Lubrizol Corporation, USA, also developed considerable quantities of additives and sunflower oil-based lubricants. However, the lack of regulatory mandates in the United States, as well as the availability of post-Desert Storm low-cost oil, made biodegradable oils too expensive to compete.

Although but biodegradable, vegetable oils have been used as lubricants for a long time, but since the introduction of mineral oils, the later have dominated the lubricant market. Today, due to growing environmental concerns, vegetable oils are again finding their way into lubricants for industrial and transportation applications. Vegetable oils can offer significant environmental advantages with respect to resource renewability, biodegradability, as well as at the same time displaying satisfactory performance in a variety of applications [2]. They show excellent tribological properties such as friction-reducing, wear controlling, improved extreme pressure, etc. when used as additives or as base stocks or [3-5].

Vegetable –based oils are liquid agricultural products and are produced from plants. They are biodegradable non toxic and derived from foods. The source of vegetable oil is a crop and they promote self –reliance as ample production capacity exists. Vegetable oils present higher flash point than mineral oils, which always a concern with flammable liquids; they are also safer to humans.

Vegetable fats and oils (known by the generic term lipids) comprise, primarily triglycerides, that is, triesters of long chain carboxylic acids combined with glycerol. Most of these oils contain at least four and sometimes as many as 12 different fatty acids. Vegetable oils are usually good boundary lubricants but the major limitations are their high cost, thermal and oxidative instability. Oxidation stability of vegetable oils depends on the level of unsaturated products present. The lower the unsaturation the better the oxidative stability but higher the melting point. For good performance, special lubricants requirements must be fulfilled, i.e. good corrosion protection, compatibility with other materials, fair oxidative and hydrolytic stability and low temperature behaviour associated with the triglyceride.

Although the lubricant identity has been trying to formulate biodegradable lubricants under similar or even better technical characteristics than that base or mineral oils reported a very narrow segment. In recent publication Franco et al has reported the use of sunflower oil bio fuels, polymeric additives such as ethylene vinyl acetate (EVA) and styrene butadiene styrene (SBS) copolymer in lubricant formulation [6].

US pat. No 5229023 disclose the synthesis and evaluation of vegetable oil based lubricant additive which can be used as thermal oxidative stability enhancers and viscosity improvers, US pat. No. 4873008 has described the synthesis and jojoba oil based lube oil additive. US pat. No. 4970010 has described a group of sulfurised derivatives of triglyceride

vegetable oils which showed acceptable lubricating properties. Sulfurised vegetable wax esters were described in US pat. No. 4152278 to act as an anti wear, friction modifier and extreme pressure additive. Because of the cost adding conversion steps and limited availability of the above oils they did not find practical application by the additive industry. Thus they are exist and ample opportunity to work this area of vegetable oil based lube oil additives for during the environmental pollution as well as to develop lube oil additives with better performance than the conventional synthetic chemical based additive.

CHAPTER II

This chapter is divided into two sections, section A and section B

Section A comprises the Synthesis, Characterization, Viscosity Studies and Performance Evaluation of Polymer of Sunflower Oil and its Copolymers in Lubricating (Lube) Oil

Section B comprises the Evaluation of Synthesized Biodegradable Polymers as Viscosity Modifier for Lube Oil

2.1 SECTION A: Synthesis, Characterization, Viscosity Studies and Performance Evaluation of Polymer of Sunflower Oil and its Copolymers in Lubricating (Lube) Oil

2.1.1 Introduction

Lubricant and additives may be petroleum, synthetic, or biological in origin. The lubricants of biological origin include vegetable oils and animal fats that are obtained from seeds, fruits, and animal tissue. Vegetable oils are obtained from renewable resources and are biodegradable. Thus they offer specific environmental benefits over mineral oil-based lubricants. This is significant in applications where the lubricant is lost in the environment, e.g., chain bar lubricants and hydraulic fluids for farm machinery. In addition to environmental benefits, vegetable oils also have certain performance advantages over conventional mineral base stocks. These include low volatility, high viscosity index, and excellent lubricity [5].

Keeping this view in mind the present invention relates to the synthesis of vegetable oil based copolymer as performance additive for lube oil, which can improve the low temperature property (i.e., can act as pour point depressant) and induce thermal stability of the additive when used in base stocks. Pour point is the temperature at which the oil is just able to flow and below which there is complete absence of flow in it. Polymeric additives known as flow improvers or pour point depressant (PPD) are generally used to lower pour point, viscosity and yield stress of lubricating oil [7-11].

Looking into the computation and the physical aspects typical vegetable oils that may be used for the derived purpose include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, canola oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, citicica oil, jojoba oil, meadow foam oil, and the like. Such oils may be partially or fully hydrogenated, if desired. In our study we chose sunflower oil as reported vegetable oil for the synthesis copolymer of it that can be made as a potential pour point depressant for lube oil.

Sunflower oil contains predominantly linoleic acid in triglyceride form. The British Pharmacopoeia lists the following profile:

- Palmitic acid: 4-9 %
- Stearic acid: 1-7 %
- Oleic acid: 14-20 %
- Linoleic acid: 48-74 %.

Sunflower oil also contains lecithin, tocopherols, carotenoids and waxes. Sunflower oil's properties are typical of vegetable triglyceride oil. Sunflower oil is produced from oil type sunflower seeds. Sunflower oil is light in taste and appearance and has high vitamin E content. It is a combination of mono-unsaturated and polyunsaturated fats with low saturated fat levels.

Physical properties of sunflower oil

Sunflower oil is liquid at room temperature. The refined oil is clear and slightly amber-colored with a slightly fatty odor.

Smoke point (refined)	332 ⁰ C	450 ⁰ F
Smoke point (unrefined)	227 ⁰ C	440 ⁰ F
Density (25 ⁰ C)	917 kg/m ³	
Refractive index (25 ⁰ C)	1.473	
Viscosity (25 ⁰ C) (unrefined)	0.049 Kg-f.s M ⁻²	

In order to have a better understanding in relation to the structure and morphology of the synthesized additive with their performance, viscometric studies of the dilute solution has also been carried out.

2.2.2 Results and discussion

^1H NMR (Figure 1) of sunflower oil indicated the presence of unsaturation (δ 5.31, 4.27 and 4.12 ppm), methyl (δ 0.87 to 1.27 ppm) and methylene protons (δ 1.59 to 2.75) ppm . Disappearance of the peaks (Figure 2) in the unsaturation region (δ 4.0 to 6.0 ppm) along with the shift in the methyl and methylene signals indicated the formation of homopolymer of the oil. Formation of copolymer of sunflower oil and styrene was indicated by the absence of unsaturation in the NMR spectrum (Figure 3) (no peak between 4 - 6 ppm) and appearance of broad multiplet centered at δ 8.2 ppm for the aromatic ring protons of styrene. Similar results were also obtained in the NMR spectrum (Figure 4 and Figure 5) of other copolymers e.g. sunflower oil – MMA and sunflower oil – DA.

IR spectra of the homo (Figure 6) and copolymer (Figure 7-9) of sunflower oil showed characteristic peaks for ester carbonyl at 1745.5 cm^{-1} and at 3408 cm^{-1} .

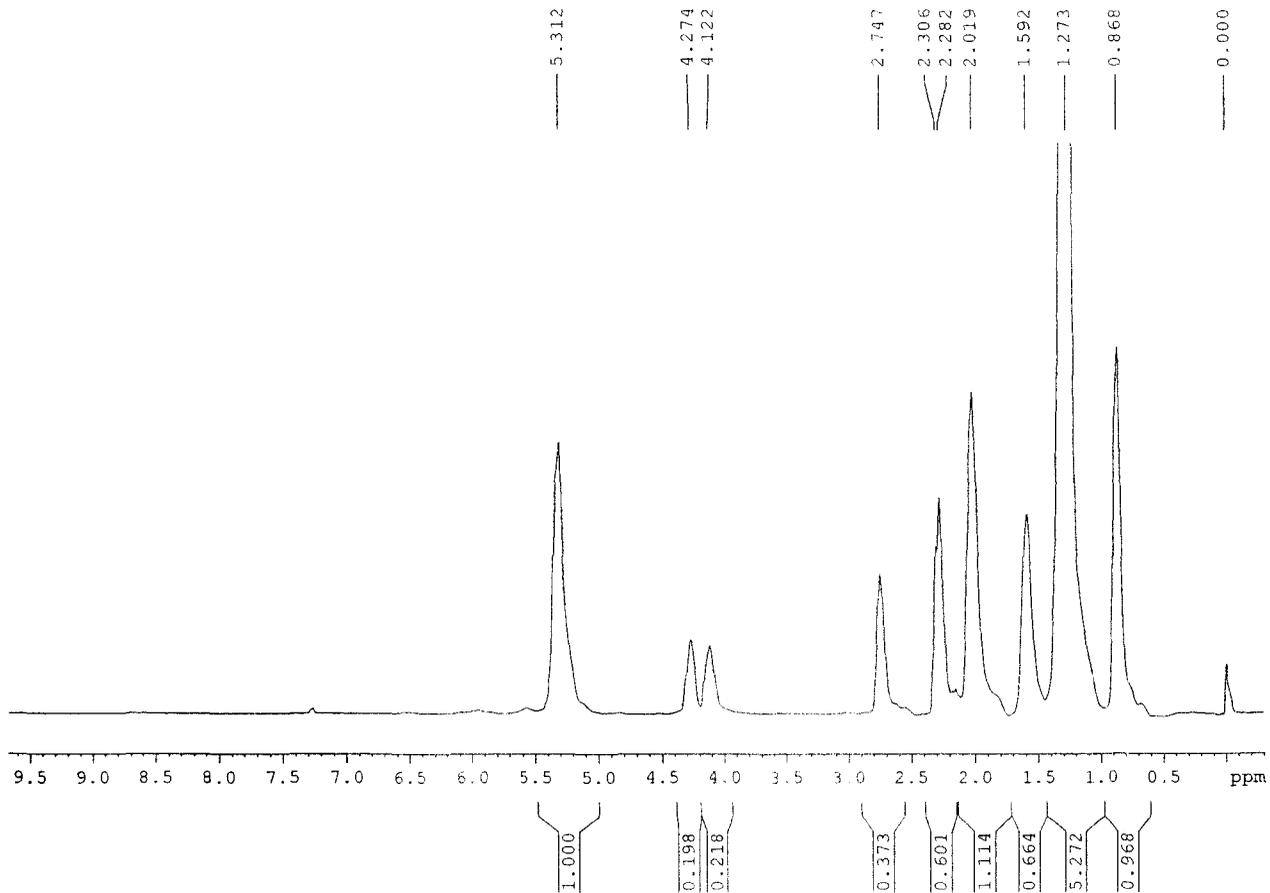
Using the graphic extrapolation method respective intrinsic viscosities and constants were evaluated. In single point determination method, SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent system. The same is used here also.

Table 1 presents intrinsic viscosity $[\eta]$ values of all prepared samples in toluene solvent. In general it has been found that intrinsic viscosity values of homopolymer are greater than copolymer (except P-3). Intrinsic viscosity increases with the increase in monomer concentration (MMA, DA and styrene). It is interesting to note that the, irrespective of the nature of polymer samples, intrinsic viscosity values obtained by using single point determination methods are always found to be greater than graphical extrapolation methods.

Although different intrinsic viscosity values may be found in graphic extrapolation of Huggins, Kraemer, Martin and SB equation (eq 2 to 5) , but in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. For the homopolymer and copolymer, $[\eta]$ value obtained by Huggins and Kraemer's equation were identical.

TD-

111



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Figure 1. ¹H NMR spectra of sunflower oil

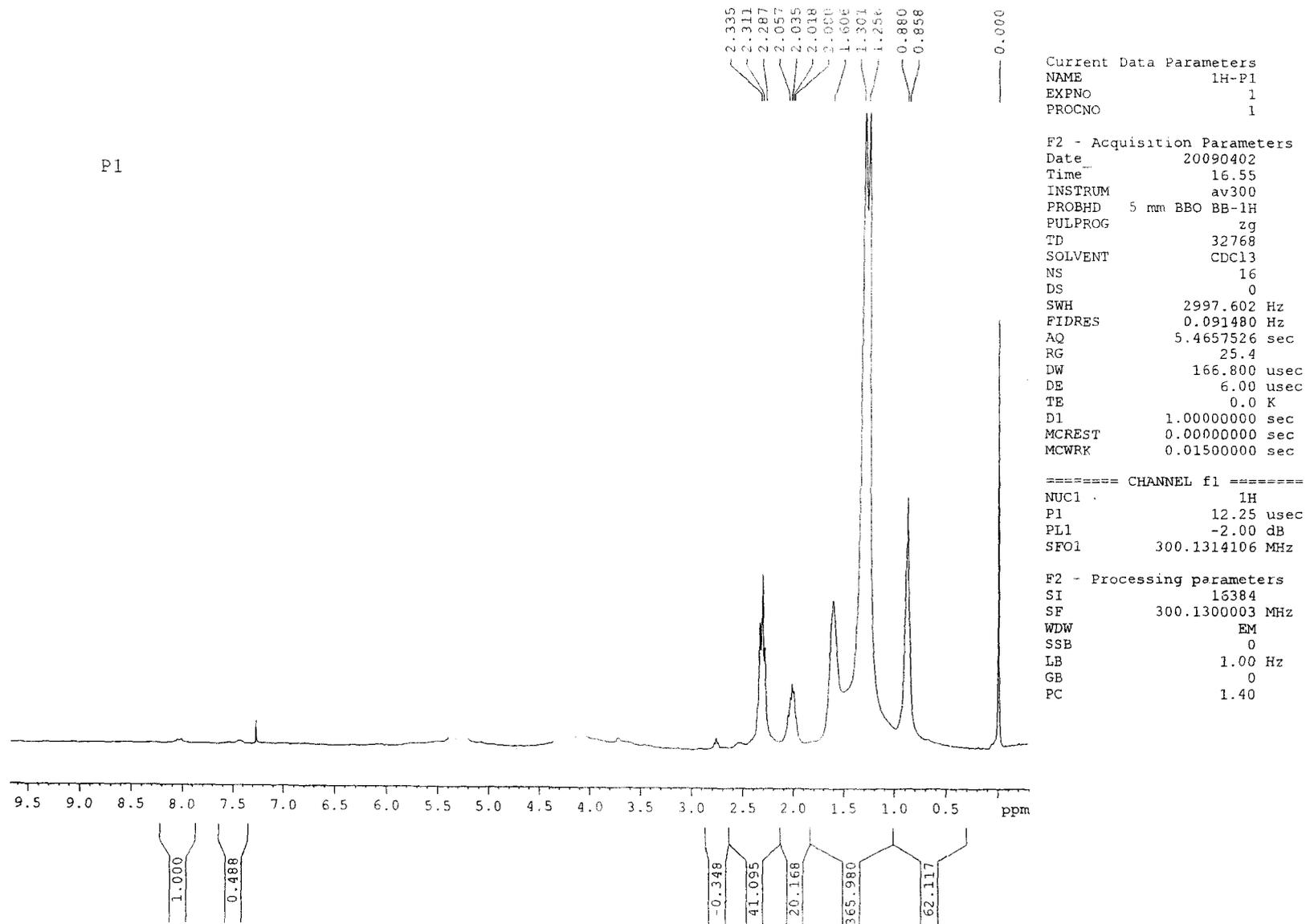


Figure 2. ^1H NMR spectra of polymer of sunflower oil

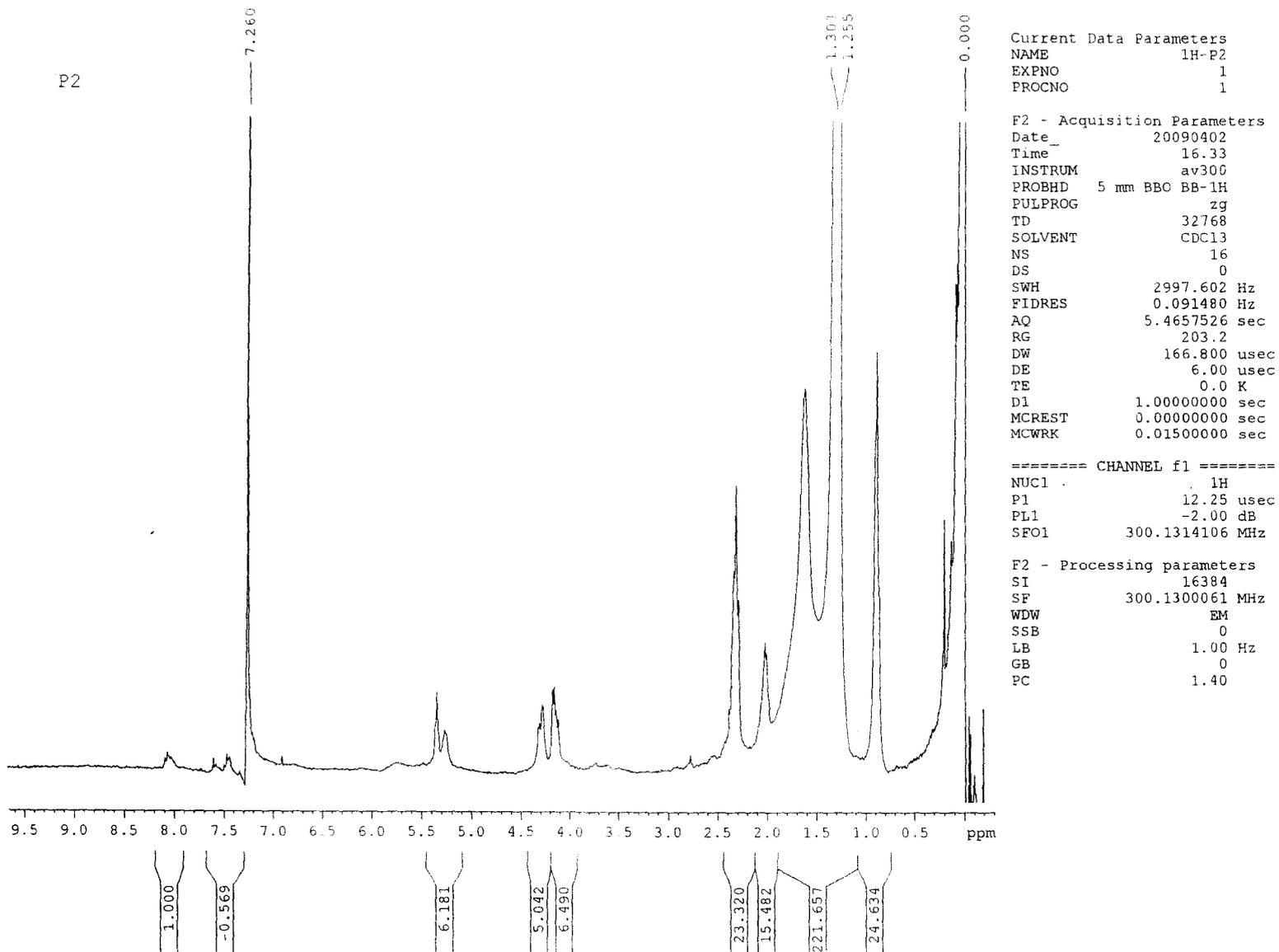
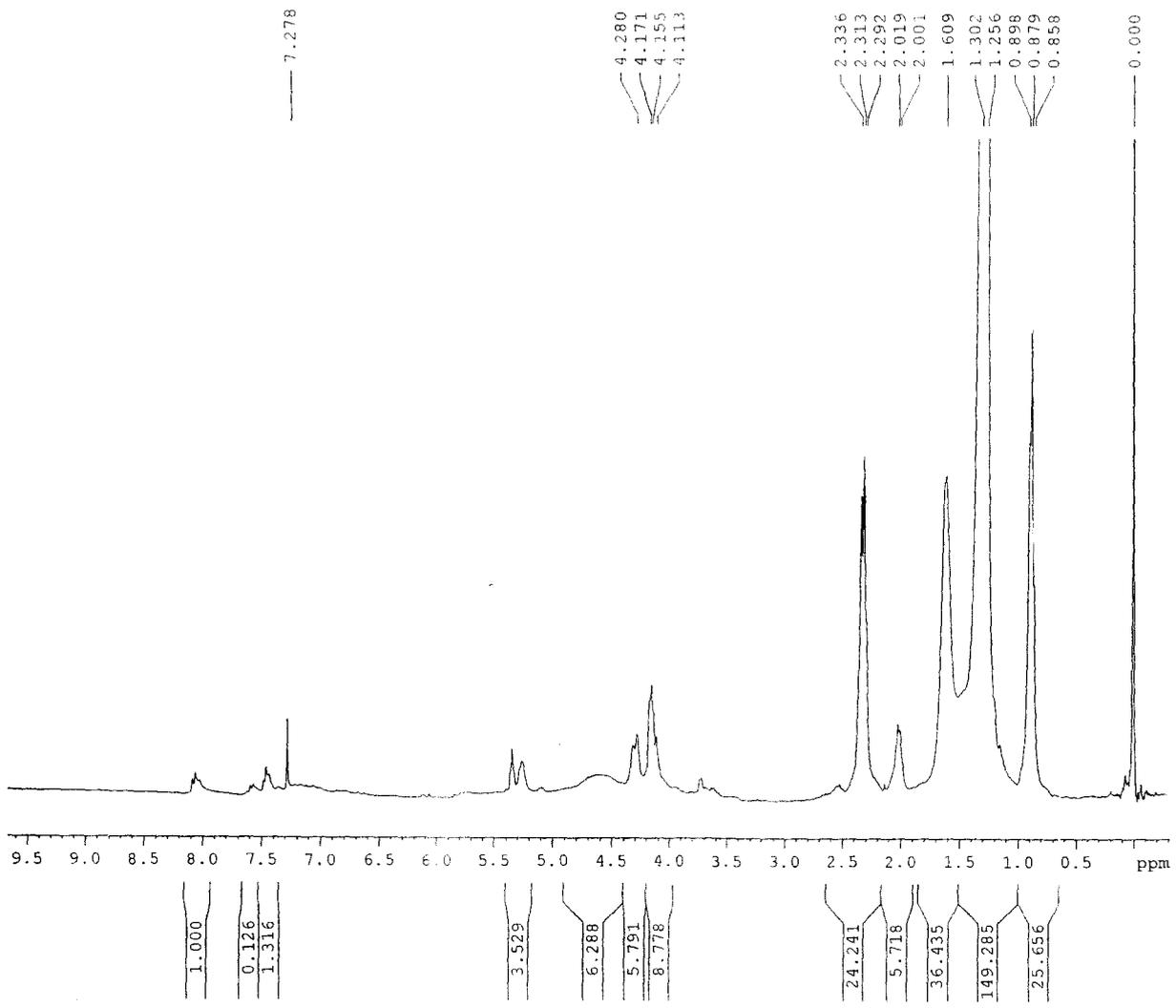


Figure 3. ^1H NMR spectra of copolymer of sunflower oil + styrene



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Figure 4. ¹H NMR spectra of copolymer of sunflower oil+ MMA

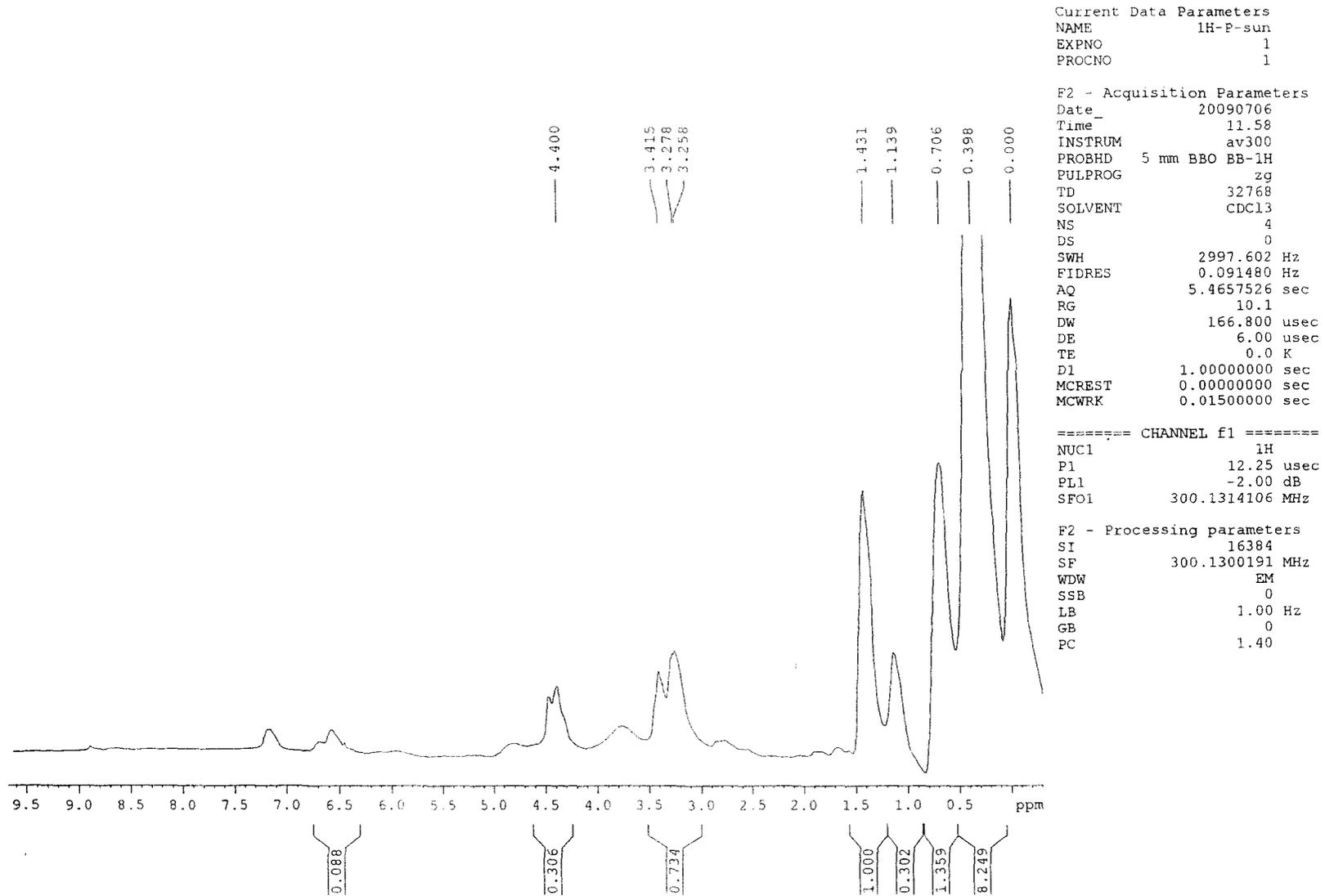


Figure 5. ^1H NMR spectra of copolymer of sunflower oil+ DA

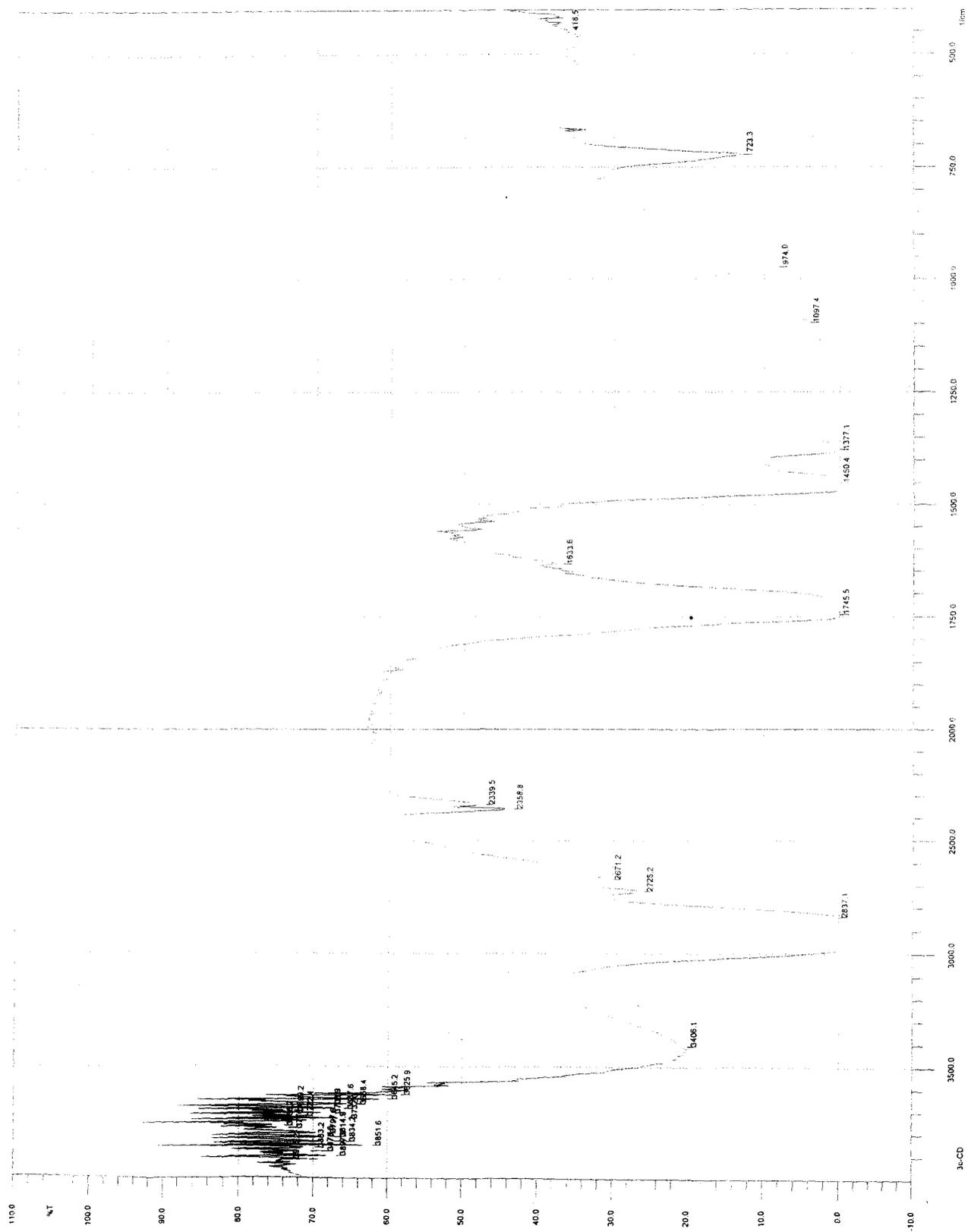


Figure 6. IR spectra of polymer of sunflower oil

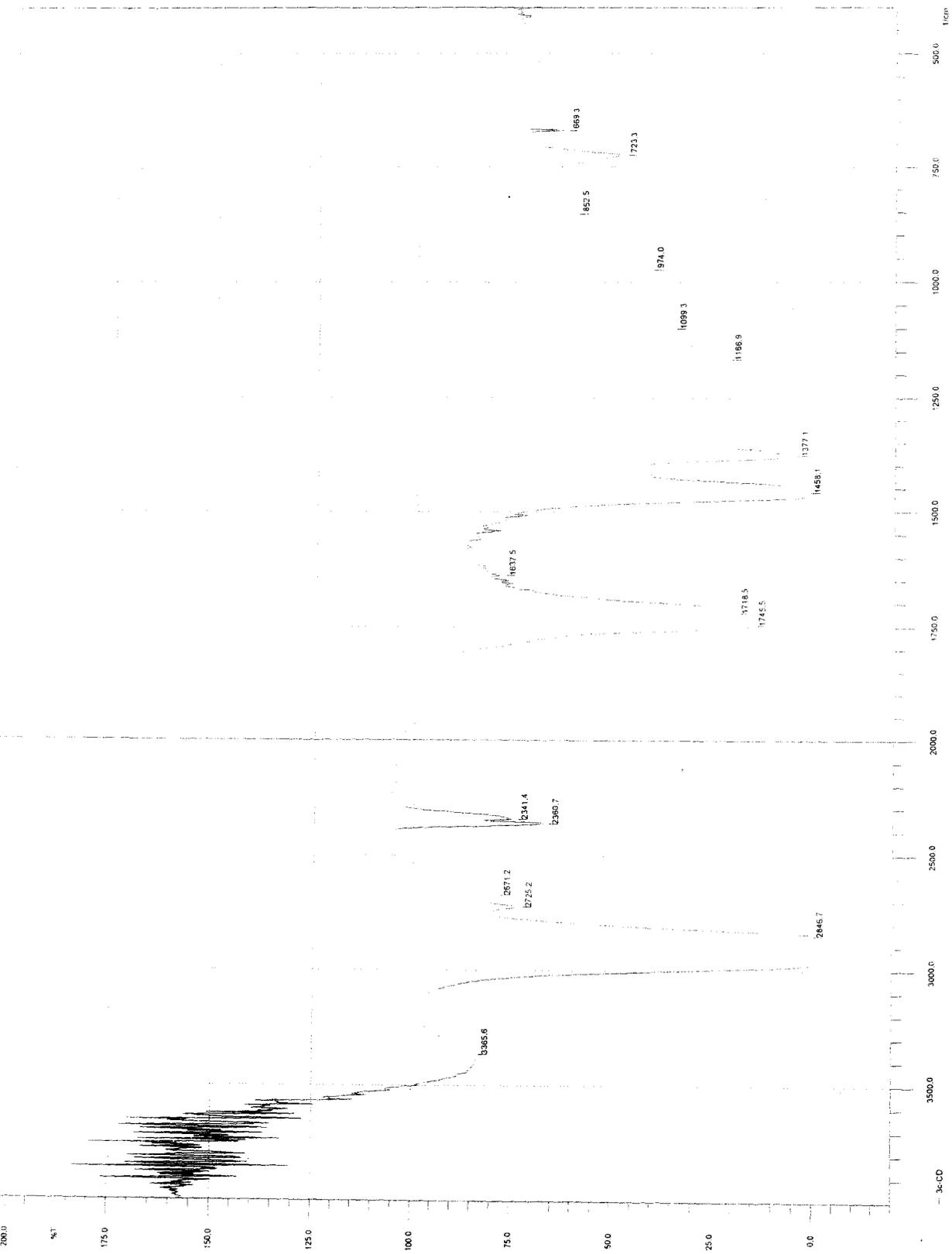


Figure 7. IR spectra of copolymer of sunflower oil + Styrene

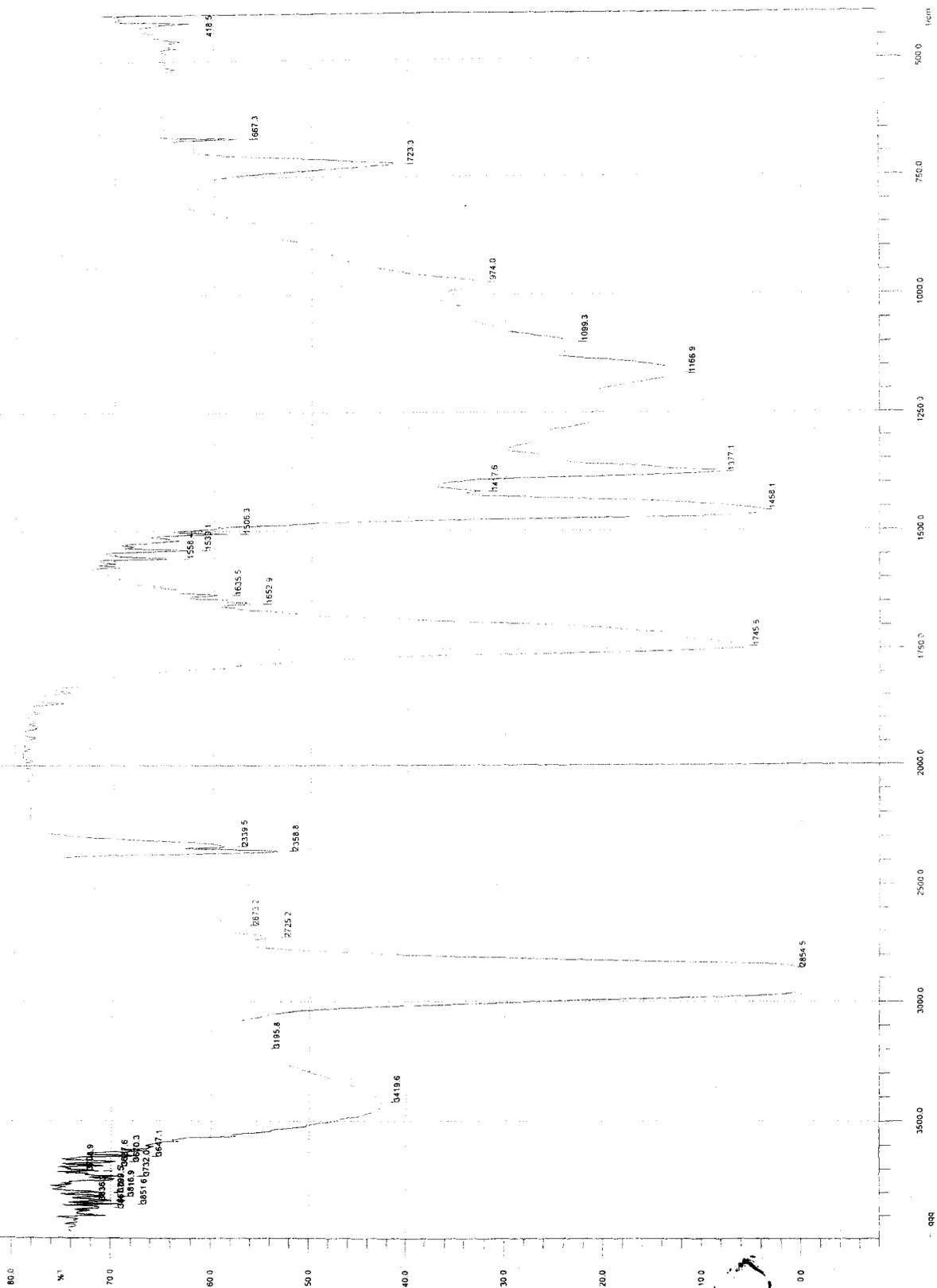


Figure 8. IR spectra of copolymer of sunflower oil + MMA

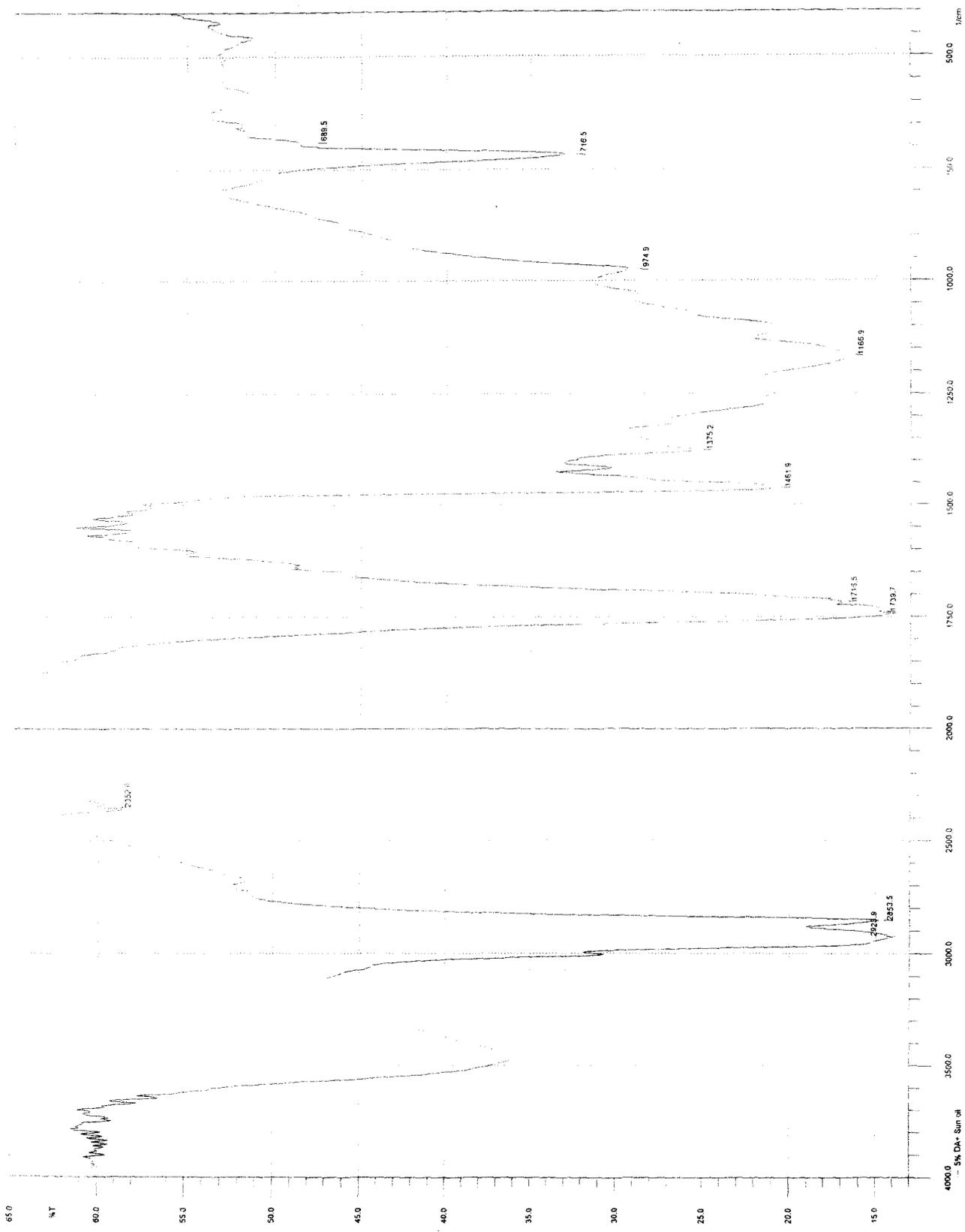


Figure 9. IR spectra of copolymer of sunflower oil + DA

Both homopolymer and copolymers in toluene medium indicating good solvation (Table 2) as is evident from their respective viscometric constant values, and this conclusion is further supported by negative values of Kraemer coefficient of the all the systems analyzed. However, it is interesting to notice that for few polymers in toluene, k_{sb} values were close to 0.28. But there appears to be a close tendency to attain the value, $k_h + k_k = 0.5$.

By comparing $[\eta]$ values (Table 3) of homo and copolymers determined through graphic extrapolation using Kraemer, Martin and SB equations and single point determination with the values determined by Huggins equation, it is observed that the range of variation ($\Delta\%$) is similar in both the cases e.g. -41.87 to 17.13 % and -4.54 to 52.80% respectively.

Table 4 presents a comparison between the value of molecular weight obtained by viscometric methods for homopolymer and copolymers analyzed. The general trend in all the cases is a gradual increase in molecular weight with increase of monomer concentration.

Table 5 presents TGA values of all the polymers. All the copolymers are thermally more stable. Increases in percent concentration of monomers increase the thermal stability.

Table 6 presents biodegradability test results obtained by using disk diffusion method. Homopolymer of sunflower oil and its copolymer with decyl acrylate showed a significant biodegradability against the fungal pathogen, *alternaria alternata*. It was further confirmed by the shift of IR frequency of the ester carbonyl to 1712 cm^{-1} after the biodegradability test. Copolymer of sunflower oil with MMA also showed biodegradability but in a smaller extent. However, significant biodegradability does not observe in case of the copolymer of sunflower oil with styrene. This may be due to the incorporation of styrene (aromatic moieties) in the polymeric chain.

Table 7 presents PPD properties of the polymers evaluated in two different base stocks (collected from two different sources S1 and S2). The results indicated that copolymers, P-2 and P-5 showed better performances in comparison to the homopolymer of sunflower oil.

2.2.3 Conclusion

Incorporation of monomers (MMA, DA and styrene) in the sunflower oil back- bone raises the thermal stability of the copolymer and the extent of monomer incorporation directly proportional to the thermal stability of the copolymer.

Intrinsic viscosity values of the copolymer are less than the corresponding homo polymer (except P-3) and the values obtained by single point determination method are higher than the values obtained by graphical extrapolation method.

Viscometric molecular weight of the copolymer is less than the homopolymer of decyl acrylate.

Pour point depressant (PPD) performance of the copolymer is always better than the homopolymer in all the base oils studied.

Table 1. Intrinsic Viscosity Values of all polymeric sample. P- 1 Polymer of sunflower oil,P- 2 copolymer of sunflower oil+ 5% MMA, P-3 copolymer of sunflower oil+10% MMA, P-4 copolymer of sunflower oil+ 5% DA ,P-5 copolymer of sunflower oil +10% DA, P-6 copolymer of sunflower oil+5% styrene, P-7 copolymer of sunflower oil + 10% styrene. A- graphic extrapolation method and b- single point determination method.

Samples	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{sb}$	$[\eta]^b_{sb}$	$[\eta]^b_{sc}$	$[\eta]^b_{dc}$
P-1	6.1	5.25	3.94	6.92	7.43	7.93	8.91
P-2	5.0	5.45	3.42	6.37	5.92	6.95	6.69
P-3	6.75	6.05	6.50	7.46	6.91	7.55	8.44
P-4	4.20	4.20	4.10	4.30	4.41	4.44	5.30
P-5	5.50	4.50	4.00	4.90	5.25	5.35	5.80
P-6	4.80	3.80	2.79	5.12	5.95	6.15	6.74
P-7	5.20	4.85	3.82	6.09	6.79	7.15	7.95

Table 2. Viscometric constant values of all sample

Samples	k_h	k_k	k_m	k_{sb}	k_h+k_k
P-1	0.88	-0.242	1.523	0.35	0.638
P-2	0.70	-0.041	1.468	0.437	0.659
P-3	0.55	-5.83×10^{-3}	0.475	0.252	0.544
P-4	0.46	-0.027	0.513	0.278	0.496
P-5	0.314	-0.187	0.78	0.35	0.127
P-6	0.89	-0.59	2.27	0.284	0.30
P-7	1.06	-0.223	1.41	0.183	0.837

Table 3. Percentual Differences of Intrinsic Viscosity ($\Delta\% = [100([\eta]/[\eta]_h) - 100]$) a- graphic extrapolation method and b- single point determination method.

Samples	K_k	K_m	K_{sb}	K_{sb}	K_{sc}	K_{dc}
P-1	-13.98	-35.36	13.48	21.74	30	46.08
P-2	-15.46	-31.6	3.40	18.6	22.08	33.74
P-3	-10.30	-3.70	10.54	2.43	30.70	25.06
P-4	-0.047	-2.33	2.44	5.0	5.74	26.19
P-5	18.18	-27.27	-10.90	-4.54	-2.70	5.49
P-6	-20.83	-41.87	6.75	23.96	28.125	40.41
P-7	-6.78	-26.54	17.13	30.57	37.5	52.80

Table 4. Viscometric molecular weight determined by using Mark -Houwink equation $[\eta] = KM^a$ where, $K = 0.00387$ and $a = 0.725$

Samples	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	25735	20906	14097	30638	33756	36956	43406
P-2	19561	15516	11585	20486	24681	25758	29211
P-3	29592	25471	28091	33979	30588	34567	40287
P-4	15365	33877	32728	35142	36462	36845	47974
P-5	33901	37578	31520	42672	47300	48665	54912
P-6	18473	13384	8783	20214	24842	26001	29503
P-7	20629	18739	13481	25658	25658	32007	37023

Table 5. TGA data of all prepared sample

Samples	Decomposition Temp.	PWL
P-1	320/350	48/80
P-2	320/350	45/75
P-3	340/385	38/82
P-4	350/390	47/78
P-5	370/410	38/82
P-6	360/400	40/75
P-7	370/410	50/80

Table 6. Results of biodegradability test by using disk diffusion method

Fungal pathogens	Polymer samples	Incubation period	Initial wt (gm)	Final wt (gm)	Wt loss (gm)
		(Days)			
<i>Calletoricheme camellie</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Fussarium equisitae</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Alterneria alternata</i>	P-1	30	1.5	0.9	0.6
	P-2	30	1.5	1.1	0.4
	P-4	30	1.5	1.4	0.1
	P-6	30	1.5	1.48	0.02
<i>Colletrichum Gleosproides</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Curvularia eragrostidies</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil

Table 7. PPD properties of base oils collected from different sources

Sample	Base oils		Pour point of Base oil	Pour point of additive doped Base oil		
				2.5%	5%	10%
P-1	BO1	S1	-3	-6	-6	-6
		S2	-3	-3	-3	-3
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-9
P-2	BO1	S1	-3	-12	-12	-12
		S2	-3	-12	-15	-15
	BO2	S1	-6	-15	-15	-15
		S2	-6	-15	-15	-15
P-3	BO1	S1	-3	-12	-12	-12
		S2	-3	-15	-15	-12
	BO2	S1	-6	-15	-12	-12
		S2	-6	-15	-12	-12
P-4	BO1	S1	-3	-15	-12	-12
		S2	-3	-15	-12	-12
	BO2	S1	-6	-15	-12	-12
		S2	-6	-15	-12	-12
P-5	BO1	S1	-3	-15	-18	-15
		S2	-3	-15	-18	-21
	BO2	S1	-6	-18	-21	-21
		S2	-6	-18	-21	-24
P-6	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-9
	BO2	S1	-6	-9	-12	-12
		S2	-6	-9	-12	-12
P-7	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-9
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-9

2.3 SECTION B: Evaluation of synthesized Biodegradable Polymers as Viscosity Modifier for Lube Oil

2.3.1. Introduction

Lubricating oil always contains different types of additives. These additives differ in quantity and quality according to the purpose for which they are needed. Lubricant additives are compounds or mixtures when incorporated in base lubricating fluids, supplement their natural characteristics and improve their field service performance in existing applications. One of the important such kind of additive is viscosity index improvers or viscosity modifier. The viscosity index (VI) express the viscosity changes of an oil when temperature is varied, i.e., the smaller changes of the viscosity named as a higher viscosity index [12-14].

The effect of the polymeric viscosity index improvers depends mainly on the behavior of polymer molecules in the dispersed phase (base oil) when the polymer dissolved in oil. It is assumed that it takes the irregular skeins. At low temperatures the skeins are packed into narrow space. As a result, they act on more and more molecules of oil and reduce their mobility. The sequence is that the viscosity of the oil is not reduced at evaluated temperatures as much as that of the undoped oil. Briefly, it is believed that the polymer molecule in solution exists as a random coil, which is swollen by the lube oil solvent. The volume of this molecule determines the viscosity increase; it may be resembled to a tangled ball of yarn, which impedes solvent flow [15]. As the temperature is raised, although the lube oil viscosity decreases, further unraveling of the polymer molecules occurs resulting in an increase of the viscosity of the mixture. This in turn decreases the change of viscosity with temperature of this mixture. Heavy petroleum fractions can be mixed with neutrals to give blends having somewhat higher viscosity index than the arithmetical mean of the initials stocks, but the use of polymeric materials, called viscosity index improvers, yields higher viscosity index values [8].

Structurally viscosity index improvers (VII) and viscosity modifiers (VMs) are long chain, high molecular weight polymers used to resist the change of viscosity of the oil by increasing the relative viscosity of oil more at high temperatures than at low temperatures [16-19].The performance of VMs is very often expressed in terms of Viscosity Index (VI),

which is an arbitrary number [20] that indicates the resistance of a lubricant to viscosity change with temperature. The higher the VI, the less the viscosity of an oil changes for a given temperature change. Its value can be calculated from the viscosity measurements of fluids at 40⁰C and 100⁰C. The performance of the VII depends on the behaviour of the polymer molecules in the oil, where the polymer solubility, molecular weight and resistant to shear degradation are determinant parameters [19].

Since reports are scanty towards the development of vegetable oil based additives to act as a potential VIIs in lubricating oil, the author under took the present investigation for the synthesis of such kind of VIIs.

Polymer of sunflower oil, poly(methyl methacrylate), poly(decyl acrylate) and copolymer of sunflower oil with methyl methacrylate and also with decyl acrylate, were prepared . Their effectiveness as a VII was examined in various base stocks and the results are reported in this section.

2.3.2 Results and Discussion

The prepared copolymers were tested for their effectiveness as viscosity index improvers in base oils (BO1, BO2 and BO3) and the results are expressed in terms of VI (ASTM D-2270-87). Kinematic viscosity of the different concentrations of additives doped base oils were determined at 40⁰C and 100⁰C. The concentrations range investigated were ranging from 0 wt % and 5 wt %. The effect of additive concentration on the VI is expressed in terms of Figure 1, 2 and 3.

Physical properties of the base oils used in the present investigation are presented in Table 1, below.

Analysis of the experimental data as given in Table 2 – 16 and the plots (Figure 1-3), indicates that the values of viscosity index (VI) increases with the increase in concentration of the additives in solution and the VI values of the copolymer (S-4 and S-5) doped base oils are slightly higher in comparison to the homopolymers (S-1, S-2 and S-3) doped base oils. A possible explanation of the above observation may be put like that, as the temperature is

raised, the lube oil viscosity decreases; meanwhile the polymer molecule expands and as a result of which its hydrodynamic volume increases. This increase in the micelle size of the solvated polymer molecules counterbalance the reduction of the viscosity of the lube oils with temperature [21, 22]. This effect is more pronounced in case of copolymers rather than homopolymers. The increase in concentration of polymer leads to an increase in the total volume of the polymer micelles in the oil solutions. Consequently, higher concentration of additive will impart higher viscosity index [23].

2.3.3 Conclusion

In general, viscosity index (VI) of the additive (both for homo and copolymer) doped base oil increases with the increase in concentration of the additives in solution, irrespective of the nature of the base oils. Again the VI values of the copolymer (S-4 and S-5) doped base oils are slightly higher in comparison to the homopolymers (S-1, S-2 and S-3) doped base oils and the prediction is not dependent on the nature of the base oils.

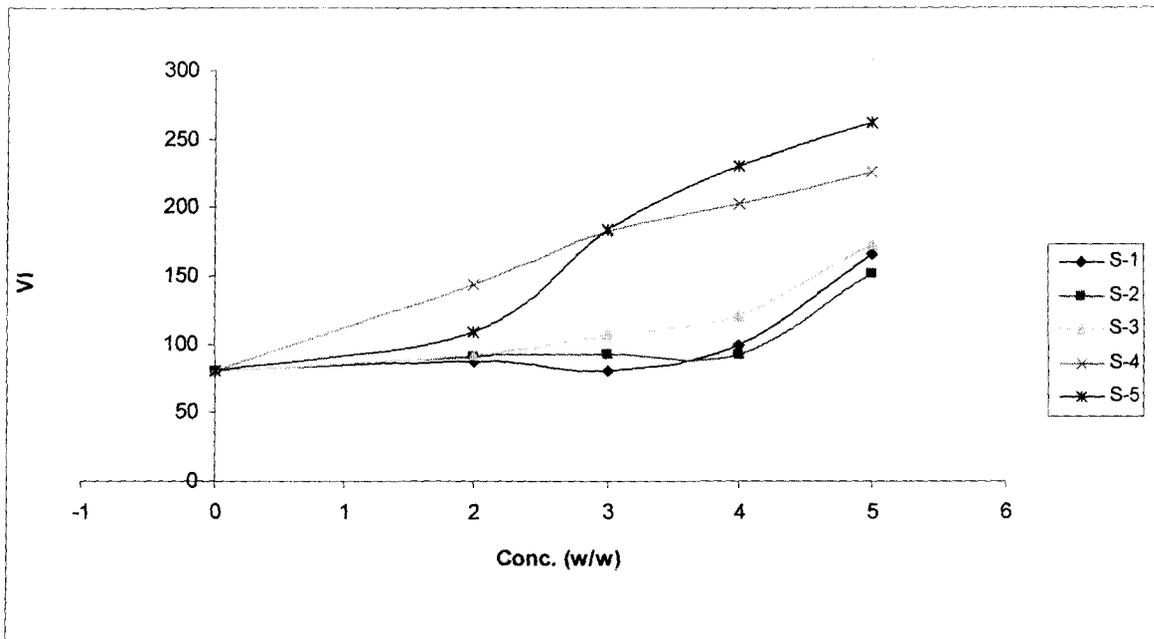


Figure 1. Plot of viscosity index (VI) vs polymer concentration in BO1 Where S-1 poly(methyl methacrylate), S-2 Poly(decylacrylate), S-3 polymer sunflower oil, S-4 copolymer of MMA+sunflower oil and S-5 copolymer of DA+ sunflower oil.

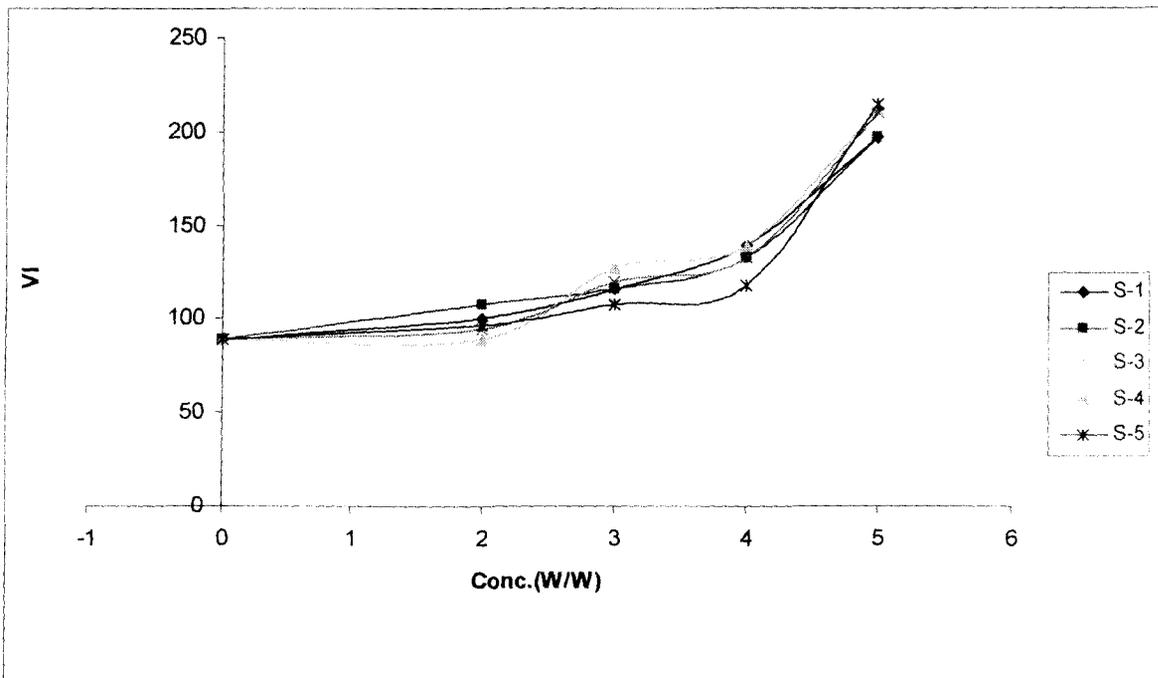


Figure 2. Plot of Viscosity index (VI) vs polymer concentration in BO2. Where S-1 poly(methyl methacrylate), S-2 poly(decyl acrylate), S-3 polymer sunflower oil, S-4 copolymer of MMA+sunflower oil and S-5 copolymer of DA+ sunflower oil.

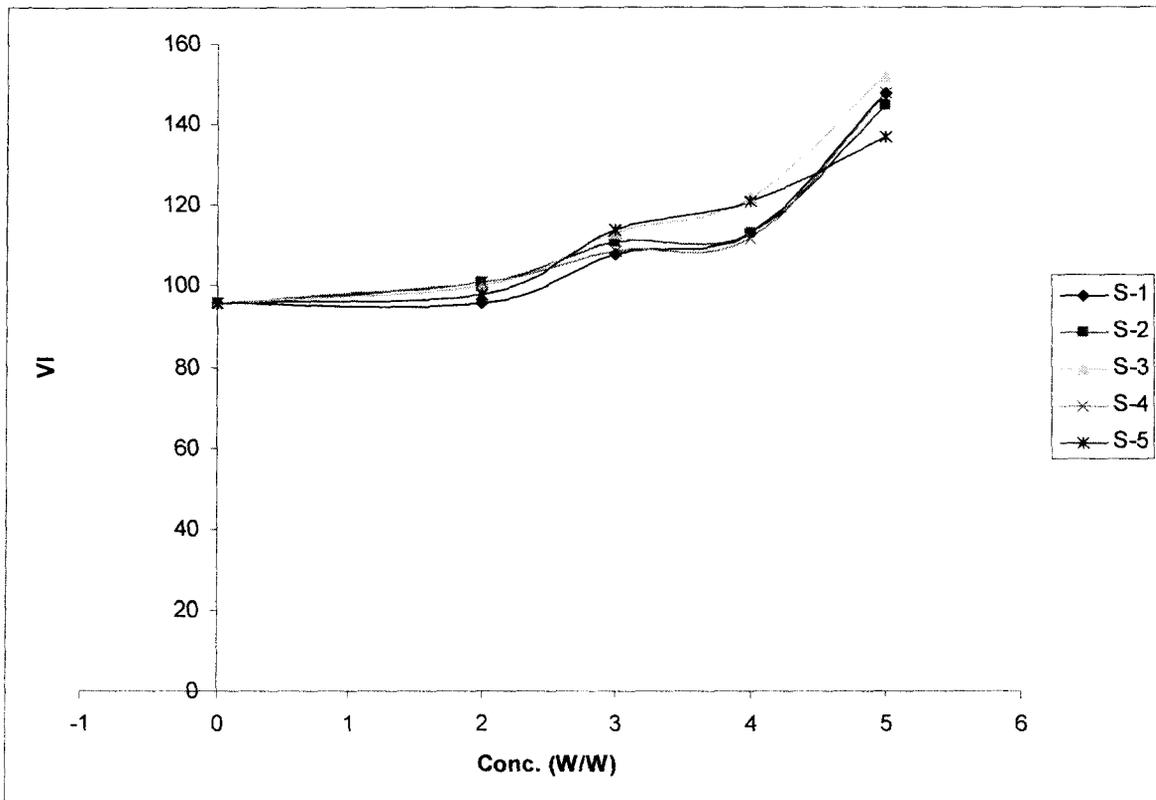


Figure 3. Plot of concentration (W/W) vs Viscosity index (VI) in BO3. . Where S-1 poly(methyl methacrylate), S-2 poly(decyl acrylate), S-3 polymer sunflower oil, S-4 copolymer of MMA+sunflower oil and S-5 copolymer of DA+ sunflower oil.

Table 1. Base oil properties

Bas oil properties	Base oils	
	BO1	BO2
Viscosity at 40 ⁰ C in cSt	6.700	24.229
Viscosity at 100 ⁰ C in cSt	2.00	4.390
Cloud point, ⁰ C	-8	-10
Pour point, ⁰ C	-3	-6

Table 2. Viscosity temperature characteristics of poly(methyl methacrylate) (S-1) – BO1 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	7.809	2.512	166
4.0	7.772	2.270	100
3.0	7.789	2.203	81
2.0	7.567	2.118	88
0.0	6.700	2.000	80

Table 3. Viscosity temperature characteristics of poly(decyl acrylate)(S-2) – BO1 blends

Additives (wt %)	Viscosity ⁰ C		Viscosity index
	40 ⁰ C	100	
5.0	8.279	2.561	151
4.0	7.881	2.264	93
3.0	7.767	2.243	93
2.0	7.267	2.143	91
0.0	6.700	2.000	80

Table 4. Viscosity temperature characteristics of polymer sunflower oil(S-3) – BO1 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	7.829	2.542	173
4.0	7.984	2.389	121
3.0	7.889	2.321	107
2.0	7.632	2.218	93
0.0	6.700	2.000	80

Table 5. Viscosity temperature characteristics of copolymer of sunflower oil with MMA(S-4) – BO1 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	8.406	2.862	226
4.0	8.058	2.697	203
3.0	7.762	2.555	182
2.0	7.3735	2.343	144
0.0	6.700	2.000	80

Table 6. Viscosity temperature characteristics of copolymer of sunflower oil with DA(S-5) – BO1 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	8.586	3.043	262
4.0	8.381	2.873	230
3.0	8.172	2.657	184
2.0	7.964	2.342	109
0.0	6.700	2.000	80

Table 7. Viscosity temperature characteristics of poly(methyl methacrylate) (S-1) – BO2 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	27.676	6.412	197
4.0	26.485	5.350	139
3.0	25.705	4.916	116
2.0	25.180	4.645	100
0.0	24.229	4.390	89

Table 8. Viscosity temperature characteristics of poly(decyl acrylate) (S-2) – BO2 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	27.626	6.394	197
4.0	26.815	5.303	133
3.0	25.807	4.936	116
2.0	25.083	4.745	108
0.0	24.229	4.390	89

Table 9. Viscosity temperature characteristics of polymer of Sunflower oil (S-3) – BO2 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	27.975	6.705	212
4.0	26.532	5.345	139
3.0	26.110	5.131	127
2.0	25.156	4.487	89
0.0	24.229	4.390	89

Table 10. Viscosity temperature characteristics of copolymer of sunflower oil with MMA (S-4) – BO2 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	28.575	6.785	210
4.0	26.927	5.309	133
3.0	26.117	5.026	120
2.0	25.176	4.576	95
0.0	24.229	4.390	89

Table 11. Viscosity temperature characteristics of copolymer of sunflower oil with DA (S-5) – BO2 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	29.396	7.025	215
4.0	28.349	5.269	118
3.0	26.940	4.952	108
2.0	24.802	4.545	97
0.0	24.229	4.390	89

Table 12. Viscosity temperature characteristics of poly(methyl methacrylate) (S-1) – BO3 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	89.152	13.147	148
4.0	87.953	11.013	113
3.0	86.713	10.654	108
2.0	85.889	9.987	96
0.0	84.714	9.918	96

Table 13. Viscosity temperature characteristics of polymer of DA(S-2) – BO3 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	90.152	13.045	145
4.0	87.983	11.048	113
3.0	87.312	10.854	111
2.0	85.789	10.221	101
0.0	84.714	9.918	96

Table 14. Viscosity temperature characteristics of polymer of sunflower oil (S-3) - BO3 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	90.252	13.405	152
4.0	88.398	11.548	122
3.0	88.301	11.085	113
2.0	84.889	10.121	100
0.0	84.714	9.918	96

Table 15. Viscosity temperature characteristics of copolymer of sunflower oil with MMA(S-4) – BO3 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	89.112	13.104	148
4.0	88.748	11.048	112
3.0	88.312	10.854	109
2.0	86.789	10.321	101
0.0	84.714	9.918	96

Table 16. Viscosity temperature characteristics of copolymer of sunflower oil with DA (S-4) – BO3 blends

Additives (wt %)	Viscosity		Viscosity index
	40 ⁰ C	100 ⁰ C	
5.0	90.552	12.645	137
4.0	87.831	11.480	121
3.0	86.312	10.952	114
2.0	85.769	10.102	98
0.0	84.714	9.918	96

CHAPTER III

3.1 Experimental

3.1.1 Materials used

Methyl methacrylate, acrylic acid and styrene were purchased from Merck India Ltd. Decyl alcohol and toluene was procured from S.D fine Chem. India Ltd. and benzoyl peroxide (BZP) from LOBA chemicals. Methyl methacrylate, toluene and benzoyl peroxide were used after purification following the method as stated in Chapter III of Part I of this thesis. Styrene, acrylic acid, decyl alcohol and Sunflower oil (commercial grade) was used as such. Base oils were collected from Indian Oil Corporation Ltd., Dhakuria, Kolkata and Bharat Petroleum Corporation Ltd., Matigara, Darjeeling.

3.1.2 Preparation of copolymer and homopolymers

The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask, desired mass of sunflower oil and initiator benzoyl peroxide (BZP) was placed followed by desired mass of styrene was added drop wise for 3 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into 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. Polymer of Sunflower oil and copolymer of sunflower oil with Decyl acrylate (DA) and also with Methyl methacrylate (MMA) were synthesis in the same way.

3.1.3 Spectroscopic measurements

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

3.1.4 Viscometric measurements

Viscometric properties were determined at 40⁰C in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at least eight different concentration of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In the single point measurement the lowest value of solution concentration was chosen for the calculation. For the viscosity – average molecular weight determination, the constants $K = 0.00387$ dl/g and $a = 0.725$ were employed in Mark Houwink – Sukurda relation [24, 25]. Determination of intrinsic viscosity and viscometric parameters by using different equation Huggins, Kraemers, Martin, Schulz-Blaske, Solomon-Ciuta, and Deb- Chanterjee equation (equation 2 to 6) and Mark Houwink – Sukurda relation (equation 1) mentioned in Part 1, Chapter 1.

3.1.5 Thermo gravimetric analysis (TGA).

The thermo grams in air were obtained on a mettler TA – 3000 system, at a heating rate of 10 ⁰C / min.

3.1.6 Biodegradability test

In this work we studied the biodegradability of the prepared polymer samples (both the copolymer and homopolymer) against five different fungal pathogens namely *Calletotricheme camellia*, *Fussarium equisetae*, *Alterneria alternate*, *Colletrichum gleosproides* and *Curvularia eragrostidies*. All experiments were performed in petridishes and were incubated at 37⁰ C for 30 days after addition of definite weight of polymer samples. The fungal growth was confirmed by a change of yellow to blackish. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. All glass apparatus, culture media were autoclaved before use. The whole process was carried out in inoculation chamber. After 30 days polymer samples were recovered from the fungal media and washed with chloroform, purified and dried in an open vessel. The dried samples were weighed [26].

3.1.7 Evaluation of prepared polymer as pour point depressant in base oils

The prepared additives were evaluated as pour point depressant using base oils (BO1 and BO2) each of them collected from two different sources (S1 and S2), through the pour point test according to the ASTM-D-97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentrations. The experimental data were noted by taking an average of three experimental results under identical conditions

3.1.8 Evaluation of prepared polymer as viscosity index improvers in base oils

The various blends were prepared by using two different types of base stock (BO1 and BO2). Viscosity index of these oils were calculated to ASTM D2270-87 method using viscosity index calculator. The kinematic viscosity of the polymer doped base oils were determined at 40⁰C and 100⁰C. Range of concentration of the additives (in lube oils) used to study the effect of concentration on VI of the lube oil, were from 1 to 5 % (w/w) .

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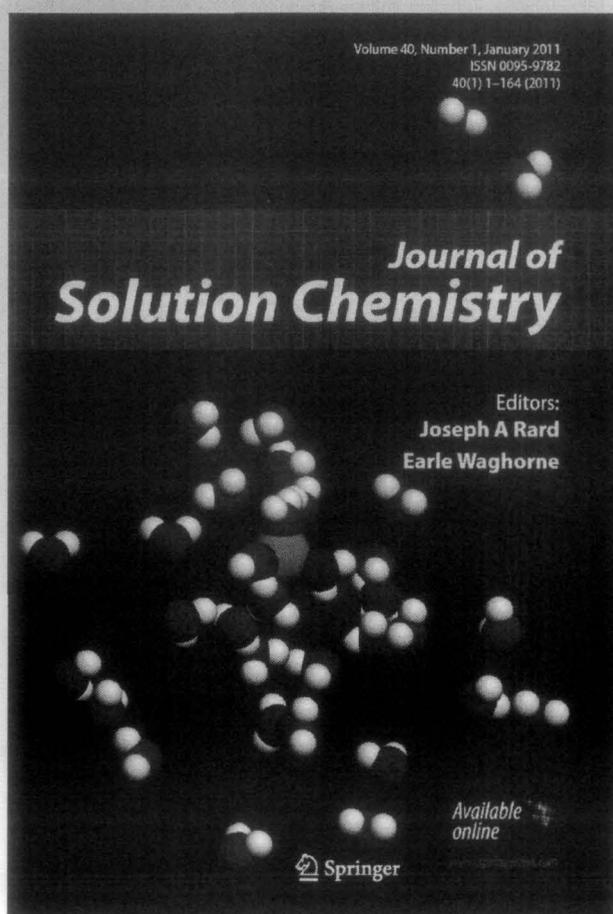
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*Synthesis Characterization and Viscosity
Studies of Homopolymer of Methyl
Methacrylate and Copolymer of Methyl
Methacrylate and Styrene*

**Journal of Solution
Chemistry**

ISSN 0095-9782
Volume 40
Number 1

J Solution Chem (2010)
40:67-78
DOI 10.1007/
s10953-010-9632-8



 Springer

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Synthesis Characterization and Viscosity Studies of Homopolymer of Methyl Methacrylate and Copolymer of Methyl Methacrylate and Styrene

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Received: 26 December 2009 / Accepted: 6 July 2010 / Published online: 4 December 2010
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Abstract A homopolymer of methyl methacrylate (MMA) and its copolymer with styrene at different compositions were synthesized and characterized. Viscosity measurements of the synthesized homopolymer and the copolymers in toluene solutions were performed at 313 K. Different equations were used to calculate the intrinsic viscosity, viscometric constants values, and molecular weight of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight obtained by the two methods (single point determination and graphical extrapolation) were compared in order to verify the validity of the single point determination for the polymers. Viscometric properties derived included the specific viscosity (it determines the contribution of the solute to the viscosity of the solution), the reduced viscosity (that provides a measure of the polymer capacity for increasing the solution viscosity), and the intrinsic viscosity.

Keywords Homopolymer · Copolymer · Intrinsic viscosity · Specific viscosity · Reduced viscosity · Rheological properties · Shear stability · Pour point depressant · Viscosity modifier

1 Introduction

Polymers of alkyl methacrylates are used as additives in lubricants for improving their viscometric and rheological properties [1–4]. They are also expected to provide additional performance characteristics such as improved low temperature fluidity and dispersancy. Although polyalkyl methacrylates (PAMAs) are the preferred type of additive in certain applications, they often contribute to the formation of deposits in the engine due to thermal instability of these additives under high temperature conditions. Any approach to overcome this shortcoming is always associated with a risk of affecting certain beneficial properties associated with normal polyalkyl methacrylates, such as pour point depressant (PPD) and good

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shear stability. Therefore, recent research on methacrylate additives has been concerned with copolymers of methacrylates with various stabilizing monomers.

It is well known that inclusion of styrene in the composition of an additive enhances the thermal stability of the copolymer compound in oil solution. Since homopolymers of styrene are insoluble in lube oil, they are introduced in the composition of the oil soluble polymer by copolymerization, which may then be useful PPD/VM (viscosity modifier) for petroleum and synthetic oil.

In this paper the results of our investigation involving the synthesis, characterization and viscometric measurement of MMA + styrene copolymers in comparison to the homopolymer of MMA will be discussed. Four copolymers from these two monomers were prepared by varying the styrene mass fractions in the monomer mixture from 2.5% to 10% and employing the free radical polymerization technique using benzoyl peroxide (BZP) as initiator in toluene as solvent. Polymerization was carried out following the procedure reported earlier [3]. A homopolymer of MMA was also prepared under identical conditions.

Physical characterization of the copolymers was carried out by employing gel permeation chromatography (GPC), thermogravimetric analysis (TGA), IR and NMR techniques. However, since performance of such additives under field conditions is very much dependent on the structure and morphology of the polymer in the desired solvent [5], viscometric studies in dilute solutions may give valuable information concerning the quality of the solvent or base stock employed and chain conformation in dilute solution. Since reports regarding such information is scanty [6, 7], and almost nil for polymers used as lube oil additives, the present research also includes a viscometric study of the copolymers as well as the homopolymer.

Viscometry is the simplest technique used to study macromolecules in solution and determine their molecular weight. According to the Houwink-Sukurda relation (Eq. 1), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = KM^a \quad (1)$$

where $[\eta]$, the intrinsic viscosity, can be calculated by using Eq. 2 to Eq. 7 below; the parameters 'K' and 'a' depends on the type of polymer, solvent, and temperature.

Because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from another technique, generally for determination of the molecular weight of samples using the available literature values of the constants used in that particular equation. A number of mathematical relations are available in the literature for the study of viscometric properties of a dilute polymer solution at a fixed temperature by graphic extrapolation [6–9]. The most commonly used equations are those of:

Huggins

$$\eta_{sp}/C = [\eta]_h + k_h[\eta]_h^2 C \quad (2)$$

Kremer

$$\ln(\eta_r/C) = [\eta]_k + k_k[\eta]_k^2 C \quad (3)$$

Martin

$$\ln(\eta_{sp}/C) = \ln[\eta]_m + k_m[\eta]_m C \quad (4)$$

and Schulz-Blaschke

$$\eta_{sp}/C = [\eta]_{sb} + k_{sb}[\eta]_{sb} \eta_{sp} \quad (5)$$

where C is the mass concentration, and $\eta_r = t/t_0$, the relative viscosity or viscosity ratio (where t is time flow of solution and t_0 is time flow of the pure solvent). The various viscosity quantities in these equations are:

$\eta_{sp} = \eta_r - 1$ specific viscosity

$[\eta]_h$ = intrinsic viscosity, respective to Huggins' equation

$[\eta]_k$ = intrinsic viscosity, respective to Kreamer's equation

$[\eta]_m$ = intrinsic viscosity, respective to Martin's equation

$[\eta]_{sb}$ = intrinsic viscosity or limiting number, respective to Schulz-Blaschke's equation

k_h, k_k, k_m and k_{sb} are the Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively.

Some relations have been proposed for determining the intrinsic viscosity in a dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analyzed in short period of time, practically in industrial laboratories. The most useful of them [6–10] are the Solomon-Ciute (SC, Eq. 6) and Deb-Chanterjee (DC, Eq. 7) relations.

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2} / C \quad (6)$$

$$[\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp})^{1/3} / C \quad (7)$$

These equations have been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$ [9].

The behavior of the polymeric additives towards a specific solvent/base stock plays a significant role in determining their action as a performance additive in their end application. Because viscometry provides very important data about the interaction of additives in base fluid and hence conformation of polymeric systems [5] in the base stock, the process of polymerization in the presence of a suitable solvent has been attracting considerable interest [11, 12].

Since the behavior of polymers, and especially copolymers, in solution is a complex phenomenon, a comparison involving the values of their intrinsic viscosity obtained by graphic extrapolation and by a single point determination should be interesting.

In this work viscometric parameters (intrinsic viscosity and the values of constants) of toluene solutions of polymethyl methacrylate and its copolymer consisting of several different percentages (wt/wt) of styrene was obtained by graphic extrapolation and single point determinations. The viscosity average molecular weights determined by using different equations are compared. The validity of the single point determination method for these types of polymers, in the investigated condition, is also discussed.

2 Experimental

2.1 Polymerization

The polymerization was carried out in a four-necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen, and a dropping funnel through which styrene was added drop wise. The desired mass of MMA and initiator (BZP), were placed in the flask followed by the drop wise addition of the desired mass of styrene over a 2 h period, in toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of this reaction time, the reaction mixture was poured into methanol

with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation from its hexane solution by methanol followed by drying under vacuum at 313 K. A homopolymer of MMA was similarly prepared and purified under the same conditions for use in the reference experiments.

2.2 Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells, and the spectra were recorded at room temperature over the wave number range (400 to 4000) cm^{-1} . NMR spectra were recorded in a Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe. CDCl_3 was used as solvent and TMS as the reference material. Average molecular weights (M_w and M_n) were obtained by SEC (GPC) using THF as mobile phase in a Water GPC system at (303 ± 1) K. The retention times were calibrated against known monodisperse polystyrene standards [5].

2.3 Viscometric Measurements

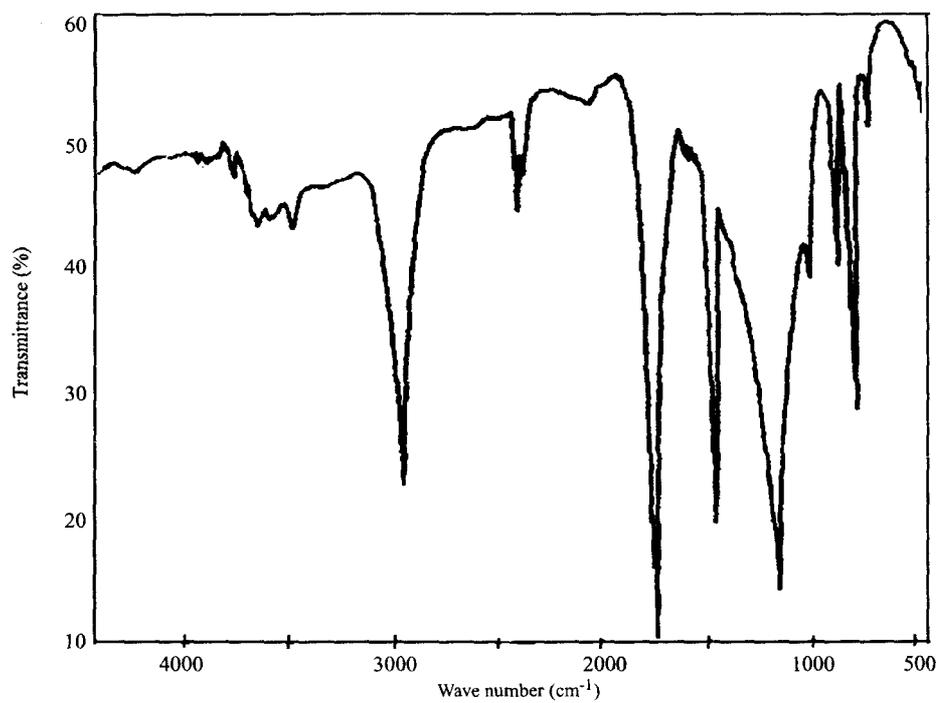
Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values $K' = 0.00268 \text{ cm}^2 \cdot \text{s}^{-2}$, $L = -19.83 \text{ cm}^2$, the volume of the bulb is 3 cm^3 and length of the capillary 11.3 cm). Experimental determinations were carried out by measuring flow times for at least nine different concentrations of $(0.2175 \text{ to } 0.087) \text{ g} \cdot \text{cm}^{-3}$ sample solutions. The flow time of the solution was manually determined by using a chronometer. In single point measurements the lowest solution concentration was chosen for the calculations. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against the viscosities of known solutions and the uncertainty was found to be nearly 0.17%. Precautions regarding prevention of evaporation of solvent were taken in all cases. For the viscosity-average molecular weight determination, the constants $K = 0.00387 \text{ dL} \cdot \text{g}^{-1}$ and $a = 0.725$ [13, 14] were employed.

2.4 Thermogravimetric Analysis (TGA)

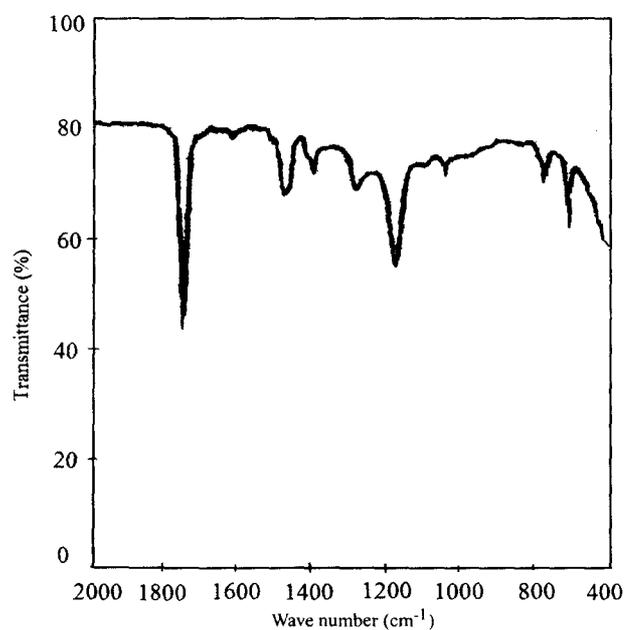
The thermograms were obtained in air on a Mettler TA-3000 system, at a heating rate of $10 \text{ K} \cdot \text{min}^{-1}$.

3 Results and Discussion

IR spectra of the homopolymer (Fig. 1a) show a peak at 1732 cm^{-1} due to the stretching vibration of an ester carbonyl group. A broad peak ranging from $(1260 \text{ to } 1000 \text{ cm}^{-1})$ appeared owing to the ester C–O stretching vibration, along with broad bands from $(950 \text{ to } 650) \text{ cm}^{-1}$ (C–H bending) and from $(3100 \text{ to } 2900) \text{ cm}^{-1}$ due to the presence of stretching vibrations. The existence of a copolymer was confirmed by IR (Fig. 1b) and NMR (Fig. 1c) analysis. The carbonyl stretching vibration at 1732 cm^{-1} of the homopolymer shifted to 1720 cm^{-1} in the copolymer. Peaks at 760 cm^{-1} and 697 cm^{-1} were attributed to the C–H bond of the phenyl group of styrene. In its ^1H NMR spectra, the presence of phenyl group in the copolymer was observed at 7.2 ppm and the $-\text{OCH}_2$ group from the acrylate at 3.9 ppm. The extent of incorporation of styrene into the polymer chain [Table 1] was determined through a comparison of the area of the $-\text{OCH}_2$ group at 3.9 ppm to the area of the signal



(a)



(b)

Fig. 1 (a) FT-IR spectrum of polymethyl methacrylate. (b) FT-IR spectrum of the copolymer of methyl methacrylate + styrene. (c) NMR spectrum of the copolymer of methyl methacrylate + styrene

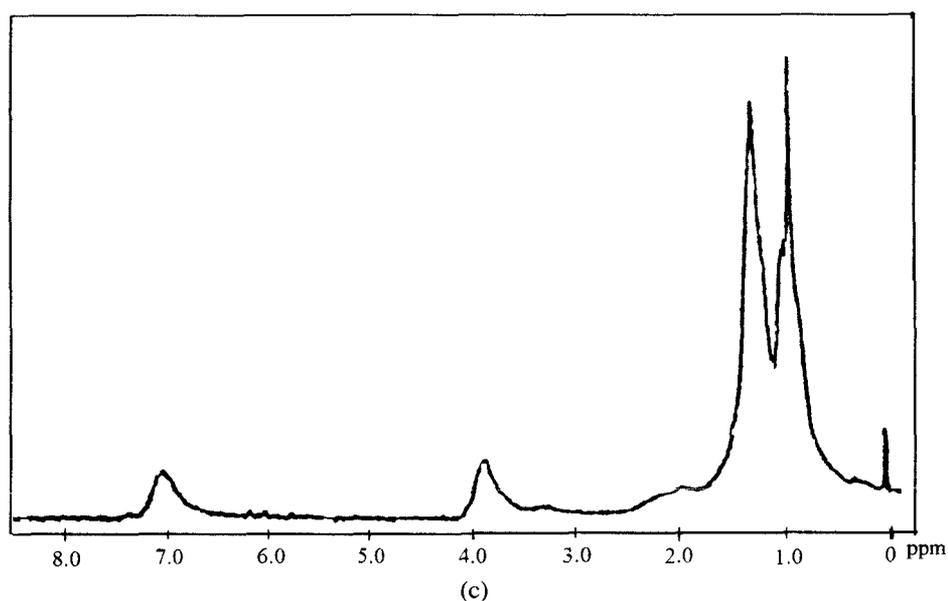


Fig. 1 (Continued.)

Table 1 Composition of the monomers in the copolymers in terms of mass fraction, determined by PMR and FT-IR spectrophotometric methods. Poly-1 is a homopolymer of methyl methacrylate (mma); Poly-2 through Poly-5 are copolymers of mma with different mass fractions of styrene

Polymer sample	Mass fraction in the feed		Mass fraction of styrene in the copolymer (PMR method)	Mass fraction of styrene in the copolymer (FT-IR method)
	MMA	Styrene		
Poly-1	1	–	–	–
Poly-2	0.975	0.025	0.01	0.015
Poly-3	0.95	0.05	0.02	0.023
Poly-4	0.925	0.075	0.035	0.037
Poly-5	0.90	0.10	0.04	0.045

due to phenyl protons at 7.2 ppm, based on earlier reports [15] as well as on the basis of our earlier paper [3], which was further verified through an analysis of FT-IR spectral data following a method also discussed in our earlier paper [3].

Table 2 presents a comparison between the values of molecular weight obtained by GPC and the TGA data for homo- and copolymers. The molecular weight increases with increase in the concentration of styrene added to the monomer. The TGA data shows that the copolymers have better thermal stability than the homopolymer.

Viscometric data were obtained using the six equations mentioned above. A linear relation for the plot of $\log_{10} \eta_{sp}$ versus $\log_{10} C[\eta]$ was obtained for all samples (Fig. 2) indicating that the measurements were performed in the Newtonian flow region [16, 17].

Using the graphic extrapolation method the respective intrinsic viscosities and constants were evaluated. In single point determinations, the SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is

Table 2 Molar mass obtained by gel permeation chromatography and thermogravimetric analysis for homo- and copolymers; M_n denotes the number average molecular weight, M_w the weight average molecular weight, and PWL the percentage weight loss

Polymer sample	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	TGA data	
			Decom. temp./°C	PWL
Poly-1	4.5	16	230/280	26/77
Poly-2	7.3	18	260/340	22/78
Poly-3	8.5	19	295/356	29/71
Poly-4	12	22	310/360	41/62
Poly-5	14.5	25	320/375	48/52

Table 3 Relative viscosity ($\eta_r = t/t_0$ where t_0 is the flow time of the pure solvent and t is the flow time of the solution) values at the concentration $0.2175 \text{ g}\cdot\text{cm}^{-3}$, for all prepared homo- and copolymer samples in toluene at 313 K, using an Ubbelohde OB viscometer having viscometer constants values of $K' = 0.00268 \text{ cm}^2\cdot\text{s}^{-2}$ and $L = -19.83 \text{ cm}^2$. The volume of the viscometer bulb is 3 cm^3 , and the length of the capillary 11.3 cm

Polymer sample	Relative viscosity ($\eta_r = t/t_0$)
Poly-1	6.890
Poly-2	4.086
Poly-3	10.464
Poly-4	13.547
Poly-5	14.122

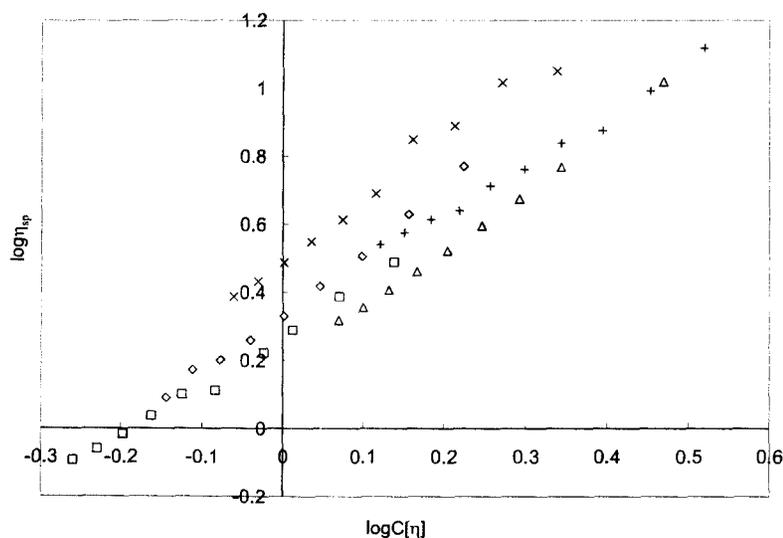


Fig. 2 Plot of $\log_{10} C[\eta]$ versus $\log_{10} \eta_{sp}$: \diamond , Poly-1; \square , Poly-2; Δ , Poly-3; \times , Poly-4, $+$, Poly-5

commonly applied in single point determination because the constant k_{sp} has been found to be very close to 0.28 for most polymer–solvent systems [6–10]. This same value is used here also.

Table 4 Intrinsic viscosity values for all prepared homo- and copolymer samples, calculated by using Eq. 2 to Eq. 7

Sample	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{sb}^a$	$[\eta]_{sb}^b$	$[\eta]_{sc}^c$	$[\eta]_{dc}^c$
Poly-1	7.69	9.38	7.75	9.71	9.83	9.95	10.72
Poly-2	6.32	7.1	6.89	7.36	7.52	7.51	7.94
Poly-3	13.5	14	14.78	15.61	15.39	15.81	17.68
Poly-4	14.4	14.69	12.18	15.91	16.53	17.94	20.35
Poly-5	15.12	15.02	16.88	18.2	16.694	18.17	21.41

^aFrom extrapolation of graph

^bSingle point determination ($k_{sb} = 0.28$)

^cSingle point determination: h, k, m, sb, sc and dc refers Huggin, Kraemer, Martin, Schulz-Blaschke, Solomon-Ciute and Deb-Chanterjee equations, respectively

Table 4 presents intrinsic viscosity values, calculated from respective relative viscosity values (Table 3), related to all equations for the studied samples. Taking into account the data for homo- and all copolymer samples, it can be noticed that, except for one or two cases, the values are consistent. Comparison among the copolymers indicated that there is a gradual increase of $[\eta]$ values with increasing styrene content in the copolymer. This indicates a more extended conformation of the copolymer chain compared to PMMA itself. Again, the change observed for Poly-3 to Poly-5 is not very significant, i.e., increasing the styrene concentration beyond 5% does not contribute much towards the $[\eta]$ value of the synthesized polymer. This may be because of the loss of flexibility of the polymer chain as the proportion of styrene increases in the copolymer. The same observation is also found in the case of Poly-2, in which the flexibility of the polymethacrylate chain may be restricted in the presence of styrene. However, beyond a concentration of 2.5% of styrene, the hydrodynamic volume exceeds that of PMMA which may reach a limiting value when the concentration of styrene is raised to 5% in the feed. Therefore, a sharp increment of $[\eta]$ is observed at 5% styrene content [18, 19].

Although different intrinsic viscosity values may be found by graphic extrapolation of the Huggins, Kraemer, Martin and SB equations (Eqs. 2 to 6), in this work the data obtained from these four equations showed a tendency to be close for the homopolymers and copolymers. For the homopolymer and copolymer, the $[\eta]_{int}$ value obtained from Huggins and Kraemer equations were similar.

Both homopolymer and copolymer viscosities in toluene medium indicate poor solvation (Table 5), as is evident from the respective viscometric constant values, and thus points to the formation of micelle or spherical structures as discussed earlier [5]. This conclusion is further supported by the positive values of the Kraemer coefficient for the all the systems analyzed. However, it is interesting to note that for all of the polymers in toluene, the k_{sb} values were close to 0.28. Thus it can be concluded that the relation $k_h + k_k \neq 0.5$ did not restrict application of the SB equation.

The relation $k_k + k_h = 0.5$ was not found for the samples analyzed (Table 5), but our findings are similar to those reported elsewhere [17]. The maximum deviation for the homopolymer of MMA may be attributed to the comparatively poor solubility of this polymer in toluene.

By comparing the $[\eta]$ values of PMMA and the copolymers determined through graphic extrapolation using the Kraemer, Martin and SB equations, with the values determined by the Huggins equation also from graphic extrapolation, it can be noticed that the range

Table 5 Viscometric constants obtained for all prepared homo- and copolymer samples where k_h , k_k , k_m and k_{sb} denote the Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively

samples	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
Poly-1	1.006	0.093	0.740	0.294	1.099
Poly-2	0.816	0.078	0.476	0.311	0.894
Poly-3	0.639	0.0006	0.377	0.247	0.640
Poly-4	0.76	0.031	0.760	0.305	0.791
Poly-5	0.678	0.038	0.356	0.227	0.716

Table 6 Percentage differences ($\Delta = ([\eta]/[\eta]_h) - 1$) obtained for intrinsic viscosity values, with Huggins' equation taken as a reference

Sample	100 Δ					
	K ^a	M ^a	SB ^a	SB ^b	SC ^b	DC ^b
Poly-1	21.97	0.78	26.31	27.88	29.39	39.36
Poly-2	12.34	9.003	16.45	19.01	18.87	25.69
Poly-3	3.70	9.48	15.55	14.01	17.11	30.96
Poly-4	2.01	-15.43	10.48	14.79	24.58	41.41
Poly-5	-0.66	11.64	20.37	10.41	20.15	41.60

^aData from extrapolation

^bData from single point determination

Table 7 Determination of molecular weight by Houwink's equation $[\eta] = KM^a$, where $K = 0.00387 \text{ dL} \cdot \text{g}^{-1}$ and $a = 0.725$

Sample	($M_h \times 10^{-4}$) ^a	($M_k \times 10^{-4}$) ^a	($M_m \times 10^{-4}$) ^a	($M_{sb} \times 10^{-4}$) ^a	($M_{sb} \times 10^{-4}$) ^b	($M_{sc} \times 10^{-4}$) ^b	($M_{dc} \times 10^{-4}$) ^b
Poly-1	3.54	4.65	3.58	4.88	4.97	5.05	5.59
Poly-2	2.70	3.17	3.04	3.33	3.43	3.43	3.70
Poly-3	7.69	8.09	8.71	9.99	9.22	9.56	11.16
Poly-4	8.41	8.64	6.67	9.65	10.17	11.38	13.54
Poly-5	8.99	8.91	10.47	11.62	10.31	11.58	14.54

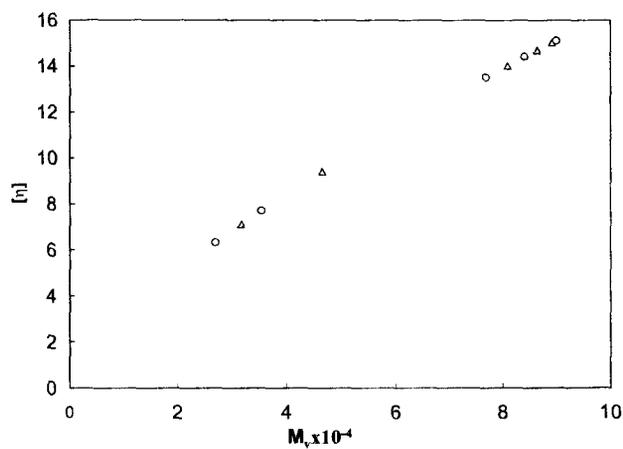
^aData from extrapolation

^bData from single point determination

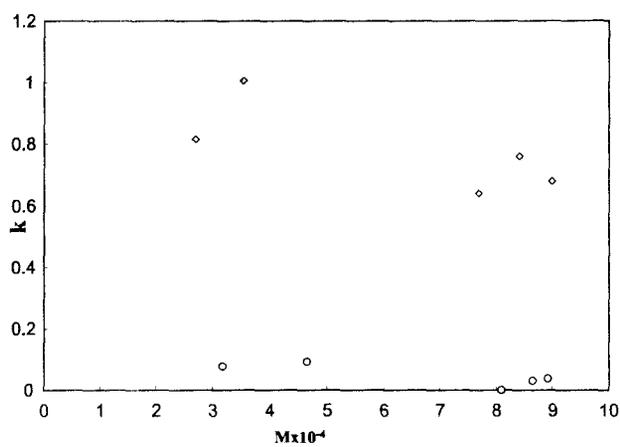
(-15.43 to 26.31%, Table 6) is narrow when compared to values obtained through the single point method using the SB, SC and DC equations (10.43 to 41.40%). Again, the percentage differences ($\Delta = ([\eta]/[\eta]_h) - 1$) for the homopolymer are always higher (except one in each case) than for the copolymer, both in graphical extrapolation and single point determinations (Table 6). This may be because the homopolymer PMMA, with lowest molecular weight ($M_n 45000 \text{ g} \cdot \text{mol}^{-1}$) in toluene (which is not a good solvent), seemed to produce higher differences, both in the graphical extrapolation and in the one point determination.

A close observation of the intrinsic viscosity values (Table 6) indicated that, for the copolymer system analyzed, the SB equation, which is widely applied in industry quality control laboratories, should be the most suitable for application in one point determinations. This table also indicates that for PMMA, the graphical extrapolation method seems to be more suitable in toluene rather than the single point determination, and the Martin equation

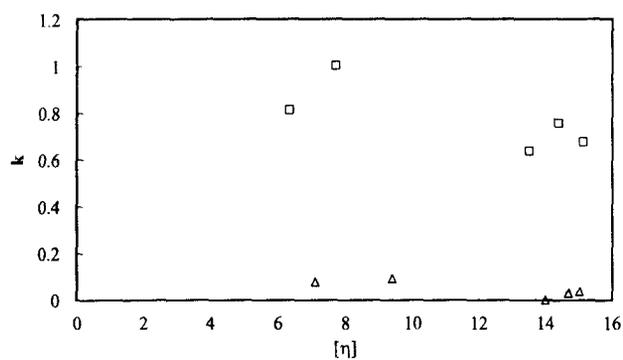
Fig. 3 (a) Plot of the intrinsic viscosity ($[\eta]$) versus the viscometric molecular weight ($M_v \times 10^{-4}$): \circ , Huggins' value; Δ , Kraemer's value. (b) Plot of the viscometric constant (k) versus the molecular weight ($M \times 10^{-4}$): \diamond , Huggins' value; \circ , Kraemer's value. (c) Plot of the viscometric constant (k) versus the intrinsic viscosity ($[\eta]$): \square , Huggins' value; Δ , Kraemer's value



(a)



(b)



(c)

Table 8 Percentage differences obtained for viscometric molecular weight values where $\Delta = (M/M_h) - 100$, Huggins' equation taken as a reference

Sample	100 Δ					
	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
Poly-1	31.52	1.07	38.02	40.38	42.67	58.06
Poly-2	17.40	12.64	23.38	27.10	26.90	37.00
Poly-3	50.14	13.30	29.80	19.80	24.34	45.12
Poly-4	2.78	-20.60	14.74	20.95	35.40	61.08
Poly-5	-0.91	16.40	29.10	14.60	28.80	61.00

^aData from extrapolation

^bData from single point determination

produced the lowest deviation values among the four when compared to those obtained from Huggins' equation.

Table 7 presents a comparison among the values of molecular weight obtained by the GPC and viscometric methods for the homopolymer and copolymers analyzed. The general trend in all cases (except Poly-2) is a gradual increase in molecular weight with increase of the styrene concentration. However, as expected, a difference was observed between the values of molecular weight obtained by GPC and viscometry. This is probably due to the differences in analysis conditions, such as solvents, temperature techniques and standards employed [20].

By comparing the viscosity molecular weight with the number average molecular weight obtained by GPC, it can be seen that the graphical extrapolation values are closer to the SEC values rather than to the single point determination values. The percentage differences ($\Delta = (M/M_h) - 1$), obtained for viscometric molecular weight values, are shown in Table 8. These values were calculated taking M_v values determined by Huggins' equation as a reference. The Martin equation showed the smallest Δ differences.

Plot of M_v and $[\eta]$ obtained by both the Huggins and Kraemer equations, the most commonly employed relations in viscometry, showed a linear relationship (Fig. 3a). However, the plots involving M_v and $[\eta]$ versus the respective constant, k , showed a similar relation but it was not linear (Fig. 3b and c). Thus, the nature and extent of interactions involving the solvent and polymers (homo- and copolymers), used as additives for lubricating oil, at different concentrations cannot be predicted by these two equations. However the intrinsic viscosity values may be correlated with the viscosity average (M_v) molecular weight.

4 Conclusions

Viscometric parameters determined by graphic extrapolation and by single point determinations point towards greater compatibility of the copolymers with the solvent in comparison to the homopolymer. Thus, introduction of styrene enhances the solubility and thermal stability, and thus it may also enhance the performance of the polymer as well when used in field applications as a performance additive (like VM or PPD). The study also indicates that performance evaluation of this kind of additive may be done in a very simple way (viscometric method) when the other types of equipment are not available.

Acknowledgements Thanks are due to University Grants Commission, New Delhi for financial assistance.

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Synthesis of Copolymers and Homopolymers of Methyl Methacrylate and Styrene and Studies on their Viscometric Properties in Three Different Solvents

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Abstract

Homopolymer of methyl methacrylate (PMMA) and styrene (PS) and their copolymers were synthesized and characterized. The viscometric measurements of the synthesized homopolymers as well as the copolymers were performed in three different solvents. Different equations were used to calculate intrinsic viscosity and viscometric constant values of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight obtained by the two methods (single point determination and graphical extrapolation) were compared. Measurements of viscometric properties included the determination of specific viscosity (it determines the contribution of solute to the viscosity of the solution), the reduced viscosity (that provides the measurements of the polymer capacity of increasing the solution viscosity) and intrinsic viscosity.

Keywords: Homopolymer, Copolymer, Intrinsic viscosity, Specific viscosity, Reduced viscosity, Rheological properties, Shear stability, Pour point depressant, Viscosity modifier.

Introduction

Polymers of alkyl methacrylate are used in lubricant compositions for improving the viscometric and rheological properties of the lubricant^{1, 2}. They are also looked upon to provide additional performance characteristics such as improved low temperature fluidity and dispersancy. However, owing to the presence of quaternary C-atom in the polymer chain, they readily undergo depolymerization with a constant decrease of the oil viscosity compounded with these polymers. Therefore, the recent research on methacrylate additives has been concerned on copolymers of it with stabilizing monomer. Since it is well known that inclusion of styrene in the composition of an additive increases the thermal stability of the co polymer, copolymerization of methyl methacrylate with different concentration of styrene has been carried out which may be useful as a pour point depressant or viscosity modifier for petroleum and synthetic oil.

Again, since the performance of such kind of additives in the field condition is very much dependent on the structure and morphology of the polymers in dissolved solvent³, viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation of the polymer in dilute solutions are concerned. Therefore, the study may be very useful for evaluating the performance of polymer blended oil as an additive for lube oil, where the structure and morphology plays a significant role. Despite this, such information regarding lube oil additives is not yet emphasized.

Several mathematical equations available in literature⁴⁻⁸ may also be applied here to determine the viscometric parameters of the polymer blended solvent / oil at determined temperature either by graphic extrapolation (equation 1-4) or by single point determination (equation 5-6).

$$\text{Huggins (H): } \eta_{sp}/C = [\eta]_h + k_h[\eta]_h^2 C \quad \dots(1)$$

$$\text{Kraemer (K): } \ln \eta_r/C = [\eta]_k - k_k[\eta]_k^2 C \quad \dots(2)$$

$$\text{Martin (M): } \ln(\eta_{sp}/C) = \ln[\eta]_m + k_m[\eta]_m C \quad \dots(3)$$

$$\text{Schulz-Blaschke (SB): } \eta_{sp}/C = [\eta]_{sb} + k_{sb}[\eta]_{sb}\eta_{sp} \quad \dots(4)$$

$$\text{Solomon-Ciuta (SC): } [\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2}/C \quad \dots(5)$$

$$\text{Deb-Chanterjee (DC): } [\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp})^{1/2}/C \quad \dots(6)$$

where, $\eta_r = t/t_0$ relative viscosity or viscosity ratio (efflux time ratio between the solution in a determined concentration and the solvent); η_{sp} specific viscosity ($\eta_{sp} = \eta_r - 1$); $\eta_{sp}/C = \eta_{red}$ reduced viscosity or viscosity number; $\ln \eta_r/C = \eta_{inh}$ inherent viscosity or logarithmic viscosity number; $[\eta]_h = \lim_{c \rightarrow 0} \eta_{red}$ intrinsic viscosity or limiting viscosity number, respective to Huggins equation; $[\eta]_k = \lim_{c \rightarrow 0} \eta_{inh}$ intrinsic viscosity or limiting viscosity number, respective to Kraemer equation; $[\eta]_m = \lim_{c \rightarrow 0} \ln \eta_{red}$ intrinsic viscosity or limiting viscosity number, respective to Martin equation and $[\eta]_{sb} = \lim_{c \rightarrow 0} \eta_{red}$ intrinsic viscosity or limiting viscosity number respective to Schulz-Blaschke equation; k_h , k_k , k_m and k_{sb} are Huggins, Kramer, Martin and Schulz-Blaschke coefficients respectively. It has been observed that $k_{sb} = 0.28$ for many systems in dilute solution.⁴⁻⁸

The method of single point determination (equation 5-6) has the advantage of being considerably faster and can be adequate when a large number of samples are to be analyzed in short periods of time, particularly in industry laboratories. The use of these equations has been derived under the supposition of the validity of the relationship⁷ $k_b + k_k = 0.5$.

Polymer samples may present the same molecular mass but may also be linear or branched showing different sizes and shapes. The conformation of the chain in solution and, consequently, the volume it occupies in the solvent medium, is completely dependent on the type of solvent and the temperature of the measurement. The better is the solvent, the higher extended conformation the chain will assume¹. Thus the viscometric study, which is a function of molecular size and not the molecular mass, of the polymer solutions in different solvents may yield very useful parameters required for the choice of end application of the polymers.

Huggins and Kraemer coefficients are adequate to evaluate the quality of the solvent. Huggins coefficient (k_h) is accepted as a parameter related to polymer-solvent interactions. Experimental results indicate that the higher is the affinity between polymer and solvent, the lower is the k_h value. A range varying from 0.25 to 0.5 is attributed to good solvation whereas values above 0.5-1.0 are found for poor solvents and theta solvents³⁻⁷. At the same time, negative values for the Kraemer coefficient (k_k) indicate good solvents and positive values indicate poor ones³⁻⁵.

Taking into account the complex behavior of copolymers in solution, a comparison involving the values of intrinsic viscosity obtained by graphic extrapolation and by a single point determination should be interesting. In this case, an evaluation involving deviations between both values and the possibility of applying the latter measurement, which is faster, in copolymer samples should be considered.

Material and Methods

Polymerization: The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel to add styrene drop wise. In the flask was placed desired amount of methyl methacrylate (MMA) and initiator benzoyl peroxide (BZP) followed by the desired weight of styrene added drop wise for 2 hr in the presence of toluene as solvent. The reaction temperature was maintained at 80°C for 6 hr. At the end of the reaction time, the reaction mixture was poured into 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 40 °C. Homopolymer of MMA and styrene was similarly prepared under the same conditions for use in reference experiments.

Measurements: IR spectra were recorded on a Shimadzu FT IR - 8300. NMR spectra were recorded on a Bruker 300 MHz FT NMR, using $CDCl_3$ as solvent. Average molecular weights (M_w and M_n) were obtained by SEC (GPC) using THF as mobile phase in a Water GPC system at 30 ± 1 °C. The retention times were calibrated against known monodisperse polystyrene standards.³

Viscometric measurements: Viscometric properties were determined at 25 °C in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at least with nine different concentration of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. For the viscosity - average molecular weight determination, the constants $k = 0.00387$ dl/g and $a = 0.725$ were employed.^{13,14}

Thermo gravimetric analysis (TGA): The thermo grams in air were obtained on a mettler TA - 3000 system, at a heating rate of 10 °C / min.

Results and Discussion

In its IR spectra the homopolymer, PMMA showed a peak at 1722 cm^{-1} for the ester carbonyl function. IR and NMR analysis confirmed the existence of the copolymer. The IR spectra showed a peak at 1720 cm^{-1} which was attributed to the carbonyl group of the methyl methacrylate whereas the absorption bands at 760 and 697 cm^{-1} were attributed to the C - H band of the phenyl group of styrene.

¹H NMR spectra indicated the presence of a phenyl group at 7.2 ppm and a -OCH₂ group from the acrylate at 3.9 ppm. The absence of signals between 5 and 6 ppm indicated the absence of vinylic protons of styrene.

Table I presents a comparison between the values of molecular mass obtained by GPC for homo polymer and copolymers along with the polydispersity. As reported earlier⁹, the molecular weight increases with the increase in the concentration of styrene in the monomer composition. Higher values of polydispersity were observed for the copolymers.

Viscometric data were acquired using the six equations mentioned. Linear relationship for the plot of $\log h_{sp}$ vs. $\log c$ [h] (Fig 1a-1c) indicated that the measurements were performed in Newtonian flow¹⁰⁻¹². Huggins (H), Kraemer (K), Martin (M) and Schulz-Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz-Blaschke (SB), Solomon-Ciuta (SC) and Deb-Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz-Blaschke (SB) equation

is commonly applied in single point determinations because it was found that $k_{sb} = 0.28$ for many polymer-solvent systems⁴⁻⁸. In this work, this value has been used.

Tables IIA-IIC present intrinsic viscosity values related to all equations for the samples analyzed. Considering the different solvent employed (CHCl_3 , Toluene, CCl_4) and comparing $[\eta]$ for homo and copolymers, it is noticed that the higher values were obtained in chloroform followed by carbon tetrachloride and toluene. Thus considering all the polymers (homo polymer and co polymers), chloroform appeared to be more compatible to the polymer, leading to more extended conformations of the polymers. Carbon tetrachloride leads to the lowest values for the homo and copolymers, which varied in a small range in comparison to the other solvents, indicating similar contracted structures with a star like conformation⁹. Variation of $[\eta]$ obtained by graphic extrapolation method (equation 1-4) was found to be less compared to those obtained by single point determination method (equation 5-6) without any restriction of solvent.

As expected, the copolymer and also the homo polymers did not show a correlation or a constant variation as far as $[\eta]$ values, molecular weights and compositions are concerned³. It is also observed that $[\eta]$ values increase with the increase in styrene concentration except in one or two cases. $[\eta]$ values obtained by using DC equation are always higher irrespective of the nature of the solvent. PMMA was insoluble in CCl_4 .

Tables IIIA – IIIC present the viscometric constant calculated for homo and co polymers in CHCl_3 , k_b and k_k fitted in the range of good solvents, whereas CCl_4 medium produced results indicating poor solvation suggesting the formation of micellar spherical structure.³

Although k_{sb} values found for the samples were different from 0.28, the use of these value for the single point determination produced $[\eta]_{sb}$ values close to the ones obtained by extrapolation. It is also interesting to notice that for the best solvent CHCl_3 , k_{sb} values for the co polymer were close to 0.28. It is also important to observe that the relation $k_b + k_k = 0.5$ was not found for the great majority of the samples analyzed. However, both $[\eta]_{sc}$ and $[\eta]_{dc}$ were similar to $[\eta]_b$, $[\eta]_k$, $[\eta]_m$ and $[\eta]_{sb}$ which were obtained by graphic extrapolation with small percentage differences. So values different from 0.5 did not put any restriction for the application of SC equation.

Tables IVA-IVC present percentage differences ($\Delta\%$) calculated from intrinsic viscosity values obtained by K, M, SB, SC and DC equations when compared with the values produced by H equation.

As expected different $[\eta]$ values were obtained by graphic extrapolation of H, K, M and SB equations³⁻⁷ in all

the three solvents analyzed. In CHCl_3 the percentage differences of $[\eta]$ values obtained for both the homo and copolymers when K, M and SB equations (graphic extrapolation) were compared to H equation, varied in the range from -23.07 to 14.38 and are less compared to the values (-12.53 to 92.89) obtained by using SB, SC and DC equations (single point determination method). In toluene, the variation ranges are from -20.00 to 66.96 and 23.45 to 66.96 respectively. In CCl_4 the percentage variation is much higher in both the cases. This suggests that the contracted structure of the homo and copolymers in CCl_4 solvent produces higher differences, both in graphic extrapolation and in one point determinations.

In comparison to graphic extrapolation method, the determination employing single point led to higher percentage differences in the values of intrinsic viscosities for all the polymers (homo and copolymers) in all the solvents analyzed and SB equation seems to be better than the other two methods SC and DC.

Table V presents the thermal stability of the polymers. As expected, the TGA data showed that the copolymers are better in thermal stability than the homopolymers. Table VI presents the molecular weight obtained by viscometric methods (Mv) for homo polymer and co polymers analyzed. The general trend is a gradual increase in molecular weight with the increase of styrene concentration. However, as expected, a difference was observed in the values of molecular weight (Mv) obtained by SEC and viscometry. This is probably due to the differences in analysis conditions like solvents, temperature, techniques and standard employed¹⁵.

By comparing viscosity molecular weight (Mv) obtained in different solvents with number average molecular weight obtained by SEC, it can be seen that Mv obtained in CHCl_3 was found to be more close to the SEC values than the same obtained in other two solvents which may be attributed to the comparatively poor solubility of the polymer in these solvents as observed above in this study. It is also observed that in all the cases and irrespective of the solvents, the single point determination values are more close to that of the SEC values rather than the graphical extrapolation values.

Conclusion

Viscometric parameters are determined by graphic extrapolation and by single point determination points towards the more compatibility of the co polymers with the solvent in comparison to the homopolymer. Best results are obtained when chloroform is used as solvent for the study. Introduction of styrene enhances the solubility, the thermal stability and thus may also enhance the performance of the polymer as well when used in the field application as a performance additive (like VM or PPD). The study also

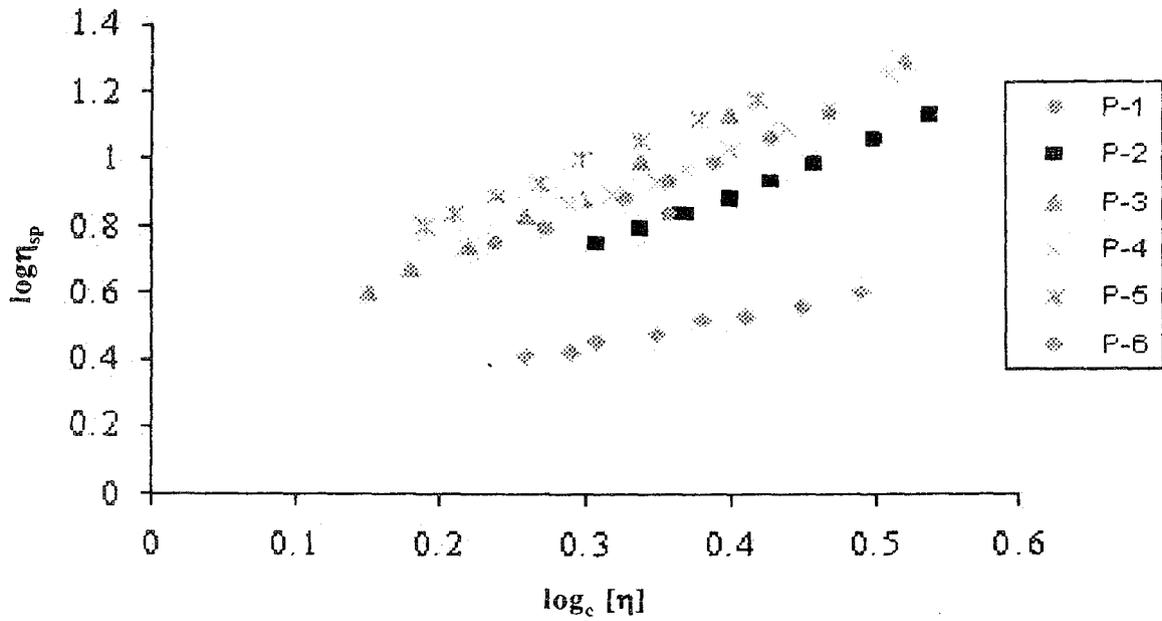


Fig. 1a: Plot of $\log \eta_{sp}$ Vs $\log_e [\eta]$ for chloroform solvent

Table I
Molecular weight of the polymers

Polymer No.	Percent styrene (w/w) in the monomer composition	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	Polydispersity
P-1 ^c	0.0	4.5	14	1.3
P-2 ^d	100.0	6.5	15	3.4
P-3 ^e	2.5	7.3	18	3.9
P-4 ^f	5.0	9.5	20	4.0
P-5 ^g	7.5	12.5	22	6.8
P-6 ^h	10.0	14.0	26	10.2

Table II A
Intrinsic Viscosity Data in chloroform solvent

Polymer No.	$[\eta]_c^a$	$[\eta]_c^b$	$[\eta]_{sp}^c$	$[\eta]_{sp}^d$	$[\eta]_{sp}^e (0.2\%)$	$[\eta]_{sp}^f$	$[\eta]_{sp}^g$
P-1 ^c	13.00	11.00	14.87	10.00	11.37	12.26	13.84
P-2 ^d	13.54	12.64	12.18	12.00	14.23	17.78	21.53
P-3 ^e	10.50	9.50	9.02	11.00	11.85	13.75	16.12
P-4 ^f	14.50	15.00	16.44	14.40	16.64	22.44	27.97
P-5 ^g	15.00	14.87	14.15	14.00	17.32	22.28	27.20
P-6 ^h	15.46	15.50	14.87	15.00	16.61	20.74	25.12

a- Graphic extrapolation method, b-single point determination method, c- homo polymer of mma, d- homo polymer of styrene, e- co polymer of mma and styrene(2.5%), f- co polymer of mma and styrene(5%), g- co polymer of mna and styrene (7.5%) . h - co polymer of mma and styrene (10%)

Table II B
Intrinsic Viscosity Data in toluene solvent

Polymer No.	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{ab}^a$	$[\eta]_{ab}^b (0.28)$	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1 ^c	5.50	5.33	4.48	4.40	6.84	6.79	7.08
P-2 ^d	12.00	13.50	10.48	10.00	15.30	15.83	17.39
P-3 ^e	6.00	7.77	6.05	5.62	9.04	9.02	9.53
P-4 ^f	9.33	12.8	9.83	8.50	13.96	14.30	15.58
P-5 ^g	10.40	13.10	11.34	9.60	14.44	14.84	16.22
P-6 ^h	11.20	14.00	10.88	9.20	14.81	15.26	16.71

Table II C
Intrinsic Viscosity Data in carbon tetrachloride solvent

Polymer No.	$[\eta]_h^a$	$[\eta]_k^a$	$[\eta]_m^a$	$[\eta]_{ab}^a$	$[\eta]_{ab}^b (0.28)$	$[\eta]_{sc}^b$	$[\eta]_{dc}^b$
P-1 ^c	-	-	-	-	-	-	-
P-2 ^d	10.00	13.00	12.18	10.00	15.19	17.22	19.96
P-3 ^e	5.00	6.40	4.95	7.00	10.31	11.04	12.42
P-4 ^f	6.25	8.00	5.85	5.70	13.17	15.14	17.69
P-5 ^g	10.00	13.00	7.39	10.00	14.17	16.84	16.25
P-6 ^h	11.00	12.80	11.02	10.50	15.75	18.08	21.11

Table III A
Viscometric constant values in chloroform

Polymer No.	k_h	k_k	k_m	k_{ab}	$k_h + k_k$
P-1 ^c	0.29	0.08	0.14	0.37	0.37
P-2 ^d	0.82	0.01	0.58	0.36	0.83
P-3 ^e	0.83	0.05	0.97	0.32	0.89
P-4 ^f	1.20	8.99×10^{-3}	0.48	0.35	1.21
P-5 ^g	1.10	3.48×10^{-3}	0.65	0.38	1.10
P-6 ^h	0.86	0.04	0.54	0.33	0.89

Table III B
Viscometric constant values in toluene

Polymer No.	k_h	k_k	k_m	k_{ab}	$k_h + k_k$
P-1 ^c	1.08	-0.42	1.69	1.33	0.66
P-2 ^d	0.97	0.02	0.96	0.73	0.99
P-3 ^e	1.90	0.07	1.33	1.15	1.97
P-4 ^f	1.59	0.05	0.72	0.88	1.64
P-5 ^g	1.27	0.05	0.70	0.79	1.32
P-6 ^h	1.09	0.08	0.08	0.81	1.17

Table III C
Viscometric constant values in carbon tetrachloride

Polymer No.	k_1	k_2	k_m	k_{ab}	k_1+k_2
P-1 ^c	-	-	-	-	-
P-2 ^d	1.73	0.11	0.24	0.57	1.84
P-3 ^e	3.51	0.41	1.8	0.60	3.92
P-4 ^f	3.84	0.36	1.87	0.99	4.20
P-5 ^g	1.57	0.03	1.41	0.48	1.60
P-6 ^h	1.52	0.03	0.83	0.55	1.55

Table IV A
Percentual difference of intrinsic viscosity with respect to Huggins intrinsic viscosity
(Using chloroform solvent)

Polymer No.	K ^c	M ^c	SB ^a	SB ^b	SC ^b	DC ^b
P-1 ^c	-15.38	14.38	-23.07	-12.53	-5.69	6.46
P-2 ^d	-6.65	-10.04	-11.37	5.09	31.31	58.93
P-3 ^e	-9.52	-14.09	4.76	12.85	30.95	53.52
P-4 ^f	3.44	13.37	-0.69	14.75	54.75	92.89
P-5 ^g	-0.86	-5.66	-6.66	15.46	48.53	81.33
P-6 ^h	0.25	-3.81	-2.97	7.37	34.15	62.41

Table IV B
Percentual difference of intrinsic viscosity with respect to Huggins intrinsic viscosity
(Using toluene solvent)

Polymer No.	K ^c	M ^c	SB ^a	SB ^b	SC ^b	DC ^b
P-1 ^c	-3.09	-18.54	-20.00	24.36	23.45	28.72
P-2 ^d	12.50	-12.66	-16.66	27.55	28.16	44.91
P-3 ^e	29.50	0.75	-6.33	50.6	50.33	58.90
P-4 ^f	37.19	5.36	-8.89	49.66	53.27	66.96
P-5 ^g	25.92	9.04	-7.69	38.87	42.98	55.90
P-6 ^h	25.00	-2.87	-17.85	32.23	36.25	49.19

Table IV C
Percentual difference of intrinsic viscosity with respect to Huggins intrinsic viscosity
(Using carbon tetrachloride solvent)

Polymer No.	K ^a	M ^a	SB ^a	SB ^b	SC ^b	DC ^b
P-1 ^c	—	-	-	-	-	-
P-2 ^d	30.00	21.80	0.00	51.92	72.20	99.60
P-3 ^e	28.00	-1.00	40.00	106.20	120.80	148.40
P-4 ^f	28	-6.4	-8.8	110	142.24	183.1
P-5 ^g	30.00	-26.10	0.00	41.69	68.40	62.50
P-6 ^h	16.36	0.18	-4.50	43.52	64.36	91.90

Table V
TGA data for homo and co polymers

Polymer No.	TGA data	
	Decom. Temp., °C	% Weight Loss
P-1 ^c	280/300	26/77
P-2 ^d	445/462	42/58
P-3 ^e	310/340	29/71
P-4 ^f	351/372	41/62
P-5 ^g	380/395	48/52
P-6 ^h	410/437	49/52

indicated that viscometric analysis may be very useful for performance evaluation of this kind of additive when the other equipments are not available.

Acknowledgement

Thanks are due to University Grants Commission, New Delhi for financial assistance.

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Table VI
Determination of molecular weight by Mark Houwinks equation $[\eta] = KM^a$
where $K = 0.00387 \text{ dl/g}$ and $a = 0.725$

Using chloroform solvent

Polymer No	$M_n^* \times 10^{-4}$	$M_w^* \times 10^{-4}$	$M_m^* \times 10^{-4}$	$M_{ab}^* \times 10^{-4}$	$M_{ab}^b \times 10^{-4}$	$M_{ac}^b \times 10^{-4}$	$M_{dc}^b \times 10^{-4}$
P-1 ^c	7.30	5.80	8.79	5.08	6.07	6.74	7.96
P-2 ^d	7.73	7.03	6.68	6.54	8.27	11.25	14.65
P-3 ^e	5.44	4.74	4.41	5.80	6.43	7.89	9.83
P-4 ^f	8.49	8.90	10.10	8.41	10.27	15.51	21.02
P-5 ^g	8.90	8.79	8.21	8.09	10.85	15.36	20.23
P-6 ^h	9.28	9.31	8.79	8.90	10.24	13.92	18.12

Using toluene

Polymer No	$M_n^* \times 10^{-4}$	$M_w^* \times 10^{-4}$	$M_m^* \times 10^{-4}$	$M_{ab}^* \times 10^{-4}$	$M_{ab}^b \times 10^{-4}$	$M_{ac}^b \times 10^{-4}$	$M_{dc}^b \times 10^{-4}$
P-1 ^c	2.23	2.13	1.68	1.64	3.01	2.98	3.16
P-2 ^d	6.54	7.69	5.43	5.09	9.15	9.59	10.91
P-3 ^e	2.51	3.59	2.54	2.29	4.42	4.41	4.76
P-4 ^f	4.62	7.15	4.97	4.07	8.06	8.33	9.38
P-5 ^g	5.37	7.38	6.05	4.81	8.45	8.77	9.91
P-6 ^h	5.95	8.09	5.71	4.56	8.75	9.16	10.33

Using carbon tetrachloride

Polymer No	$M_n^* \times 10^{-4}$	$M_w^* \times 10^{-4}$	$M_m^* \times 10^{-4}$	$M_{ab}^* \times 10^{-4}$	$M_{ab}^b \times 10^{-4}$	$M_{ac}^b \times 10^{-4}$	$M_{dc}^b \times 10^{-4}$
P-1 ^c							
P-2 ^d	5.09	7.30	6.68	5.09	9.06	10.77	13.20
P-3 ^e	1.95	2.75	1.92	3.11	5.30	5.83	6.86
P-4 ^f	2.66	3.74	2.43	2.34	7.44	9.01	11.18
P-5 ^g	5.09	7.30	3.35	5.09	8.23	10.44	9.94
P-6 ^h	5.80	7.15	5.81	5.44	9.52	11.52	14.26

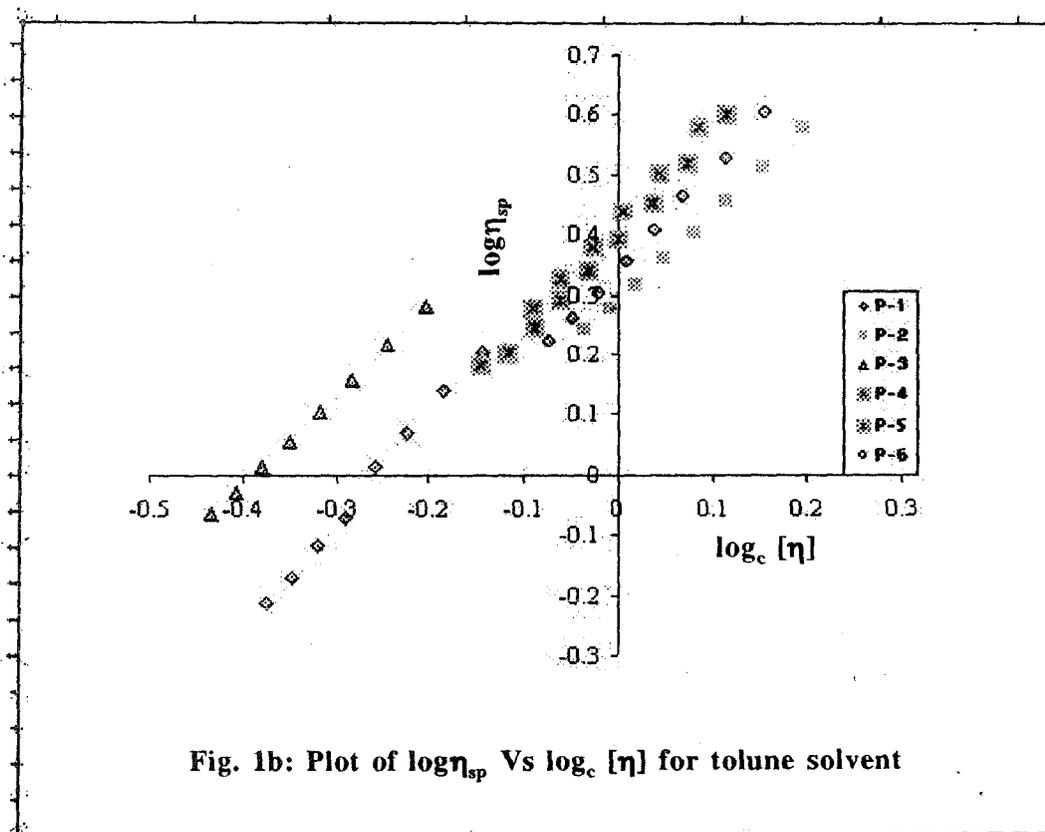


Fig. 1b: Plot of $\log \eta_{sp}$ Vs $\log_c [\eta]$ for toluene solvent

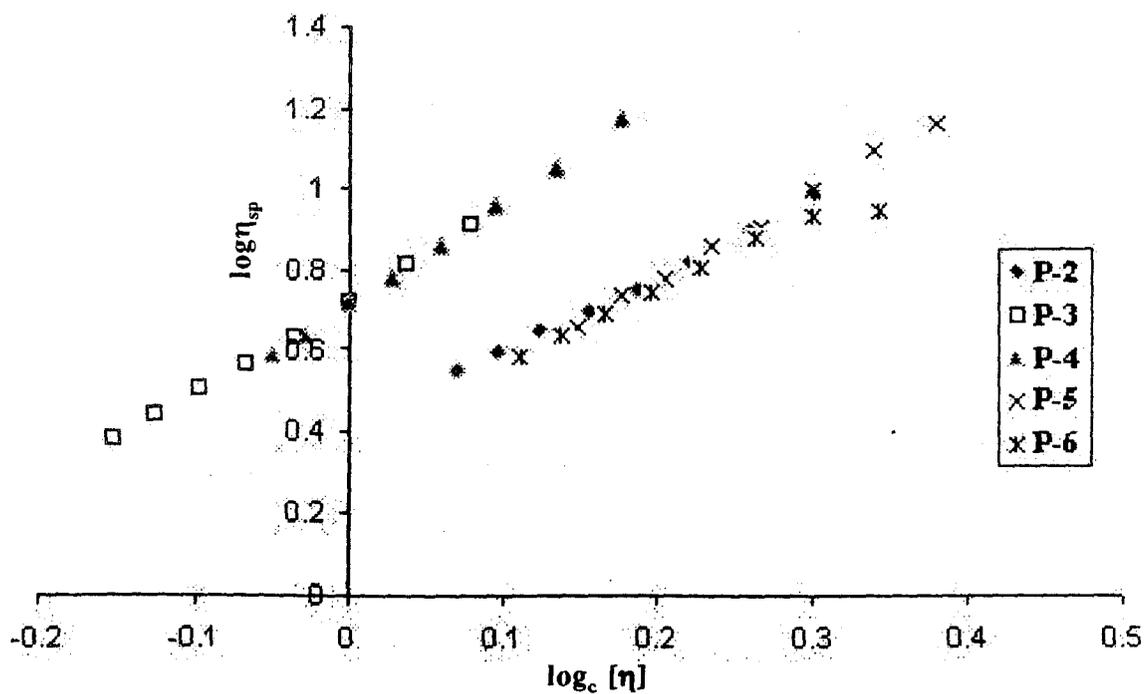


Fig. 1c: Plot of $\log \eta_{sp}$ Vs $\log_c [\eta]$ for carbon tetrachloride solvent

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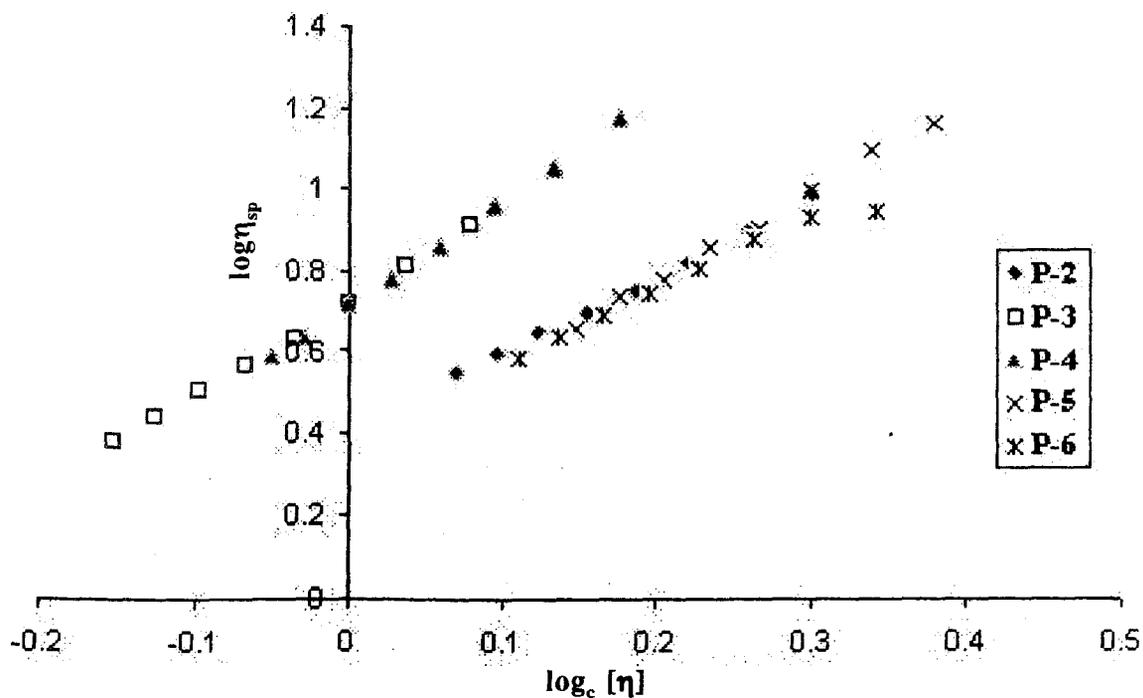
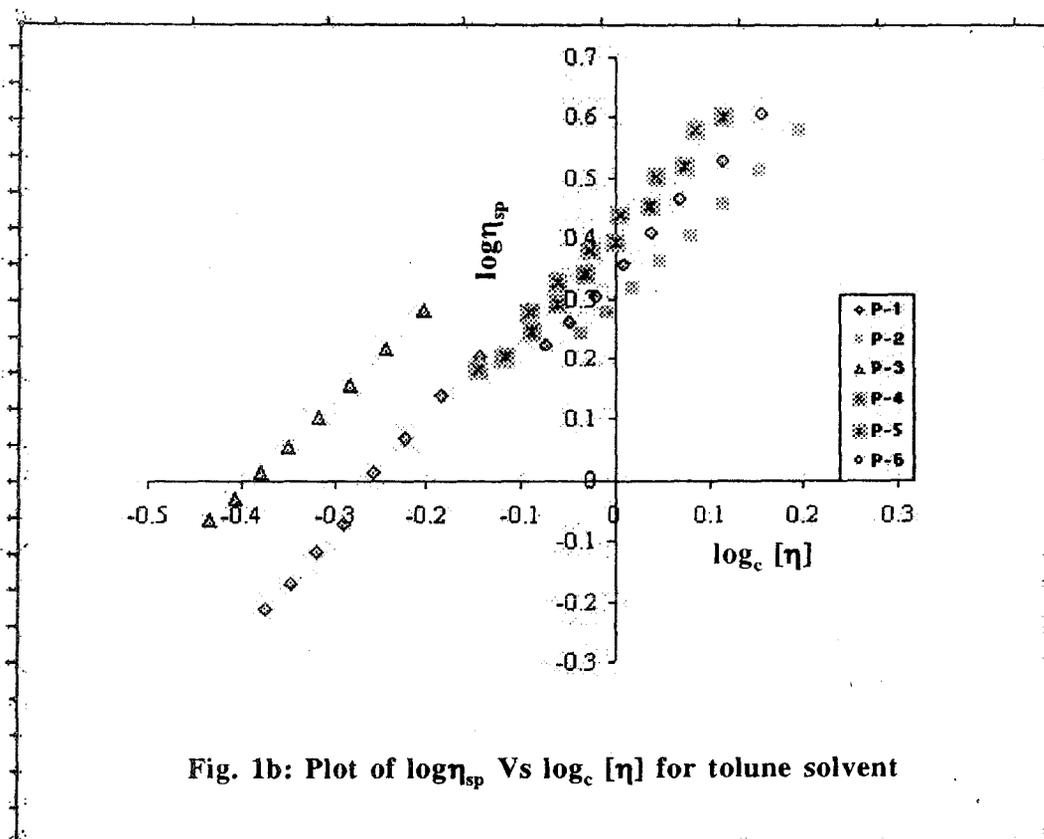


Fig. 1c: Plot of $\log \eta_{sp}$ Vs $\log_c [\eta]$ for carbon tetrachloride solvent

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(Received 1st January 2009, accepted 25th February 2009)

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Copolymer of decyl acrylate and styrene as a potential pour point depressant for lubricating oil

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ABSTRACT

The potential for use of homo polymer of decyl acrylate and its copolymer with styrene as pour point depressant (PPD) additives in lubricating compositions has been investigated. The polymers (homo and copolymers) were prepared by free radical initiator polymerization in toluene solvent, using benzoyl peroxide (BZP) as initiator and employing different levels of styrene (wt %) in the monomer mixture and were characterized employing TGA, FT-IR and FT-NMR techniques. Since the performance of such kind of additives in the field condition is very much dependent on the structure and morphology of the polymer dissolved in solvents, viscometric studies of the dilute solution of the polymers in toluene have also been employed.

The resulting copolymers were evaluated for potential use as Pour point depressant in lubricant compositions through ASTM method. Pour point depressant (PPD) performance of the copolymer is always better than the homo polymer in all the base oils studied. Increase in styrene concentration in the copolymer (up to a certain limit) induces better PPD performance into the additive. . Incorporation of styrene in the acrylate backbone raises the thermal stability of the copolymer and extent of styrene incorporation directly proportional to the thermal stability of the copolymer.

KEY WORDS: Decyl acrylate, styrene, homopolymer, copolymer, pour point, lubricating oil.

1.0 INTRODUCTION

Lubricating oils containing predominantly paraffin materials are the less soluble in water which start separating out at low temperature as small crystals. The temperature at which this phenomenon occurs is known as cloud point. Further cooling results in the formation of a rigid interlocked crystal lattice trapped in to the liquid hydrocarbon materials and prevents the flow of the oil. The lowest temperature at which the oil can still flow is termed pour point. If the pour point is not below the desired temperature, problems are encountered during storage and in actual usage of the lubricant. Chemical additives used for depressing the pour point, known as pour point depressant (PPD), reduce the size of the crystals and thereby lower the pour point. It is also known that the effectiveness of a PPD can be enhanced by increasing the number of groups per molecule which are capable of interacting with the wax either by absorption, adsorption and crystallization [1-5].

Although poly (decyl acrylate) (PDA) are preferred type of PPD in certain applications [6], very often contribute to enhance formation of deposits in the engine due to thermal instability of these additives under high temperature conditions[7]. The usual approach to overcome these shortcomings is to incorporate dispersancy property into the additive. Although they (multifunctional additives) may function as better PPD as compared to PDA, there remains always a risk of affecting certain beneficial properties offered by normal PDAs such as viscosity index and good shear stability [8]. Thus, within the category of PDA type of PPDs, considerable need and potential exists to develop polymers with improved performance.

As a part of the ongoing studies on development of poly(acrylate) based PPDs with improved performances [8], it became a matter of interest to explore alkyl acrylate and styrene copolymer as potential PPD. Exploratory studies on copolymers of styrene with alkyl acrylate or with alkyl methacrylates towards their potential application as synthetic base stocks, viscosity modifiers (VMs) and as PPDs, are reported in the literature [9-12]. However, they are being preliminary studies; the information available in these regards about the suitability of these polymers for the intended applications is

quite limited. On the basis of these literature reports, as well as from a consideration of the structure and morphology of the polymers, authors envisaged that these copolymers can exhibit improved performances as compared to PDA of corresponding molecular weight.

Again, since the performance of such kind of polymeric additives in the field condition is very much dependent on the structure and morphology of the polymers in dissolved solvent [8], viscometric studies in dilute solutions may give valuable information as far as the quality of the base stock employed and chain conformation of the polymer in dilute solutions are concerned. Therefore, the study may be very useful for evaluating the performance of polymer blended oil as an additive for lube oil, where the structure and morphology plays a significant role [9].

On the basis of the above we have under taken the present investigation comprising synthesis, characterization (including viscometric method) and performance evaluation as a pour point depressant in lube oil. A comparison of the copolymer was also made with the homopolymer of Decyl acrylate and the results of our findings is being reported here.

The commonly used equations employed to determine the viscometric parameters of the polymer are [12-17].

$$\text{Mark Houwink – Sukurda relation : } [\eta] = K M^a \quad 1$$

[where, M is the molecular weight and the values of parameter ‘K’ and ‘a’ depend on the type of polymer, solvent and temperature].

$$\text{Huggins } \eta_{sp}/C = [\eta]_h + k_h[\eta]_h^2 C \quad 2$$

$$\text{Kreamer } \ln \eta_r / C = [\eta]_k - k_k [\eta]_k^2 C \quad 3$$

$$\text{Martin } \ln (\eta_{sp} / C) = \ln [\eta]_m + k_m [\eta]_m C \quad 4$$

$$\text{Schulz-Blaschke } \eta_{sp}/C = [\eta]_{sb} + k_{sb}[\eta]_{sb}\eta_{sp} \quad 5$$

Where,

$\eta_r = t/t_0$, (t_0 is the time flow of pure solvent and t is time flow of polymer solution) is the relative viscosity or viscosity ratio ; $\eta_{sp} = \eta_r - 1$, is the specific viscosity

$[\eta]_h$ = intrinsic viscosity, respective to Huggins equation.

$[\eta]_k$ = intrinsic viscosity, respective to Kreamer equation ;

$[\eta]_m$ = intrinsic viscosity , respective to Martin equation,

$[\eta]_{sb}$ = intrinsic viscosity or limiting number, respective to Schulz – Blaschke equation;

k_h , k_k , k_m and k_{sb} Huggins , Kraemer , Martin and Schulz-Blaschke coefficients, respectively, C is the concentration.

Apart from the above, some relations have been proposed for determining the intrinsic viscosity $[\eta]$ in dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analysed in short period of time, practically in industrial laboratories. Most useful of them are Solomon- Ciute (SC, Eq. 6) and Deb –Chatterjee (DC, Eq. 7) relations

$$[\eta] = [2 (\eta_{sp} - \ln \eta_r)]^{1/2} / C \quad 6$$

$$[\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3\eta_{sp})^{1/3} / C \quad 7$$

The use of these equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$

2.0 EXPERIMENTAL

2.1 Materials used

Acrylic acid (GC Purity 99%), procured from Thomas Baker, India, Decyl alcohol (GC Purity 98%), obtained from S. D Fine Chemicals Ltd, India, Styrene obtained from Merck

Products, Germany and Hydroquinone procured from S. D Fine Chemicals Ltd, India, were used. Benzoyl peroxide (GC Purity 98%), procured from Loba Chemicals Pvt. Ltd. , India , was purified by crystallization from methanol –chloroform mixture and was used. Toluene (GC Purity 99.5 %), obtained from Emark, India, was used as a solvent.

2.2 Esterification of decylacrylate (DA) from acrylic acid and decyl alcohol

Decyl acrylate was prepared by reacting acrylic acid with decyl alcohol (1.1:1 molar ratio). The reaction was carried out in a resin kettle in the presence of catalytic amount of concentrated sulphuric acid, 0.25% hydroquinone (with respect to the monomer) as polymerization inhibitor for acrylic acid, and toluene as a solvent under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 130⁰C using a well-controlled thermostat. The progress of reaction was followed by monitoring the amount of liberated water from the reaction mixture to give the ester, decyl acrylate.

2.3 Purification of prepared ester

The prepared ester was purified according to the following procedure: a suitable amount of charcoal was added to the ester, allowed to reflux for 3 h, and then filtered off. The filtrate was washed with 0.5N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distil water to remove any traces of sodium hydroxide, the ester was then left over night on calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

2.4 Preparation of homo polymer of DA and its copolymer with styrene and their purification

The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask was placed desired mass of DA and initiator (BZP) followed by the desired mass of styrene was added drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was

maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into 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. A homo polymer of DA was similarly prepared and purified under the same conditions for use in reference experiments.

2.5 Preparation of Polymer – base oil blend

Base oils of three different viscosity grades, B1 and B2 and B3 (Table 5) were collected from two different refineries, A and B. In all the cases blending of the additives with the oils were carried out by taking required amount of polymer in the calculated amount of oil (w/w) and then heating the mixture at 60⁰C for 30 min with constant stirring.

3.0 MEASUREMENTS

3.1 Spectroscopic measurements

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

3.2 Viscometric measurements

Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values are $K' = 0.00268 \text{ cm}^2 \text{ sce}^{-2}$, $L = -19.83 \text{ cm}^2$ and volume of the bulb is 3 cm³ and length of the capillary 11.3 cm). Experimental determination was carried out by counting time flow at least six different concentration of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and uncertainty was found to be nearly 0.17 %. Precautions regarding

prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$ [17,18] were employed.

3.3 Thermo gravimetric analysis (TGA)

The thermograms in air were obtained on a mettler TA – 3000 system, at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ and in the temperature range of $90 - 450 \text{ }^{\circ}\text{C}$.

3.4 Evaluation of prepared additive as pour point depressants in base oils

The prepared additives were evaluated as pour point depressant using base oils collected from two different sources A and B, (Table 5) through the pour point test according to the ASTM–D-97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentration. The experimental data were noted by taking an average of three experimental results under identical conditions

4.0 RESULTS AND DISCUSSION

4.1 Spectroscopic analysis

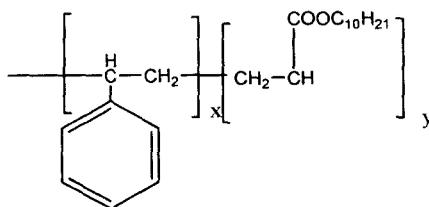
FT-IR spectrum of the homo polymer (Figure 1) exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1260 and at 1175 cm^{-1} can be explained owing to the C-O (ester bond) stretching vibration and the absorption bands at 975 , 750 and 711 cm^{-1} were due to the bending of C-H bond. The broad peak ranging from $2900\text{-}3100 \text{ cm}^{-1}$ was due to the presence of stretching vibration.

The existence of the copolymer was confirmed by FT-IR and NMR analysis. The copolymer in its IR spectrum (Figure 2) showed broad peak ranging from 1732 to 1720 cm^{-1} . This was attributed to the stretching vibration of the ester carbonyl group whereas the absorption bands at 758 , 711 , 695 and 662 cm^{-1} were due to C-H bond of the phenyl group of styrene.

In the ^1H NMR spectra (Figure 3) of one of the respective copolymers, a broad multiplet centered at 8.07 ppm indicated the presence of a phenyl group. A broad singlet

at 4.06 ppm was due to the proton of the $-\text{OCH}_2$ group. The absence of singlets between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer. Thus, as was expected, there is incorporation of styrene in the acrylate chain during copolymerization.

The proton decoupled ^{13}C NMR spectrum (Figure 4) of the above sample of copolymer was also in complete agreement with the structure as expected (structure-1)



Structure-1

The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of $-\text{OCH}_2$ group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports as well as on the basis of our earlier paper [8].

It was further verified through an analysis of FT-IR spectral data[8]. The intensity of $\text{C}=\text{O}$ absorption in FT-IR spectra of present copolymers, as compared to the carbonyl absorption in a standard, were analyzed for quantitative determination of the content of acrylate component in the copolymer. The intensity of $\text{C}=\text{O}$ adsorption in FTIR Spectra of present sample of copolymer, as compared to the carbonyl absorption in a standard, were analyzed for quantitative determination of the content of acrylate component in the copolymer blends of known quantities of an ethylene-propylene and poly (decyl acrylate) in which varied quantities of PDA was present. The comparative results obtained on comparisons are presented in Table 1.

4.2 Thermal stability of the prepared compounds

Because of the presence of a quaternary carbon atom in the copolymer chain, the acrylates readily undergo depolymerisation with a consequent decrease of the viscosity of the polymer blended oils. As a result of that recent research on acrylate additives has been focused on copolymerisation of them with various stabilising monomers [7].

Keeping this view in mind we have chosen styrene as a stabilising monomer of the present acrylate copolymer.

Thermal stability data of all prepared samples (Table 2) indicated that there is a gradual increase in thermal stability of the copolymers with the increase in styrene concentration in the copolymer feed. Thus introduction of styrene increases thermal stability of the acrylate polymer as was observed in our earlier studies [18].

4.3 Viscometric analysis

Viscometric data were obtained using the six equations mentioned. Huggins (H), Kraemer (K), Martin (M) and Schulz–Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz–Blaschke (SB) equation is commonly applied in single point determinations because it was found that $k_{sb} = 0.28$ for many polymer-solvent systems. In this work, this value was used.

Intrinsic viscosity values related to all equations for the samples analyzed in toluene (Table 3) indicated that higher intrinsic viscosity values obtained for homo polymer of decyl acrylate (PDA) compared to the copolymers. Intrinsic viscosity values decreases with increase in styrene incorporation. This indicates less extended conformation of the polymer chain compared to PDA itself, which may be due to the introduction of aromatic ring in the polymer chain. Values obtained by single point determination method were higher than the values obtained by graphic extrapolation method as was observed earlier [17].

Viscometric molecular weight (M_v) obtained by using Mark Houwink equation, is presented in Table 4. As is expected, the homo polymer showed higher Viscometric Molecular weight (M_v) compared to the copolymers [18]. There is also a gradual decrease of M_v with the increase in styrene concentration in case of the copolymers.

4.4 Performance of the homo and copolymers as PPD

Pour point of the different levels of additive doped lube oils were tested and tabulated in Tables 6. It indicated that the prepared copolymer samples are more efficient as pour point depressant than the homo polymer and the efficiency increases with the increase in concentration of additive up to a certain limit.

The greater hydrodynamic volume of the copolymer may restrict the formation of wax deposition network in the base oil, which is responsible for their poor flow ability at a lower temperature [18-21].

This is further supported by the intrinsic viscosity $[\eta]$ and viscometric molecular weight (M_v) values obtained by viscometric analysis with the copolymer and homo polymer samples. Both the parameters showed lesser values in case of copolymer than that of the homo polymer. Since the structure and morphology of the polymer chain plays a significant role for an additive to act as an effective PPD [8], incorporation of aromatic ring in the acrylate chain may be responsible for this encouraging PPD performance of the copolymer. The greater hydrodynamic volume, not only made the polymer less compatible with the solvent (less $[\eta]$ values) but at the same time prevents the formation of wax crystal network, which is responsible for reducing flow ability of the base oils.

5.0 CONCLUSIONS

Incorporation of styrene in the acrylate back bone raises the thermal stability of the copolymer and extent of styrene incorporation directly proportional to the thermal stability of the copolymer. Intrinsic viscosity values of the copolymer are less than the corresponding homo polymer and the values obtained by single point determination method are higher than the values obtained by graphical extrapolation method. Viscometric molecular weight of the copolymer is less than the homo polymer of decyl acrylate. Pour point depressant (PPD) performance of the copolymer is always better than the homo polymer in all the base oils studied. Increase in styrene concentration in the copolymer (up to a certain limit) induces better PPD performance into the additive.

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Table 1: Composition of the monomers in the co polymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. P-1 is homopolymer of decyl acrylate (DA); P-2 to P-4 is the copolymer of DA+ different mass fractions of styrene

Sample No	% of weight in the feed		% of weight in copolymer	
	DA	Styrene	By PMR	By FT-IR

	method			
P-1	100	00		
P-2	95	5	1	1.5
P-3	90	10	2	2.1
P-4	85	15	3	3.5

Table 2: Thermal Gravimetric Analysis Data of all prepared samples

Sample	Decomp.Temp	PWL
P-1	250/340	23/86
P-2	300/400	45/84
P-3	320/430	60/85
P-4	320/440	62/85

Table 3: Intrinsic viscosity values of all prepared samples calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{sb}$	$[\eta]^b_{sb}$	$[\eta]^b_{sc}$	$[\eta]^b_{dc}$
P-1	4.335	5.004	4.180	5.368	6.490	6.697	7.340
P-2	2.677	3.538	3.375	3.760	4.106	4.105	4.350
P-3	2.445	3.248	3.087	3.430	3.768	3.758	3.963
P-4	2.401	3.225	3.001	3.38	3.634	3.619	3.8

Table 4: Determination of molecular weight by Mark Houwinks equation $[\eta] = KM^a$
where, $K = 0.00387 \text{ dl.g}^{-1}$ and $a = 0.725$

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{DC}^b
P-1	16051	19563	15264	21554	28004	29244	33186
P-2	8255	12128	11364	13190	14893	14888	16127
P-3	7285	10778	10048	11623	13229	13180	14182
P-4	7105	10673	9664	11387	12584	12513	13384

Table 5: Base oil properties

Bas oil properties	Base oils					
	B1		B2		B3	
	A	B	A	B	A	B
Density (g.cm ⁻³) at 40 ⁰ C	0.85	0.89	0.90	0.93	0.98	0.97
Viscosity at 40 ⁰ C in cSt	7.47	8.01	20.25	21.00	112.05	112.80
Viscosity at 100 ⁰ C in cSt	3.52	3.81	5.54	5.79	10.82	11.33
Cloud point, ⁰ C	-8	-8	-10	-10	-14	-12
Pour point, ⁰ C	-3	-3	-6	-6	-9	-9

Table 6: Pour Point of additive doped Base oils

Base Oil	PPD Sample	Pour Point (⁰ C) of base oils containing different % (W/W) of PPD							
		0.025		0.05		0.01			
		A	B	A	B	A	B		
B1	P1	-9	-9	-9	-9	-9	-12		
	P2	-12	-12	-15	-15	-15	-15		
	P3	-12	-15	-21	-21	-21	-24		
	P4	-15	-15	-24	-21	-24	-24		
B2	P1	-9	-9	-9	-9	-12	-12		
	P2	-15	-15	-21	-24	-24	-21		
	P3	-12	-15	-21	-21	-21	-24		
	P4	-15	-15	-24	-21	-24	-24		
B3	P1	-12	-12	-9	-12	-12	-12		
	P2	-15	-18	-18	-18	-15	-18		
	P3	-18	-21	-21	-21	-21	-21		
	P4	-21	-24	-27	-24	-27	-24		

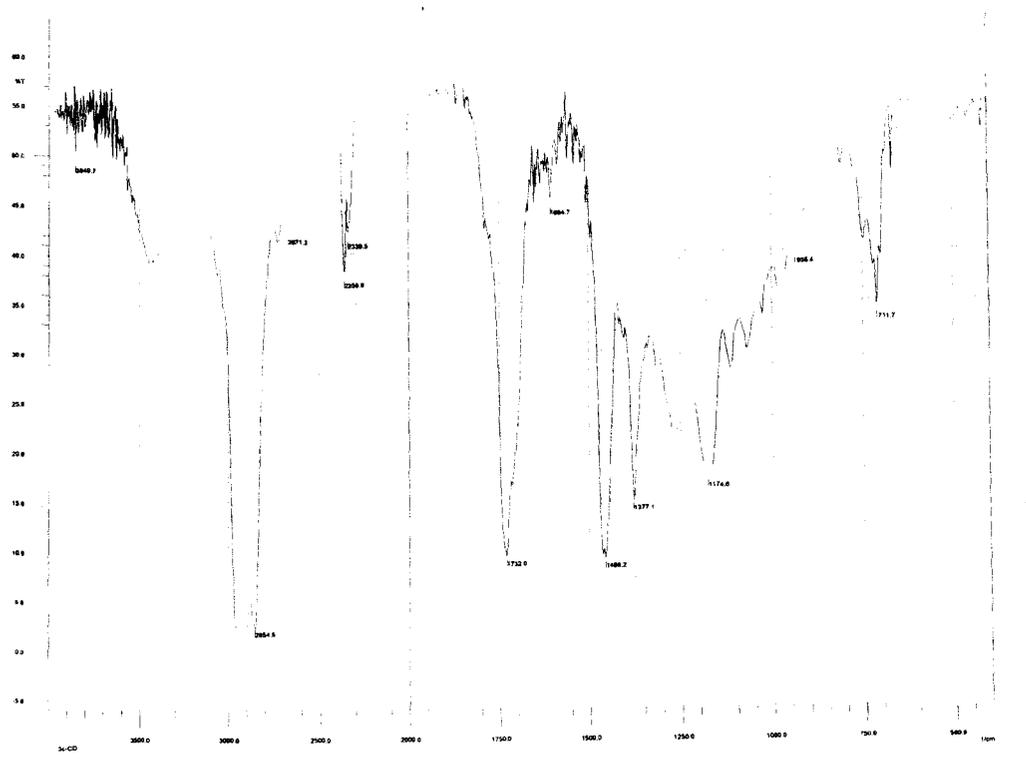


Figure 1 : FT- IR spectrum of homodecyl acrylate

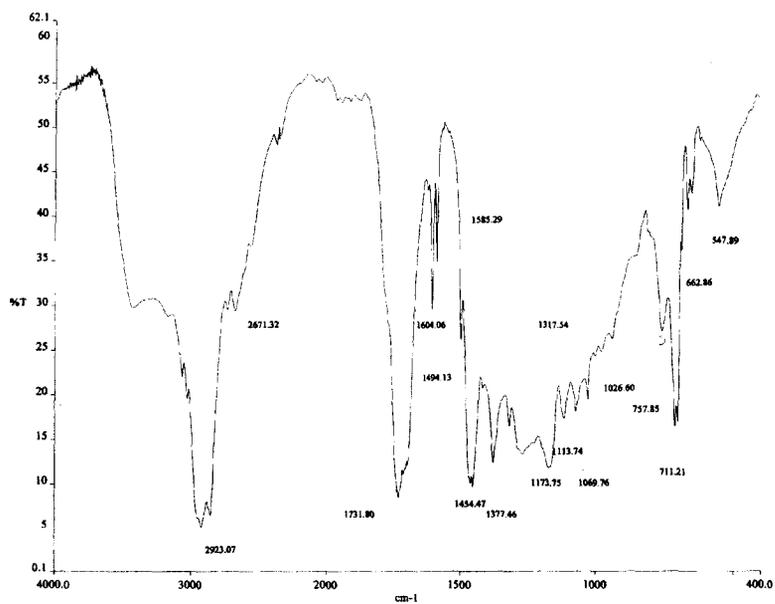


Figure 2: FT- IR spectrum of copolymer of Decylacrylate with styrene

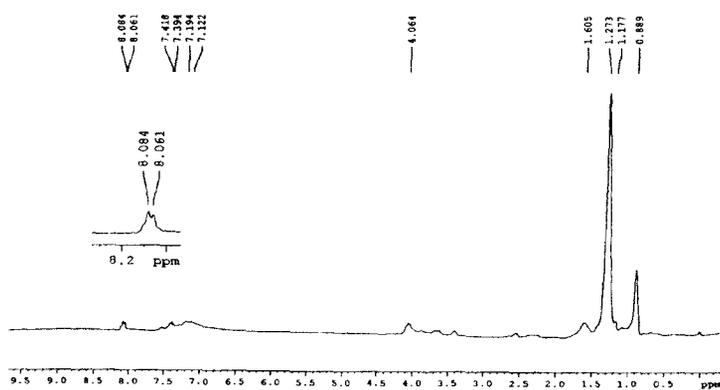


FIGURE 3: ¹H NMR spectrum of copolymer of Decylacrylate with styrene

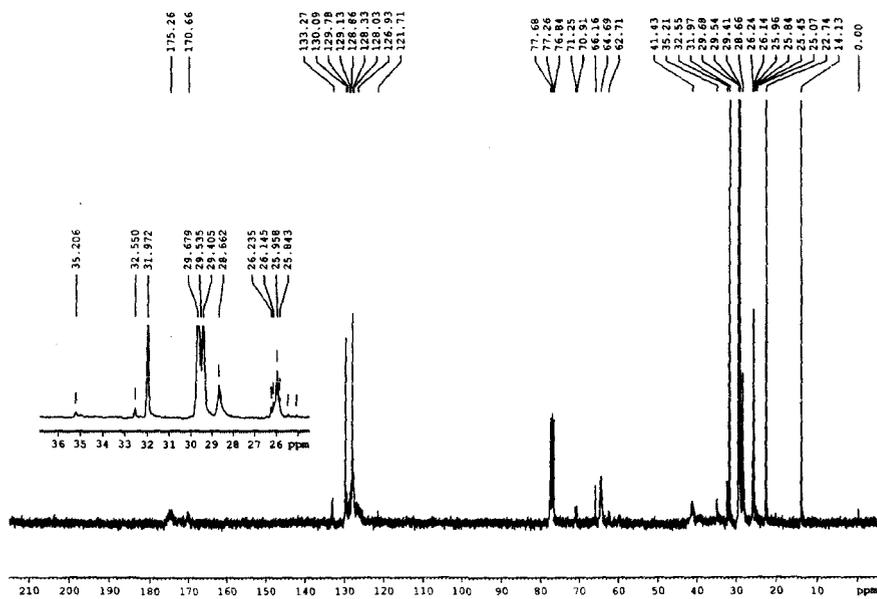


FIGURE 4: ^{13}C NMR spectrum of copolymer of Decylacrylate with styrene

Synthesis, Characterization and Viscosity Studies of Acrylate based Homo and Co-polymers

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Abstract

Homopolymer of isodecyl acrylate and dodecyl acrylate and their copolymer using different compositions of styrene were synthesised and characterised. Viscosity measurements of synthesised polymers in the toluene solution at 313K were performed. Six different equations viz. Huggins, Kraemer, Martin and Schulz-Blaschke (graphic extrapolation method) and Solomon-Ciuta, Deb-Chatterjee and Schulz-Blaschke (by a single point determination method) were used to calculate intrinsic viscosity, viscometric constants values of the polymer solutions. Molecular weights of the synthesized polymers were determined by Mark Houwink – Sukurda equation. The values of intrinsic viscosity and viscosity average molecular weight, obtained by the two methods (single point determination and graphical extrapolation) were compared in order to verify the validity of the single point determination for the polymers.

Keywords: Homopolymer, Co-polymer, Rheological properties, Pour point depressant, Viscosity Modifier

Introduction

Lubrication is simply the use of materials to improve the smoothness of movement of one surface over another and the material that is used in this way is called a lubricant. Quality of the lubricating oil can be improved by using various kinds of polymeric additives. In addition, additives play an important role in compounding of lubricants for steam turbines, gas turbines, jet aircraft turbines, railroads and stationary piston engines.

The followings are the main types of lube oil additives: viscosity index improver (VII), pour point depressants (PPD), detergents, dispersants, antioxidants, corrosion inhibitors and extreme pressure agents. Some polymeric additives like poly acrylates and poly alkyl acrylates show multifunctional properties. Additives for the future lubricants will be required to maintain oil consumption control over the life of the equipment while providing a high level of thermal stability and enhancing low temperature fluidity. The viscosity index (VI) expresses the viscosity changes of an oil when temperature is varied that is the smaller changes of viscosity named as a higher viscosity index. As a rule, the VI of lubricating oil, obtained from mineral oils, according to conventional

process is not sufficiently high for satisfying the very severe specifications relating to viscosity which are required by modern engines. The polymer molecules in solution exist as random coil which are swollen by the solvent. The volume of this molecule determines the viscosity increase as a function of solvation power which is related to the temperature.

The polymeric additives dissolved in the lube oil resemble a tangled ball at which some of the solvent molecules are incorporated forming a micelle. As the temperature is raised, the lube oil viscosity decreases. Meanwhile, the polymer molecule expands due to the increase in the micelle size, counterbalancing the reduction of the viscosity of the lube oil and hence reducing the changes of viscosity with temperature of the mixture. Consequently, the performance of VII depends on the behaviour of the polymer molecule in the oil where the polymer solubility, molecular weight and resistant to shear degradation are determinant parameters.

The pour point of oil is considered to be the temperature at which the oil begins to lose its fluidity under the effect of gravity under prescribed conditions. This phenomenon may be due to either the crystallisation or separation of solid substances, which are soluble at higher temperature or to increase the viscosity. The use of materials to depress the pour points of lube oils is common and such materials make possible the production of low pour point oil without extensive dewaxing. When paraffinic oils are cooled, the wax crystals separate out from the oil forming a network of crystals. Pour point depressant appears to function by depositing or adsorbing on the wax crystals network by markedly reducing the size of the wax crystals formed. These depressants obstruct the lateral crystal growth.

Many types of additives are used to improve the viscosity index and pour point depressants for lubricating oil. Additives are mainly polymers with molecular weights ranging from 25,000 to over one million, the most widely known among them are polyisobutene and polyalkylmethacrylates. It is anticipated that suitably tailored copolymers of these types can exhibit a better performance as lube oil additives. Styrene is one of the least expensive and most readily available monomers. It is used extensively in the synthesis of various polymeric products for lube oils¹⁻³.

Co-polymers were prepared by varying the styrene concentration in the monomer mixture and employing free

radical polymerization technique using benzoyl peroxide (BZP) as initiator in toluene solvent. Polymerization was carried out following the procedure as reported earlier⁴. Homo polymer of IDA and DDA were also prepared under identical condition.

Physical characterization of the copolymers was carried out employing Viscometrical Analysis, Thermo Gravimetric Analysis (TGA), IR and NMR techniques. However, since performance of such kind of additives in field condition is very much dependent on the structure and morphology of the polymer in desired solvent⁵, viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution is concerned. Viscometry is the simplest technique used to study the macromolecules in solution and determine their molecular weight. According to Mark Houwink – Sukurda relation (Eq. 1), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = KM^a \quad (1)$$

where 'K' and 'a' depend on the type of polymer, solvent, and temperature. The higher is the molecular weight, the more viscous will be the polymer solution.

When a polymer has a higher molecular weight, it has a bigger hydrodynamic volume; that is, the volume that the coiled up polymer takes up in solution. Being bigger, the polymer molecule can block more motion of the solvent molecules. It might be said that it can block off more lanes of the highway. Also, the bigger a polymer is, the stronger its secondary forces are. So the higher is the molecular weight, the more strongly the solvent molecules will be bound to the polymer. This enhances the slowing-down of the solvent molecules. Because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from other techniques, generally in determination of molecular mass of samples. A number of mathematical relations are available in literature for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation⁵⁻⁹. The most commonly used equations are:

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

$$\text{Kraemer (K)} \quad \ln \eta_r / C = [\eta]_k - k_k[\eta]_k^2 C \quad (3)$$

$$\text{Martin (M)} \quad \ln(\eta_{sp}/C) = \ln[\eta]_m + k_m[\eta]_m C \quad (4)$$

$$\text{Schulz- Blaschke (SB)} \quad \eta_{sp}/C = [\eta]_{sb} + k_{sb}[\eta]_{sb}\eta_{sp} \quad (5)$$

where $\eta_r = t/t_0$, relative viscosity or viscosity ratio; $\eta_{sp} = \eta_r - 1$, specific viscosity; $[\eta]_h$ = intrinsic viscosity, respective to Huggins equation; $[\eta]_k$ = intrinsic viscosity, respective to Kraemer equation; $[\eta]_m$ = intrinsic viscosity, respective to Martin equation; $[\eta]_{sb}$ = intrinsic viscosity or limiting number respective to Schulz – Blaschke equation; k_h , k_k , k_m and k_{sb} Huggins, Kraemer, Martin and Schulz-Blaschke coefficients respectively.

Some relations have been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination method. This method has the advantage of being considerably faster and can be adequate when a large number of samples must be analysed in short period of time, practically in industrial laboratories. Most useful of them⁵⁻⁹ are Solomon- Ciuta (SC, Eq. 6) and Deb –Chatterjee (DC, Eq. 7) relations.

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2} / C \quad (6)$$

$$[\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp})^{1/3} / C \quad (7)$$

The use of these equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$ ⁹. The behaviour of the polymeric additives towards a specific solvent / base stock plays a significant role in their action as a performance additive in their end application. Since, viscometry provides very important data about the interaction of additive in base fluid and hence conformation of polymeric system⁵ in the base stock, the process of polymerization in the presence of a suitable solvent has been attracting great interest now-a-days^{10,11}. Since the behaviour of polymers especially the co polymers in solution is a complex phenomenon, a comparison involving the values of their intrinsic viscosity obtained by graphic extrapolation and by a single point determination should be interesting. In this work, viscometrical parameters (intrinsic viscosity and the value of constants) in toluene solution of the sample of poly acrylate and co-polymer having different percentage (w/w) of styrene are obtained by graphic extrapolation and single point determination method. The viscosity average molecular weight determined by using different equations were compared.

Material and Methods

Esterification: Isodecyl acrylate was prepared by reacting 1 mole of acrylic acid with 1 mole of isodecyl alcohol. The reaction was carried out in a resin kettle in presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid and toluene as a solvent. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 403 K using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester, isodecyl acrylate (IDA). Under the same procedure, dodecyl acrylate was also prepared from acrylic acid and dodecyl alcohol.

Purification of prepared ester: A suitable amount of charcoal was added to the ester, allowed to reflux for 3 h, and then filtered off. The filtrate was washed with 0.5N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide. the ester was then

left overnight on calcium chloride and was then removed by distillation and was used in the polymerization process.

Preparation of copolymer and homo polymer: The copolymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which styrene is added drop wise. In the flask, desired mass of IDA and initiator (BZP) were placed followed by addition of the desired mass of styrene drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 4 h. At the end of the reaction time, the reaction mixture was poured into 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. Homopolymer of IDA, homopolymer of DDA and copolymer of DDA with styrene were similarly prepared and purified under the same conditions for use in reference experiments.

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

Viscometrical measurements: Viscometrical properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow for at least eight different concentrations of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In the single point measurement, the lowest value of solution concentration was chosen for the calculation. For the viscosity-average molecular weight determination, the constants $K = 0.00387 \text{ dl/g}$ and $a = 0.725$ were employed in Mark Houwink – Sukurda relation^{7,12}

Thermo gravimetric analysis (TGA): The thermograms in air were obtained on a Mettler TA – 3000 system at a heating rate of 10 $^{\circ}\text{C} / \text{min}$.

Results and Discussion

Spectral analysis: FT-IR spectra of homopolymer of isodecyl acrylate exhibited absorption at 1732 cm^{-1} for the ester carbonyl stretching vibration along with other peaks at 1456.2, 1379, 1260 and 1166.9 cm^{-1} , owing to the CO stretching vibration and absorption bands at 750 and 710 cm^{-1} were due to the bending of C-H bond. In its ^1H NMR spectra, homo isodecyl acrylate showed a broad singlet centred at 4.02 ppm due to the proton of $-\text{OCH}_2$ group, a broad singlet at 0.86 ppm was due to methyl's of isodecyl chain.

The existence of its copolymer with styrene was confirmed by FT-IR, ^1H -NMR and ^{13}C -NMR analysis. In its FT-IR spectra, the copolymer showed a broad peak ranging from 1722-1732 cm^{-1} along with other peaks at 753.56, 712.15, 700.75, 667.98 cm^{-1} which were due to C-H bond of the phenyl group of styrene. In the ^1H NMR spectra of the copolymer, a broad multiplet ranging from 7.23 to 7.58 ppm indicated the presence of phenyl group of styrene. Broad singlet at 4.06 ppm was due to the proton of $-\text{OCH}_2$ group. Methyls of the isodecyl chain appeared between 0.81 to 0.86 ppm. The absence of singlets between 5 and 6 ppm indicated the absence of any vinylic proton in the copolymer. The existence of copolymer was further confirmed by the presence of aromatic carbon ranging between 124 to 141 ppm in the ^{13}C -NMR spectrum of the polymer. The carbonyl carbon appears at 174.47 ppm along with other carbons. The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of signal of $-\text{OCH}_2$ group at 4.6 ppm. Area of signal of phenyl group at 7.40 ppm is based on earlier reports⁴. It was further confirmed through FT-IR spectral data. The intensity of carbonyl absorption in FT-IR spectra of the copolymer was analysed for quantitative determination of the content of acrylate component in the copolymer (Table I).

FT-IR spectra of the homopolymer of Dodecylacrylate exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration along with other peaks at 1456, 1260, 1164.9, 1112, 1028 and 711 cm^{-1} due to the bending of C-H bond. ^1H NMR spectra of the homopolymer indicated the existence of $-\text{OCH}_2$ group at 4.02 ppm (broad singlet) along with the methyl protons ranging between 0.86 to 0.90 ppm together with methylene proton ranging between 1.3 to 1.6 ppm. The proton decoupled ^{13}C -NMR of the above sample was in complete agreement with the homopolymer.

The existence of copolymer of Dodecyl acrylate with styrene was confirmed by the analysis of FT-IR, ^1H NMR and ^{13}C -NMR spectra of the copolymer. FT-IR spectra of the copolymer showed sharp peak at 1732 cm^{-1} for the ester carbonyl along with other peaks at 1028, 900, 760, 700 due to C-H bond of phenyl group of styrene. ^1H NMR spectra of the copolymer showed broad singlet at 4.02 ppm due to $-\text{OCH}_2$ protons. A broad multiplet centered at 7.45 ppm was due to aromatic protons. The absence of singlet between 5 to 6 ppm indicated the absence of vinylic protons in the copolymer. ^{13}C -NMR spectrum of the above sample showed the presence of ester carbonyl at 173 ppm with the aromatic carbon appearing in the range 125 to 134 ppm. The extent of incorporation of styrene in the polymer chain was also determined by the method as applied earlier and tabulated as in table I.

Viscometrical analysis: Viscometrical data were obtained using the six equations mentioned. A linear relation for the plot of $\log \eta_{sp}$ vs. $\log c[\eta]$ obtained for all samples (Fig.1) indicated that measurements were performed in Newtonian

flow¹²⁻¹⁴. Using the graphic extrapolation method, respective intrinsic viscosities and constants were evaluated. In single point determinations, SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent systems⁶⁻⁹. Table II presents intrinsic viscosity values related to all equations for the samples analysed. Taking into account of the data for homo and all copolymer samples, it can be noticed that in both cases (P-1 to P-4 and P-5 to P-6), values are consistent. Comparison among the copolymers indicated that there is a gradual increase of $[\eta]$ values with the increase of styrene content in the monomer composition. This indicates more extended conformation of the polymer chain compared to poly isodecyl acrylate and poly dodecyl acrylate itself.

Although different intrinsic viscosity values may be found by graphic extrapolation of Huggins, Kraemer, Martin and SB equation (eq 2 to 6), but in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. For the homopolymer and co-polymer $[\eta]$ values obtained by Huggins and Kramer's equation were similar. Both homopolymer and copolymers in toluene medium indicated poor salutations (Table III) as is evident from the respective viscometrical constant values and thus point towards the formation of micelle or spherical structures as discussed earlier⁵.

However, it is interesting to notice that for all the polymers in toluene, k_{sb} values were not close to 0.28 and $k_h + k_k$ values were not found close to 0.5 in most of the cases. But negative value of kraemers coefficient for all copolymeric samples did not put any restriction to explain better solubility of copolymer in toluene.

Table IV presents the percentual differences ($\Delta \% = 100([\eta] / [\eta]_h) - 100$) of intrinsic viscosity $[\eta]$ values of homopolymers and the copolymers determined through

graphic extrapolation using Kraemer, Martin and SB equations with respect to Huggins equation. It can be noticed that the range (1.881 to 17.290 %) was narrow when compared to the values obtained through a single point using SB, SC and DC equation (5.538 to 24.192 %). Again, the percentage differences in case of polymers of dodecyl acrylate are higher than those of polymers of isodecyl acrylate both in graphic extrapolation and single point determination method (except P-3 and P-7).

Table V presents a comparison between the value of molecular weight obtained by viscometrical methods for homopolymers and co-polymers analyzed. In general, there is a gradual increase in molecular weight with increase of styrene concentration in both cases. Table VI presents the percentual difference ($\Delta \% = [100(M/M_h)] - 100$), obtained for viscometrical molecular weight values. These values were calculated taking M determined by Huggins equation as a reference. Martin equation showed the smallest Δ differences except P-1. Table VII presents a comparison between the TGA data for homo and copolymers. The TGA data show that the co-polymers are better in thermal stability than the homopolymers in the both cases.

Conclusion

Co-polymers showed better thermal stability than the corresponding homopolymers. Also, co-polymers showed gradual increase of intrinsic viscosity values with the increase of styrene content in the feed. Negative values of Kraemer coefficient indicate good salvation for copolymers analysed, although $k_h + k_k \neq 0.5$ and $k_{sb} \neq 0.28$ for them. In both cases homo polymers have higher molecular weight compared to their co-polymers. There is gradual increase in molecular weight with increase of styrene concentration.

Acknowledgement

Authors are grateful to CSIR, New Delhi, for financial support.

Table I

Composition of the monomers in the co polymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. P-1 and P-5 are homopolymer of IDA, P-2 to P-4 are the copolymer of mma + different mass fractions of styrene

Polymer sample	Mass fraction in the feed		Mass fraction of styrene in co polymer by PMR method	Mass fraction of styrene in co polymer by FT- IR
	IDA/DDA	Styrene		
P-1	1	-	-	-
P-2	0.975	0.025	0.01	0.015
P-3	0.95	0.05	0.02	0.023
P-4	0.925	0.075	0.035	0.037
P-5	1	-	-	-
P-6	0.975	0.025	0.01	0.015
P-7	0.95	0.05	0.02	0.023
P-8	0.925	0.075	0.035	0.037

Table II

Intrinsic viscosity values for all prepared homo and co polymer samples calculated by using different equation (eq. 2 to eq.7). a- extrapolation of graph, b- single point determination ($k_{sb}=0.28$), c- single point determination. h, k, m, b, sc and dc refers Huggin, Kraemer, Martin, Schulz- Blaschke, Solomon- Ciuta and Deb –Chatterjee respectively

Sample	$[\eta]^a_b$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{sb}$	$[\eta]^b_{sb}$	$[\eta]^c_{sc}$	$[\eta]^c_{dc}$
P-1	3.774	3.845	3.881	3.945	4.02	3.983	4.119
P-2	2.737	2.876	2.846	2.930	3.074	3.046	3.110
P-3	2.877	3.167	3.099	3.229	3.505	3.474	3.573
P-4	3.004	3.287	3.222	3.378	3.561	3.529	3.623
P-5	4.059	4.361	4.336	4.512	4.637	4.599	4.773
P-6	2.621	2.752	2.724	2.772	2.882	2.857	2.933
P-7	3.211	3.522	3.452	3.626	3.784	3.750	3.876
P-8	3.424	3.859	3.766	4.016	4.128	4.091	4.230

P-1 Homo isodecyl acrylate, P-2 copolymer of isodecyl acrylate + 10 % styrene, P-3 copolymer of isodecyl acrylate + 15 % styrene, P-4 copolymer of isodecyl acrylate + 20 % styrene, P-5 Homo dodecyl acrylate, P-6 copolymer of dodecyl acrylate +10 % styrene, P-7 copolymer of dodecyl acrylate +15 % styrene, P-8 copolymer of dodecyl acrylate +20 % styrene.

Table III

Viscometrical constants obtained for all prepared homo and copolymer samples. k_h , k_k , k_m and k_{sb} Huggins, Kraemer, Martin and Schulz- Blaschke coefficients respectively

Sample	k_h	k_k	k_m	k_{sb}	k_h+k_k
P-1	0.475	0.107	0.359	0.294	0.582
P-2	0.850	- 0.044	0.604	0.462	0.806
P-3	1.140	- 0.089	0.694	0.501	1.051
P-4	1.103	- 0.084	0.683	0.480	1.019
P-5	0.76	0.044	0.478	0.347	0.804
P-6	0.802	- 0.017	0.572	0.465	0.785
P-7	1.057	- 0.057	0.649	0.453	1.000
P-8	1.194	- 0.065	0.670	0.441	1.129

Table IV

Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values, Huggins equation taken as a reference. a- data from extrapolation; b – data from single point determination

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
P-1	1.881	2.835	4.531	6.518	5.538	9.141
P-2	5.079	3.982	7.052	12.313	11.290	13.628
P-3	10.080	7.716	12.235	21.828	20.751	24.192
P-4	9.421	7.257	12.450	18.542	17.477	20.606
P-5	7.440	6.824	11.160	14.240	13.304	17.591
P-6	5.074	3.930	5.761	9.958	9.004	11.904
P-7	9.685	7.505	12.924	17.845	16.786	20.710
P-8	12.704	9.988	17.290	20.561	19.480	23.540

Table V

Determination of molecular weight by Mark Houwinks equation $[\eta] = KM^a$ where $K = 0.00387$ and $a = 0.725$.

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	13,270	13,616	13,792	14,107	14,478	14,295	14,972
P-2	8,520	9,122	8,991	9,359	10,000	9,874	10,162
P-3	9,127	10,419	10,112	10,702	11,984	11,838	12,306
P-4	9,687	10,968	10,670	11,389	12,249	12,097	12,544
P-5	14,672	16,199	16,071	16,977	17,630	17,431	18,347
P-6	8,026	8,593	8,464	8,671	9,149	9,039	9,373
P-7	10,620	12,064	11,734	12,558	13,319	13,154	13,768
P-8	11,603	13,684	13,232	14,458	15,017	14,473	15,531

Table VI

Percentual differences obtained for viscometric molecular weight values ($\Delta \% = [100(M/M_h)] - 100$)

Sample	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	2.607	3.934	6.307	9.103	7.724	12.826
P-2	7.066	5.528	9.847	17.371	15.892	19.272
P-3	14.156	10.792	17.256	31.303	29.703	34.831
P-4	13.224	10.148	17.570	26.448	24.879	29.493
P-5	10.408	9.535	15.710	20.161	18.805	25.048
P-6	7.065	5.457	8.036	13.992	12.621	16.783
P-7	13.597	10.490	18.249	25.414	23.861	29.642
P-8	17.935	14.039	24.606	29.423	24.735	33.853

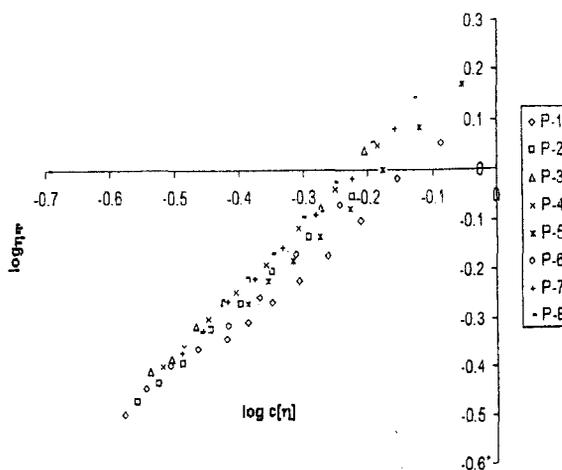
Table VII

Thermal gravimetric analysis data for homo and co-polymers. PWL is percent weight loss.

Sample	TGA data	
	Decom. Temp./°C	PWL
P-1	180/300	15/86
P-2	200/340	25/80
P-3	230/400	29/90
P-4	240/410	32/92
P-5	230/330	32/91
P-6	230/340	30/70
P-7	230/380	15/60
P-8	240/400	15/60

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Fig. 1: Plot of $\log c [\eta]$ vs. $\log \eta_{sp}$ (Received 22nd April 2010, accepted 10th September 2010)

Communicated to Jordan Journal of Chemistry

Copolymer of Decyl acrylate and Styrene – Synthesis, Characterization and viscometric studies in Different Base stocks

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Received [Dates will be filled in by the Editorial office]

In continuation of our studies towards the development of polymeric additives for lubricating oil we report herein the synthesis, characterization and viscometric studies of homo polymer of decyl acrylate and its copolymer with styrene in different base stocks at 40⁰C. In order to get more information about the structure and morphology of the polymer when dissolved in base stocks (ie in field application), viscometric measurements of the synthesized homo polymer as well as that of the co polymer were performed in the base oils at 40⁰C. Different equations were used to calculate intrinsic viscosity and viscometric constants values and molecular weight of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight obtained by the two methods (single point determination and graphical extrapolation) were compared. Measurements of viscometric properties included the determination of specific viscosity (it determines the contribution of solute to the viscosity of the solution), the reduced viscosity (that provides the measurements of the polymer capacity of increasing the solution viscosity) and intrinsic viscosity.

Keywords: Homopolymer, copolymer, viscometric measurements, pour point depressant, lubricating oil.

Introduction

Base oil also known as lubricant 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 medium to high values, very low volatility and with high viscosity index. The proportions of different hydrocarbon components determine the characteristics of the base oils.

The performance of lubricant base oils is often governed by their rheological properties such as low temperature fluidity, viscosity and viscosity temperature relationship. For example, to provide an effective performance at low temperatures as well as at high temperatures, an engine lubricant should have good low temperature fluidity and minimal variations of its viscosity with temperature.

Properties of such base oils can be improved by the incorporation of suitable performance polymer, generally called additives.

They added to base oils to impart specific property to the oil. Some of them impart new and useful properties to the lubricant, and others enhance properties already present. These additives are more active than the base oils. However, some of their properties are very often controlled by the chemical compositions of the base oils whereas some properties are controlled by the structure of the chemical additives designed for that purpose.

Acrylate based polymers and copolymers used in lubricant compositions for improving the viscometric and rheological properties of the lubricant (Mortier et al., 1997 and Chatterjee et al.,1995). They also looked upon to provide additional performance characteristics such as improved low temperature fluidity and dispersancy. However, owing to less thermal stability, they readily undergo depolymerization with a constant decrease of the oil viscosity compounded with these polymers. Therefore, the recent research on acrylate based additives has been concerned on copolymerization of it with stabilizing monomers. Since it is well known that inclusion of styrene in the composition of an additive increases the thermal stability of the co polymer, copolymerization of decyl

acrylate with two different mass concentration of styrene has been carried out which may be a very useful performance additive such as pour point depressant or viscosity modifier for petroleum and synthetic oil.

Recent research (Ivana, i. mello et al.,2006) towards the understanding of additives performance in base oils indicated that the performance of additives when used in lubricating oil and applied in field conditions are very much dependent on the structure and morphology of the polymer dissolved in it. Therefore, viscometric studies (that can be carried out in any laboratory owing to the simplicity of equipment required), with these additives in base oils may give valuable information as far as the base stock employed and morphological feature of the polymer in a dilute solution in the base oils is concerned (Delpech et al.,2002). Therefore, the study may be very useful for predicting the performance of the additive in base oils of different compositions.

The commonly used equations employed to determine the viscometric parameters of the polymer are (Delpech,2002; Schoff, 1999; Abdel-Azim, 1998; Khan,1983)

$$\text{Mark Houwink – Sukurda: } [\eta] = KM^a \quad (1)$$

Where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, the values of parameter 'K' and 'a' depends on the type of polymer, solvent, and temperature.

$$\text{Huggins} \quad \eta_{sp} / C = [\eta]_h + k_h[\eta]_h^2 C \quad (2)$$

$$\text{Kreamer} \quad \ln \eta_r / C = [\eta]_k - k_k[\eta]_k^2 C \quad (3)$$

$$\text{Martin} \quad \ln (\eta_{sp}/C) = \ln[\eta]_m + k_m[\eta]_m C \quad (4)$$

$$\text{Schulz-Blaschke} \quad \eta_{sp}/C = [\eta]_{sb} + k_{sb}[\eta]_{sb} \eta_{sp} \quad (5)$$

Where,

$\eta_r = t/t_0$, (t_0 is the time flow of pure solvent and t is time flow of polymer solution) relative viscosity or viscosity ratio ; $\eta_{sp} = \eta_r - 1$ specific viscosity

$[\eta]_h =$ intrinsic viscosity, respective to Huggins equation.

$[\eta]_k =$ intrinsic viscosity, respective to Kreamer equation ;

$[\eta]_m$ = intrinsic viscosity , respective to Martin equation,

$[\eta]_{sb}$ = intrinsic viscosity or limiting number, respective to Schulz – Blaschke equation;

k_h, k_k, k_m and k_{sb} Huggins , Kraemer , Martin and Schulz- Blaschke coefficients, respectively, C is the concentration.

Apart from the above, some relations have also been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analysed in short period of time, particularly in industrial laboratories. Most useful of them (Delpech,2002; Schoff, 1999; Abdel-Azim, 1998; Khan,1983; Qian, 2001) are Solomon- Ciute (SC, Eq. 6) and Deb –Chatterjee (DC, Eq. 7) relations

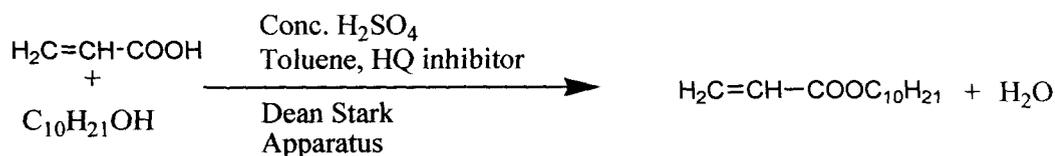
$$[\eta] = [2(\eta_{sp} - \ln\eta_r)]^{1/2}/C \quad (6)$$

$$[\eta] = (3\ln\eta_r + 3/2\eta_{sp}^2 - 3\eta_{sp})^{1/3}/C \quad (7)$$

The use of these equations has been derived under the supposition of the validity of the relationship (Delpech,2002) $k_h + k_k = 0.5$

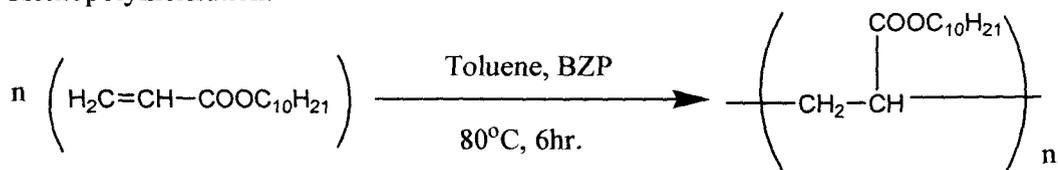
Scheme I

Esterification:



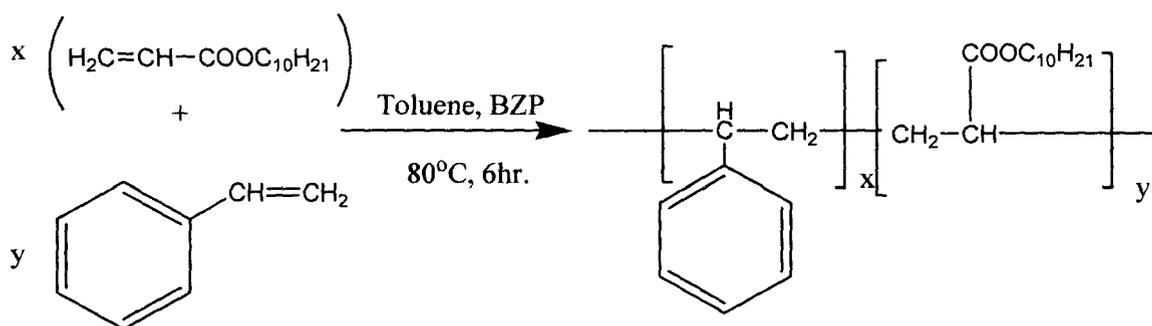
Scheme-II

Homopolymerisation:



Scheme-III

Copolymerisation:



Experimental

Esterification of decylacrylate (DA) from acrylic acid and decyl alcohol

Decyl acrylate was prepared by reacting acrylic acid with decyl alcohol (1.1:1 molar ratio). The reaction was carried out in a resin kettle in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid, and toluene as a solvent under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 130⁰C using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester, decyl acrylate.

Purification of prepared ester

The prepared ester was purified according to the following procedure: a suitable amount of charcoal was added to the ester, allowed to reflux for 3 h, and then filtered off. The filtrate was washed with 0.5N sodium hydroxide in a separating funnel and then shaken well. The entire process was repeated several times to ensure complete removal of unreacted acid. The purified ester was then washed several times with distilled water to remove any traces of sodium hydroxide; the ester was then left overnight on calcium chloride and was then removed by distillation under reduced pressure and was used in the polymerization process.

Preparation of homo polymer of DA and its copolymer with styrene and their purification

The polymerization was carried out in a four-necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask was placed desired mass of DA and initiator (BZP) followed by the desired mass of styrene was added drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into 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 313K. A homo polymer of DA was similarly prepared and purified under the same conditions for use in reference experiments.

Preparation of Polymer –base oil blend

Base oils of two different viscosity grades, BO1 and BO2 (Table 1) were collected from two different refineries, A and B. In all the cases blending of the additives with the oils were carried out by taking required amount of polymer in the calculated amount of oil (w/w) and then heating the mixture at 60°C for 30 min with constant stirring.

Measurements

Spectroscopic measurements

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

Viscometric measurements

Viscometric properties were determined at 313 K in different base stocks, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting time flow at least five different concentration of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and uncertainty was found to be nearly 0.17 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl/g}$ and $a = 0.725$ (Ivana, i. mello, 2006; Srivastava, 2003.) were employed in Mark Houwink – Sukurda relation

Thermo gravimetric analysis (TGA)

The thermograms in air were obtained on a mettler TA – 3000 system, at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$.

Results and discussion

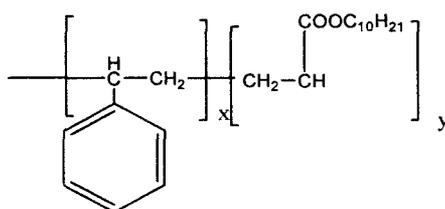
FT-IR spectrum of the homo polymer (Fig.1) exhibited absorption at 1732 cm^{-1} due to ester carbonyl stretching vibration. Peak at 1260 and at 1175 cm^{-1} can be explained

owing to the C-O (ester bond) stretching vibration and the absorption bands at 975, 750 and 711 cm^{-1} were due to the bending of C-H bond. The broad peak ranging from 2900-3100 cm^{-1} was due to the presence of stretching vibration.

The existence of the copolymer was confirmed by FT-IR and NMR analysis. The copolymer in its IR spectrum (Fig. 2) showed broad peak ranging from 1732 to 1720 cm^{-1} . This was attributed to the stretching vibration of the ester carbonyl group and to C-H bond of the phenyl group of styrene.

In the ^1H NMR (Fig. 3) spectra of one of the respective copolymers, a broad multiplet centered at 8.07 ppm indicated the presence of a phenyl group. A broad singlet centered at 4.06 ppm was due to the proton of the $-\text{OCH}_2$ group. The absence of singlets between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer.

The proton decoupled ^{13}C NMR spectrum (Fig. 4) of the above sample of copolymer was in complete agreement with the original structure-I



Structure-I

The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of $-\text{OCH}_2$ group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports (Bataille et al., 1994) as well as on the basis of our earlier paper (Ghosh, et al., 1998).

It was further verified through an analysis of FT-IR spectral data (Abdel-Azim, et al., 1998). The intensity of C=O absorption in FT-IR spectra of present copolymers, as compared to the carbonyl absorption in a standard, were analyzed for quantitative determination of the content of acrylate component in the copolymer. The comparative results obtained on comparisons are presented in Table-2.

Viscometric data were obtained using the six equation mentioned. A linear relation for the plot of $\log \eta_{sp}$ vs $\log c[\eta]$ obtained for all samples [Fig. 5a & 5b] indicated that measurements were performed in Newtonian flow (Gundert, 1986; Morris, 1984)

Huggins (H), Kraemer (K), Martin (M) and Schulz–Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz–Blaschke (SB) equation is commonly applied in single point determinations because it was found that $k_{sb} = 0.28$ for many polymer-solvent systems (Delpech,2002; Schoff, 1999; Abdel-Azim, 1998; Khan,1983; Oliveira 1991). In this work, this value was used.

Thermogravimetric analysis (TGA) in Table 3 showed that introduction of styrene raises the thermal stability of the copolymer in comparison to the homopolymer.

Table 4-5 presents intrinsic viscosity $[\eta]$ values of polymer solution in base oils BO1 and BO2 related to all equations for the samples analysed. Considering the oils (BO1 and BO2) and comparing the values of $[\eta]$ for homo and copolymers, it is noticed that the higher values were obtained in BO2 oil compared to BO1 oil. Thus considering all the polymers (homo and copolymers), oil BO2 appeared to be more compatible to the polymer and thus pointing towards providing more extended conformations of the polymers. This fact is further supported by the respective k_h+k_k values, which is well within 0.5 (Table 7). Lower values in BO1 oil in comparison to the BO2 oil, indicating contracted structures with star like conformation for the additive in this oil. Variation of $[\eta]$ obtained by graphic extrapolation method (equation 2-5) was found to be less compared to those obtained by single point determination method (equation 6-7) without any restriction to lubricating oil .

It is also observed that $[\eta]$ values decrease with the incorporation of styrene, but increases with increases in styrene concentration in case of oil BO2 and decreases in oil BO1. $[\eta]$ values obtained by using DC equation are always higher irrespective of the nature of the base stock.

It is also observed that there is a drop in intrinsic viscosity values in case of copolymer when added to base oils, particularly in BO1 oil, in comparison to the homopolymer. However, it does not change much with increase in styrene concentration in BO2 oil. Although the change is similar in BO1 oil, but the drop in intrinsic viscosity

values of the copolymer is more than what was observed in oil BO2 and the reduction in intrinsic viscosity values gradually increases with the increase in styrene concentration.

Table 6 & 7 presents values of viscometric constants calculated for homo and copolymers in BO1 and BO2 oil respectively, k_h and k_k fitted in the range of good solvents, whereas sample P-3^e in BO1 oil indicating more incompatibility. Although k_{sb} values found different from 0.28 in case of BO1 oil, but it has a close tendency to acquire this value (except p-3^e) in case of oil BO2. It is also important to observe that the relation $k_h+k_k=0.5$ was not found for the great majority of samples analyzed. However, intrinsic viscosities obtained by using single point determination methods were similar to values obtained by using graphic extrapolation method with small percentage differences. So values different from 0.5 did not put any restriction for the application of SC and DC equation.

Table 8 - 9 presents the percentual differences of intrinsic viscosity values where Huggins value taken as references. In both the oils it is observed that that differences is smaller in graphic extrapolation method compared to single point determination method. It is also observed that the differences is smaller in oil BO2 compared to oil BO1

Table 10 – 11 presents viscometric molecular weight of all the polymers (homo and copolymer). Homopolymer showed higher molecular weight than the copolymer. As expected the molecular weights are greater in oil BO2 compared to oil BO1. Again in oil BO1, a gradual decrease in viscometric molecular weight of the copolymer was observed with increase in styrene concentration although such a variation was not observed in oil BO2.

Conclusions

Viscometric analysis of the polymer may be carried out in lubricating oil to get more information about their morphological structure when added to the oil as a performance additive. Oil compatibility of the additive can be predicted easily through Viscometric analysis. Study also indicated that styrene incorporation enhances the thermal stability of this acrylate copolymer used as performance additive in lubricant formulation. This work is probably the first report of viscometric studies of polymeric additives in base oils.

Acknowledgment

Thanks are due to University Grants Commission, New Delhi for financial assistance

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Table 1. Base oil properties

Base oil	Density (g.cm ⁻¹)at 40 ⁰ C	Viscosity at 40 ⁰ C	Viscosity at 100 ⁰ C	Cloud point	Pour point
BO1	0.848	7.47	3.5	-8	-3
BO2	0.904	20.25	5.5	-10	-6

Table 2. Composition of the monomers in the co polymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. P-1 is homopolymer of decyl acrylate (DA); P-2 to P-3 is the copolymer of DA+ different mass fractions of styrene

Sample No	% of weight in the feed		% of weight in copolymer	
	DA	Styrene	By PMR method	By FT-IR
P-1	100	00		
P-2	95	5	1	1.5
P-3	90	10	2	2.1

Table 3. Thermal Gravimetric Analysis Data of all prepared samples

Sample	Decomp.Temp	PWL
P-1	250/340	23/86
P-2	300/400	45/84
P-3	320/430	60/85

Table 4. Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method.

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{SB}$	$[\eta]^b_{SB}$	$[\eta]^b_{SC}$	$[\eta]^b_{DC}$
P-1	2.691	3.075	2.974	2.931	3.515	3.544	3.649
P-2	1.967	2.036	2.054	1.938	2.162	2.18	2.213
P-3	1.294	1.020	1.118	1.343	1.974	1.99	2.005

Table 5. Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method.

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]^a_m$	$[\eta]^a_{SB}$	$[\eta]^b_{SB}$	$[\eta]^b_{SC}$	$[\eta]^b_{DC}$
P-1	4.642	4.303	4.609	4.571	4.718	4.687	4.746
P-2	3.317	3.538	3.602	3.684	3.836	3.832	3.821
P-3	3.501	3.187	3.430	3.555	3.925	3.921	3.917

Table 6. Viscometric constant values in BO1 oil

Sample	k_h	k_k	k_m	k_{sb}	$k_h+k_k=0.5$
P-1	1.08	3.64×10^{-3}	0.692	0.74	1.083

P-2	0.80	-0.186	3.374	1.72	0.614
P-3	0.70	-5.103	0.513	0.524	-4.40

Table 7. Viscometric constant values in BO2 oil

Sample	k_h	k_k	k_m	k_{sb}	$k_h+k_k= 0.5$
P-1	0.063	0.245	1.474	0.107	0.308
P-2	0.66	-0.376	-8.89×10^{-3}	0.77	0.284
P-3	0.535	-0.432	1.44	0.705	0.103

Table 8. Percentual differences ($\Delta \% = 100 \times [\eta]/[\eta]_h - 100$) of intrinsic viscosity values (In BO1 oil), Where Huggins value taken as a reference.

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
P-1	14.27	10.52	8.92	30.62	31.70	35.6
P-2	3.51	4.42	-1.47	9.91	10.83	12.51
P-3	-21.17	-13.6	3.79	52.55	53.79	54.95

Table 9. Percentual differences ($\Delta \% = 100 \times [\eta]/[\eta]_h - 100$) of intrinsic viscosity values (In BO2 oil), Where Huggins value taken as a reference.

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
P-1	-7.30	-0.71	-1.53	1.64	0.97	2.24
P-2	6.66	8.59	11.06	16.46	15.53	15.19
P-3	-8.97	-2.03	1.54	12.11	11.99	11.88

Table 10. Viscometric molecular weight of all prepared sample in BO1 oil by using Mark –Houwink equation $[\eta] = KM^a$, Where $K = 0.00387$ and $a = 0.725$.

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{DC}^b
--------	---------	---------	---------	------------	------------	------------	------------

P-1	8315	9995	9545	9355	12019	12156	12656
P-2	5396	5659	5729	5287	6148	6219	6349
P-3	3029	2181	2475	3188	5423	5484	5541

Table 11. Viscometric molecular weight of all prepared sample in BO2 oil by using Mark –Houwink equation $[\eta] = KM^a$, Where $K= 0.00387$ and $a = 0.725$.

Sample	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{DC}^b
P-1	17639	15887	17467	16951	18039	17876	18187
P-2	11095	12128	12432	12824	13559	13540	13486
P-3	11954	10500	11620	12208	13995	13975	13956

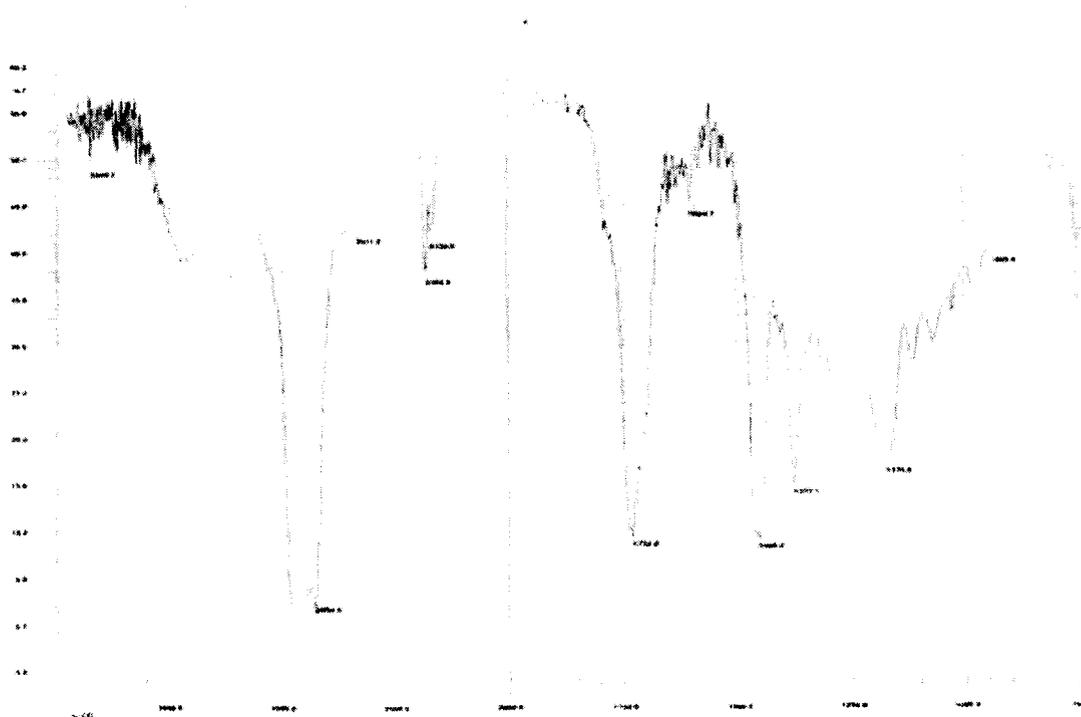


Figure 1. FT-IR spectrum of poly decylacrylate

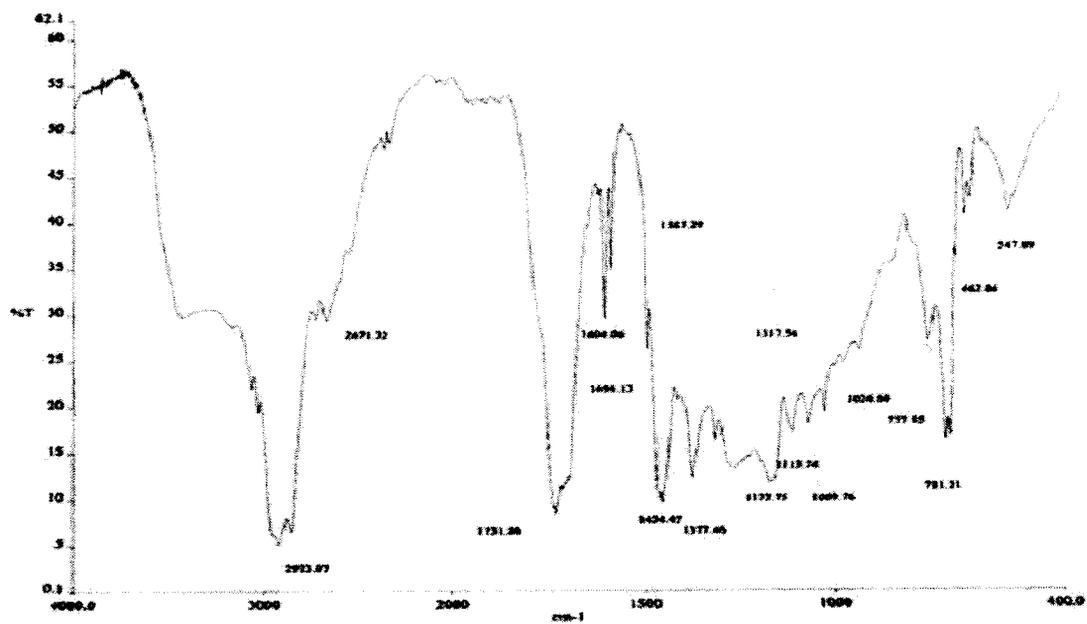
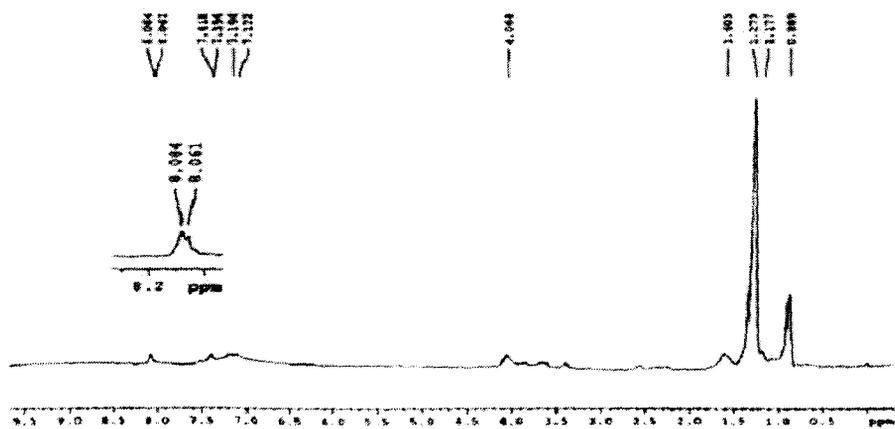


Figure 2. FT-IR spectrum of copolymer of decyl acrylate with styrene



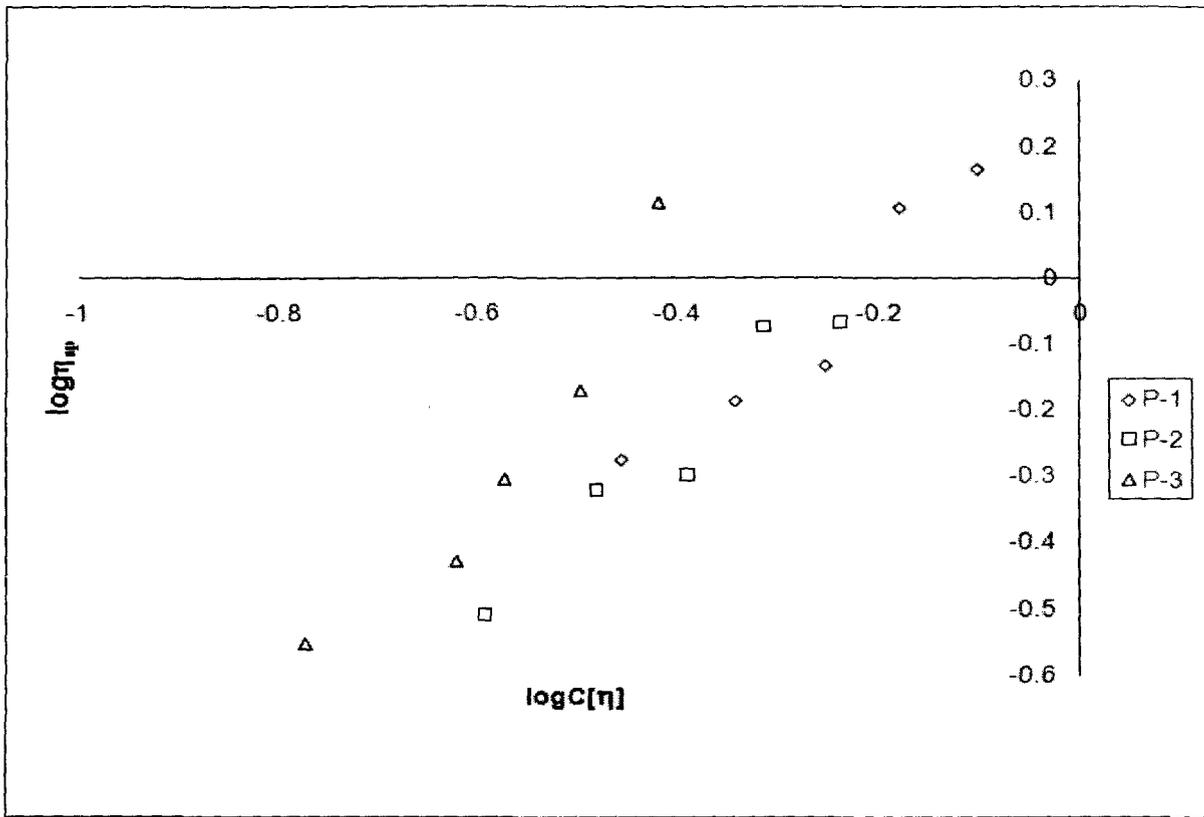


Figure 5a. Plot of $\log \eta_{sp}$ vs $\log C[\eta]$ for BO1.

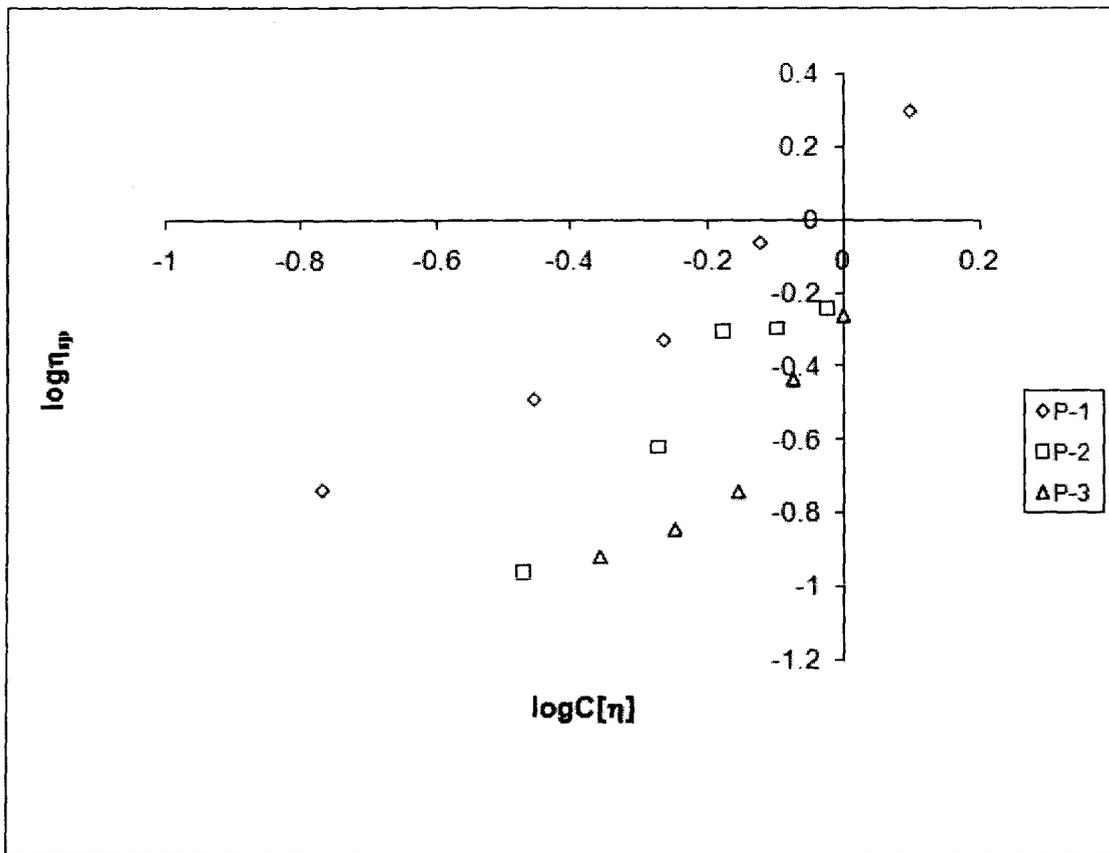


Figure 5b. Plot of $\log \eta_{sp}$ vs $\log C[\eta]$ for BO2.

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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713647664>

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Online publication date: 15 October 2010

To cite this Article Ghosh, Pranab , Das, Tapan , Nandi, Debabrata , Karmakar, Gobinda and Mandal, Amitava(2010) 'Synthesis and Characterization of Biodegradable Polymer - Used as a Pour Point Depressant for Lubricating Oil', *International Journal of Polymeric Materials*, 59: 12, 1008 – 1017

To link to this Article: DOI: 10.1080/00914037.2010.504156

URL: <http://dx.doi.org/10.1080/00914037.2010.504156>

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Synthesis and Characterization of Biodegradable Polymer - Used as a Pour Point Depressant for Lubricating Oil

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Additives based on polymers of alkyl methacrylate used in lubricant composition improve the viscometric and rheological properties of the lubricant and provide fuel economy. They are also looked upon to provide additional performance characteristics such as improved low temperature fluidity, dispersancy and thickening. However, the recent demand for eco-friendly technology guided us to incorporate the sunflower chemistry into the acrylate skeleton through the process of copolymerization in anticipation of getting an ideal blend of performance as well as eco-friendly chemistry. The present investigation comprises the homo and copolymerization of sunflower oil with different mass fraction of methyl methacrylate (MMA), decyl acrylate (DA) and styrene, characterizations and their evaluations as a pour point depressant in base oils.

Keywords base oil, biodegradable additives, copolymer, pour point, viscometric studies

Received 2 March 2010; accepted 11 May 2010.

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INTRODUCTION

The use of oil-soluble additives in lubricating oil to improve their performance is well-known. They improve performances by either enhancing the desirable properties already present or by introducing new properties into the oil without disturbing its original performance.

The decreasing of the natural resources of mineral oil and increasing environmental awareness have increased investigation into new environmental lubricant and additive chemistry. Keeping this view in mind, people have already started working in this direction to meet the above needs [1]. The use of biodegradable vegetable oils was known for a long time. Today, due to growing environmental concern, these oils are again finding application in lubricants for transportation as well as for industrial applications. They can offer significant environmental advantages with respect to fuel consumption, biodegradability and displaying satisfactory performance in field application. They are also reported to show excellent tribological properties when used as base stocks or as additives [2]. But the major limitations are their high cost and thermal and oxidative instability. Keeping this in mind and in continuation of our studies towards the development of chemical additives for lubricating and crude oils, in the present investigation an attempt has been made to synthesize a pour point additive based on sunflower oil.

Pour point is the temperature at which lubricating oil is just able to flow and below which there is complete absence of flow in it. Polymeric additives known as flow improvers or pour point depressants are generally used to lower the pour point, viscosity and yield stress of lubricating oil [3–7].

Since performance of such additives in field conditions is very much dependent on the structure and morphology of the polymer in the desired solvent [8], viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution are concerned. Since reports regarding such information are scanty [9,10] and almost nil for polymers used as lube oil additives the present research also include a viscometric study of the copolymers as well as the homopolymer.

According to the Mark Houwink–Sukurda relation (Eq. (1)), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = K M^a \quad (1)$$

where $[\eta]$, the intrinsic viscosity, can be calculated by using (Eq. (2) to Eq. (7)), parameter 'K' and 'a' depends on the type of polymer, solvent, and temperature.

Because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from another technique, generally in

determination of the molecular mass of samples with the available literature value of the constants used in the particular equation. A number of mathematical relations are available in the literature for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation [11–17]. The most commonly used equations are:

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

$$\text{Kraemer } \ln \eta_r/C = [\eta]_k - k_k [\eta]_k^2 C \quad (3)$$

$$\text{Martin } \ln(\eta_{sp}/C) = \ln [\eta]_m + k_m [\eta]_m C \quad (4)$$

$$\text{Schulz-Blaschke } \eta_{sp}/C = [\eta]_{sb} + k_{sb} [\eta]_{sb} \eta_{sp} \quad (5)$$

where $\eta_r = t/t_0$, relative viscosity or viscosity ratio; η_{sp} = specific viscosity

$[\eta]_h$ = intrinsic viscosity, respective to Huggins equation;

$[\eta]_k$ = intrinsic viscosity, respective to Kraemer equation;

$[\eta]_m$ = intrinsic viscosity, respective to Martin equation;

$[\eta]_{sb}$ = intrinsic viscosity or limiting number, respective to Schulz-Blaschke equation; k_h , k_k , k_m and k_{sb} Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively.

Some relations have been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analyzed in a short period of time, practical in industrial laboratories. Most useful [13–17] are the Solomon-Ciute (SC, Eq. (6) and Deb-Chanterjee (DC, Eq. (7) relations.

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2}/C \quad (6)$$

$$[\eta] = (3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3\eta_{sp})^{1/3}/C \quad (7)$$

The use of these equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$ [15].

EXPERIMENTAL

Measurements

Spectroscopic: IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells and the spectra were recorded 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 a solvent and TMS as reference material.

Viscometric Measurements

Viscometric properties were determined at 40°C in a toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting the time flow of at least eight different concentrations of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In the single point measurement the lowest value of solution concentration was chosen for the calculation. For the viscosity – average molecular weight determination, the constants $K = 0.00387$ dl/g and $a = 0.725$ were employed in Mark Houwink – Sukurda relation [15–17].

Thermogravimetric Analysis (TGA)

The thermograms in air were obtained on a Mettler TA – 3000 system, at a heating rate of 10°C/min.

Biodegradability Test

In this work we studied the biodegradability of the prepared polymer samples (both the copolymer and homopolymer) against five different fungal pathogens namely *Colletotrichum camelliae*, *Fusarium equisetiae*, *Alternaria alternata*, *Colletotrichum gloeosporioides* and *Curvularia eragrostidis*. All experiments were performed in petri dishes and were incubated at 37°C for 30 days after the addition of definite weight of polymer samples. The fungal growth was confirmed by a change of yellow to blackish color. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. All glass apparatus and culture media were autoclaved before use. The whole process was carried out in an inoculation chamber. After 30 days polymer samples were recovered from the fungal media and washed with chloroform, purified and dried in an open vessel. The dried samples were weighed [18].

Evaluation of Prepared Polymer as Pour Point Depressant in Base Oils

The prepared additives were evaluated as a pour point depressant using base oils (BO1 and BO2), each of them collected from two different sources (S1 and S2), through the pour point test according to the ASTM–D-97 method using WIL-471 cloud and pour point test apparatus model 3 (India). The effect of additive concentration was investigated by using different doping concentrations. The experimental data were noted by taking an average of three experimental results under identical conditions.

RESULTS AND DISCUSSION

^1H NMR of sunflower oil indicated the presence of unsaturation (δ 5.31, 4.27 and 4.12 ppm) along with other peaks due to methyl and methylene protons (δ 0.87 to 1.27 ppm) and (δ 1.59 to 2.75) ppm), respectively. The existence of homopolymer was indicated by the disappearance of the peaks in the unsaturation region (δ 4.0 to 6.0 ppm) along with a shift in the methyl and methylene signals. Formation of copolymer of sunflower oil and styrene was indicated by the absence of unsaturation in the NMR spectrum (no peak between 4–6 ppm) and the appearance of broad multiplet centered at δ 8.2 ppm for the aromatic ring protons of styrene. Similar results were also obtained in the NMR spectrum of other copolymers, e.g., sunflower oil – MMA and sunflower oil – DA.

IR spectra of the homo and copolymer of sunflower oil showed characteristic peaks for ester carbonyl at 1745.5 cm^{-1} and at 3408 cm^{-1} .

Using the graphic extrapolation method, respective intrinsic viscosities and constants were evaluated. In single point determinations, SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent system. The same is used here also.

Table 1 presents intrinsic viscosity values of all prepared samples in toluene solvent. In general it has been found that intrinsic viscosity values of homopolymer are greater than the copolymer except (P-3). Increase in monomer concentration (MMA, DA and styrene) intrinsic viscosity increases. It is interesting to note that by using several equations, values are identical for each polymer. For all polymeric samples intrinsic viscosity values obtained by using single point determination method are found to be greater than graphical extrapolation method.

Table 1: Intrinsic viscosity values of all polymeric samples. P-1 polymer of sunflower oil, P-2 copolymer of sunflower oil +5% MMA, P-3 copolymer of sunflower oil +10% MMA, P-4 copolymer of sunflower oil +5% DA, P-5 copolymer of sunflower oil +10% DA, P-6 copolymer of sunflower oil +5% styrene, P-7 copolymer of sunflower oil +10% styrene (a) graphic extrapolation method, and (b) single point determination method.

Samples	$[\eta]_{\text{n}}^{\text{a}}$	$[\eta]_{\text{k}}^{\text{a}}$	$[\eta]_{\text{m}}^{\text{a}}$	$[\eta]_{\text{sb}}^{\text{a}}$	$[\eta]_{\text{sb}}^{\text{b}}$	$[\eta]_{\text{sc}}^{\text{b}}$	$[\eta]_{\text{dc}}^{\text{b}}$
P-1	6.1	5.25	3.94	6.92	7.43	7.93	8.91
P-2	5.0	5.45	3.42	6.37	5.92	6.95	6.69
P-3	6.75	6.05	6.50	7.46	6.91	7.55	8.44
P-4	4.20	4.20	4.10	4.30	4.41	4.44	5.30
P-5	5.50	4.50	4.00	4.90	5.25	5.35	5.80
P-6	4.80	3.80	2.79	5.12	5.95	6.15	6.74
P-7	5.20	4.85	3.82	6.09	6.79	7.15	7.95

Table 2: Viscometric constant values of all samples.

Samples	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
P-1	0.88	-0.242	1.523	0.35	0.638
P-2	0.70	-0.041	1.468	0.437	0.659
P-3	0.55	-5.83×10^{-3}	0.475	0.252	0.544
P-4	0.46	-0.027	0.513	0.278	0.496
P-5	0.314	-0.187	0.78	0.35	0.127
P-6	0.89	-0.59	2.27	0.284	0.30
P-7	1.06	-0.223	1.41	0.183	0.837

Although different intrinsic viscosity values may be found by graphic extrapolation of Huggins, Kraemer, Martin and SB equation (Eqs. 2 to 6), in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. For the homopolymer and copolymer, the $[\eta]$ values obtained by Huggins and Kraemer's equation were identical.

Both homopolymer and copolymers in a toluene medium indicate good solvation (Table 2) as is evident from the respective viscometric constant values, and this conclusion is further supported by the negative values of the Kraemer coefficient of the all the systems analyzed. However, it is interesting to notice that for a few polymers in toluene, k_{sb} values were close to 0.28. But there is a close tendency to attain the $k_h + k_k = 0.5$.

By comparing $[\eta]$ values (Table 3) of homo and copolymers determined through graphic extrapolation using Kraemer, Martin and SB equations and single point determination with the values determined by the Huggins equation, it is observed that the range of variation ($\Delta\%$) is similar in both the cases, e.g., -41.87 to 17.13% and -4.54 to 52.80%, respectively.

Table 4 presents a comparison between the value of molecular weight obtained by viscometric methods for the homopolymer and copolymers analyzed. The general trend in all the cases is a gradual increase in molecular weight with an increase of monomer concentration.

Table 3: Percentual differences of intrinsic viscosity ($\Delta\% = (100((\eta)/(\eta)_h) - 100)$) (a) graphic extrapolation method, and (b) single point determination method.

Samples	K_k	K_m	K_{sb}	K_{sb}	K_{sc}	K_{dc}
P-1	-13.98	-35.36	13.48	21.74	30	46.08
P-2	-15.46	-31.6	3.40	18.6	22.08	33.74
P-3	-10.30	-3.70	10.54	2.43	30.70	25.06
P-4	-0.047	-2.33	2.44	5.0	5.74	26.19
P-5	18.18	-27.27	-10.90	-4.54	-2.70	5.49
P-6	-20.83	-41.87	6.75	23.96	28.125	40.41
P-7	-6.78	-26.54	17.13	30.57	37.5	52.80

Table 4: Viscometric molecular weight determined by using the Mark—Houwink equation ($\eta_r = KM^a$) where, $K = 0.00387$ and $a = 0.725$.

Samples	M_h^a	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
P-1	25735	20906	14097	30638	33756	36956	43406
P-2	19561	15516	11585	20486	24681	25758	29211
P-3	29592	25471	28091	33979	30588	34567	40287
P-4	15365	33877	32728	35142	36462	36845	47974
P-5	33901	37578	31520	42672	47300	48665	54912
P-6	18473	13384	8783	20214	24842	26001	29503
P-7	20629	18739	13481	25658	25658	32007	37023

Table 5: TGA data of all prepared samples.

Samples	Decomposition temperature	PWL
P-1	320/350	48/80
P-2	320/350	45/75
P-3	340/385	38/82
P-4	350/390	47/78
P-5	370/410	38/82
P-6	360/400	40/75
P-7	370/410	50/80

Table 6: Results of biodegradability test.

Fungal pathogens	Polymer samples	Incubation period (Days)	Initial wt (gm)	Final wt (gm)	Wt loss (gm)
<i>Colletotrichum camelliae</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Fusarium equisetiae</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Alternaria alternata</i>	P-1	30	1.5	0.9	0.6
	P-2	30	1.5	1.1	0.4
	P-4	30	1.5	1.4	0.1
	P-6	30	1.5	1.48	0.02
<i>Colletotrichum gloeosporioides</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Curvularia eragrostidis</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil

Table 5 presents TGA values of all the polymers. All the copolymers are thermally more stable. Increases in % concentration of monomers increase the thermal stability.

Table 6 presents biodegradability test results obtained by using the disk diffusion method. Homopolymer and copolymer of sunflower oil with decyl acrylate showed that sunflower oil was found to have significant biodegradability against the fungal pathogen, *Alternaria alternata*. It was further confirmed by the shift of IR frequency of the ester carbonyl to 1712 after the biodegradability test. Copolymer of sunflower oil with MMA also shows biodegradability but in a smaller extent. Biodegradability was not found in the copolymer of sunflower oil with styrene. The presence of styrene (aromatic moieties) may be key to the observed less biodegradability.

Table 7 presents PPD properties of the polymers evaluated in two different base stocks, each of them collected from two different sources (S1 and S2), and indicates that P-2 and P-5 showed best performance in both the base oils. The

Table 7: PPD properties of base oils collected from different sources.

Sample	Base oils	Pour point of base oil	Pour point of additive-doped base oil			
			2.5%	5%	10%	
P-1	BO1	S1	-3	-6	-6	-6
		S2	-3	-3	-3	-3
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-9
P-2	BO1	S1	-3	-12	-12	-12
		S2	-3	-12	-15	-15
	BO2	S1	-6	-15	-15	-15
		S2	-6	-15	-15	-15
P-3	BO1	S1	-3	-12	-12	-12
		S2	-3	-15	-15	-12
	BO2	S1	-6	-15	-12	-12
		S2	-6	-15	-12	-12
P-4	BO1	S1	-3	-15	-12	-12
		S2	-3	-15	-12	-12
	BO2	S1	-6	-15	-12	-12
		S2	-6	-15	-12	-12
P-5	BO1	S1	-3	-15	-18	-15
		S2	-3	-15	-18	-21
	BO2	S1	-6	-18	-21	-21
		S2	-6	-18	-21	-24
P-6	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-9
	BO2	S1	-6	-9	-12	-12
		S2	-6	-9	-12	-12
P-7	BO1	S1	-3	-9	-9	-9
		S2	-3	-9	-9	-9
	BO2	S1	-6	-9	-9	-9
		S2	-6	-9	-9	-9

values are always better than the respective homopolymer and both of them are made from sunflower oil.

CONCLUSIONS

The incorporation of monomers (MMA, DA and styrene) in the sunflower oil backbone raises the thermal stability of the copolymer and extent of monomer incorporation directly proportional to the thermal stability of the copolymer.

Intrinsic viscosity values of the copolymer are less than the corresponding homopolymer (except P-3) and the values obtained by single point determination method are higher than the values obtained by graphical extrapolation method.

Viscometric molecular weight of the copolymer is less than the homopolymer of decyl acrylate.

Pour point depressant (PPD) performance of the copolymer is always better than the homopolymer in all the base oils studied.

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*Oral Presentation*

PREPARATION, CHARACTERIZATION AND EVALUATION OF ACRYLATE POLYMERS AS POUR POINT DEPRESSANT FOR LUB OIL

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ABSTRACT

The potential for the use of poly acrylates and their co polymer as pour point depressant in lubricating oil is well documented. In the present work free radical homo polymerization of methyl methacrylate (MMA) and co polymerization with styrene were performed at 70°C with BZP as initiator in toluene. The molecular weight of the polymer was determined by GPC and viscometric methods. Resulting polymers were characterized by intrinsic viscosity, FT-IR and ¹H NMR spectroscopy. All the resulting polymers will be tested for their PPD performance in lubricating oil as well as in crude oils

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Ionic conductivity and phase transition Behaviour in $4\text{AgI}_{(1-x)}\text{PbI}_{2-2x}\text{CuI}$ system

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Abstract

Samples of general formula $4\text{AgI}_{(1-x)}\text{PbI}_{2-2x}\text{CuI}$, $x = 0-0.4$, have been prepared and studied by X-ray diffraction, DSC and electrical conductivity techniques. X-ray diffractograms showed the presence of binary system consisting of AgI and PbI_2 in the sample $x = 0$. Cu-substituted samples showed very similar diffractograms to that of the pure compound which indicates that no effect for the substitution on the nature of the binary system. DSC Curves showed the presence of phase transition whose temperature increased with Cu^+ ratio in the system. Ionic conductivity measurements confirmed the occurrence of the phase transition and showed that the high temperature phase is superionic conducting whose conductivity increases with the increasing Cu^+ amount in the system.

Keywords: Ionic conductivity; Phase transition; XRD; DSC

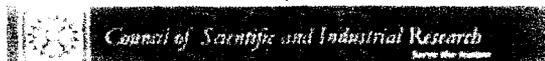
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SYNTHESIS AND CHARACTERIZATION OF POLYMERIC P1 ADDITIVES FOR LUBRICATING OIL

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ABSTRACT

Methacrylate based polymeric additives were prepared by free radical polymerization using toluene as a solvent. Resulting polymers were characterized by viscometric measurements and spectroscopic analysis. Thermal behaviors of the additives to be tested by TGA to find the suitability of the polymers in operating condition. Their performance as a viscosity index improver and pour point depressant will be tested following ASTM procedures. Effect of initiator concentration and temperature of polymerization on the performance of the additives will also be studied.

Similar study will be carried out of the homo and copolymer of acrylate esters.

Copolymer Of Sun Flower Oil With Alkyl Acrylates - Synthesis, Characterization And Performance Evaluation In Lubricating Oil

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Different kinds of polymeric additives are used in lubricant composition for improving the viscometric and rheological properties of the lubricant [1- 4]. They prolong the useful life of machines, achieve greater performance and provide fuel economy. However, the present specification laid down by the Original Equipment Manufacturer (OEM) led us to synthesize additives which are eco-friend or less hazardous to the environment, without disturbing their performances. Due to this present demand of greener technology, many researchers are embarking on the viability of the vegetable-based lubricants [5] and recently, much effort has been focused on research and development of new types of biodegradable lubricating oil additives to adapt new requirements and demands. Keeping this view in mind and to overcome the shortcoming always associated with the existing additive chemistry, we undertook a study to synthesize vegetable based lubricating oil additives by the copolymerization of alkyl acrylates with sun flower oil - their characterization and evaluation in lubricating oil. This paper comprises the results of our recent investigation which will be presented in the symposium.

Keywords:

Additives, Lubricating Oil, Viscometric and Rheological properties, Copolymerization, Original Equipment Manufacturer,

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Synthesis, Characterization and Viscometric Studies of Homo and Copolymer of Decylacrylate

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ABSTRACT

Homopolymer of decylacrylate (DA) and its copolymer using different concentrations of styrene were synthesized, characterized and evaluated for their performance as lubricating oil additives. of the co polymers was carried out employing GPC, TGA, IR and NMR. However, since performance of such kind of additives in field condition is very much dependent on the structure and morphology of the polymer in desired solvent [1,2], viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution are concerned. Since report regarding such information is scanty [3, 4] and almost nil for polymers used as lube oil additives – present research also include viscometric study of the synthesized polymers. The viscometric measurements of the synthesized homopolymer as well as the co polymers in different base stocks at 400 C were performed [5]. Results are interesting and will be presented in the Symposium.

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