

SYNTHESIS, CHARACTERIZATION AND EVALUATION OF ACRYLATE - BASED POLYMERIC ADDITIVES FOR LUBRICATING OIL

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Dedicated to My Parents

DECLARATION

I hereby declare that the thesis entitled "**SYNTHESIS, CHARACTERIZATION AND EVALUATION OF ACRYLATE - BASED POLYMERIC ADDITIVES FOR LUBRICATING OIL**" completed and written by me under the guidance of Dr. Pranab Ghosh, Associate Professor of Department of Chemistry, University of North Bengal. This thesis or any part of it 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, Characterization and Evaluation of Acrylate-based Polymeric Additives for Lubricating oil**”, submitted by **Sri Debabrata Nandi**, who got his name registered on **18.05.09** for the Ph.D. (Science) Degree of the University of North Bengal, is entirely based on 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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SUMMARY OF THE WORK

The work embodied in the thesis has been divided into three parts and each of them contained three chapters. The first chapter of every part presented a brief review of the titled work, the second chapter of each part comprises the results and detailed discussion about the present investigation and the last chapter consists of detailed experimental procedures and references.

PART - I

Synthesis, Characterization and Viscosity Analysis of Homo and copolymer of Methyl acrylate and Evaluation of their Viscosity index improver and Pour Point Depressant Properties in Lubricating Oils

This Part has been divided into three chapters: **Chapter I**, **Chapter II** and **Chapter III**

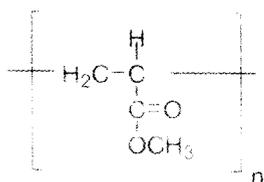
Chapter - I: It describes a brief review of the present investigation

Chapter - II: This chapter contains only one section

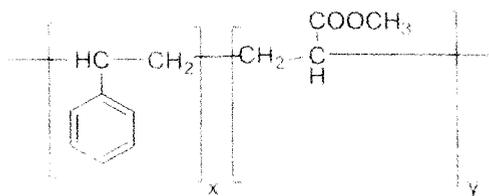
Synthesis, Characterization and Viscosity Analysis of Homo and Copolymer of Methyl Acrylate and Evaluation of their Pour Point Depressant and Viscosity Index Improver properties in different Base Stocks

Homopolymer of methyl acrylate (MA) and its copolymer with styrene were synthesized. The effect of solvents and initiator concentrations on percent yield, solubility, molecular weight and viscometric properties of each of the homopolymer and the copolymer were studied and compared. The characterization of the homopolymer and copolymer samples was carried out by FT-IR and FT-NMR spectroscopic method. The solubility test was performed in thirteen different solvents for the homopolymer and the copolymer samples prepared in three different solvents. The viscosity measurements of the synthesized homopolymers as well as that of the copolymers in the toluene solution at 303K, 313K and 323K were performed and compared. 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 in increasing the solution viscosity) and intrinsic viscosity. Then the homopolymers of methyl acrylate and the copolymers of methyl acrylate with styrene prepared in three different solvents were evaluated as pour point depressant and viscosity index improver in two different base oils.



Homopolymer of methyl acrylate



Copolymer of methyl acrylate with styrene

Chapter - III: This chapter consists of detailed of experimental procedures and References

PART II

Synthesis, Characterization and Viscosity Studies of Homo polymer of Methyl Methacrylate and Copolymers of Methyl Methacrylate with Styrene and 1-Decene and Comparative Performance Evaluation of these Polymers as Pour Point Depressant (PPD) and Viscosity Index Improvers (VII) in Lubricating Oils.

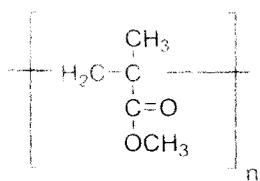
This Part has been divided into three chapters, **Chapter I**, **Chapter II** and **Chapter III**

Chapter – I: This chapter comprises a brief review of the titled work

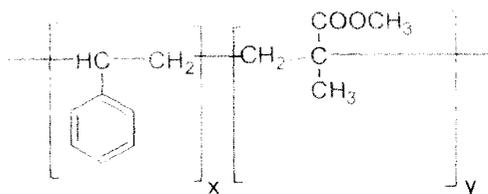
Chapter – II: This chapter is divided into three sections, **Section A**, **Section B** and **Section C**

Section A: It Comprises the **Synthesis, Characterization and Viscosity Studies of Homopolymer of Methyl Methacrylate and its Copolymers with Styrene and 1-Decene.**

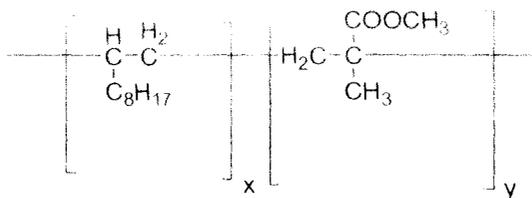
Homopolymer of methyl methacrylate (MMA) and its copolymer using different compositions of styrene and 1-decene were synthesized and characterized. The viscosity measurements of the synthesized homopolymer as well as the copolymer in the toluene solution at 313K were performed. Different equations were used to calculate 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 determination of specific viscosity (η 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.



Homopolymer of methyl methacrylate



Copolymer of methyl methacrylate with styrene



Copolymer of methyl methacrylate with 1-decene

Section B Comprises **Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate and Evaluation of their Pour Point Depressant properties in Lubricating (Lube) Oils.**

The degradation stability towards mechanical shearing (shear stability) of the homopolymer of methyl methacrylate (MMA) and its copolymer with styrene at different level of concentrations have been investigated. With a view to understanding the relationship between the thickening performance (percent increase in viscosity of the solvent in the additive of the unit weight of polymers) and shear stability of the polymer, the thickening abilities of the polymer were also determined and compared. Pour point depressant properties of the copolymers in comparison to the homopolymer were also tested in different base stocks

Section C Comprises **Comparative Performance Evaluation of Homopolymer of Methyl Methacrylate and Copolymer of Methyl Methacrylate with Styrene and 1-Decene as Pour Point Depressant and Viscosity Index Improver in three different Base Oils.**

The homopolymer of methyl methacrylate (MMA), copolymer of MMA with styrene and copolymer of MMA with 1-decene were synthesized and comparatively evaluated as viscosity index improver (VII) and pour point depressant (PPD) for three different lube oils. It was observed that the copolymers performed better as VII and PPD than the homopolymer. It was also observed that the occurrence of maximum performance depends on the mineral base oil used and the type and concentration of the polymers. The result of the work indicated the dependence of the performance of the polymeric additives on the chemical composition and structural characteristics of the polymer, the length of the alkyl side chains and molecular weight of the polymer.

Chapter III: This chapter consists of experimental procedures and References

PART III

Preparation, Characterization, Viscometric Analysis, Compatibility Studies and Evaluation of Homopolymer of Decyl Acrylate and its Copolymer with Styrene along with their Blends as Lubricating Oil Additives

This Part has been divided into three chapters, **Chapter I**, **Chapter II** and **Chapter III**

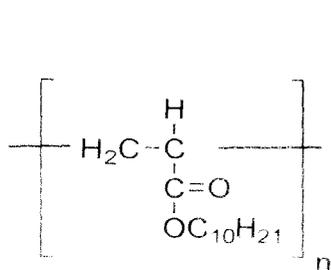
Chapter I A brief review of the titled work

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

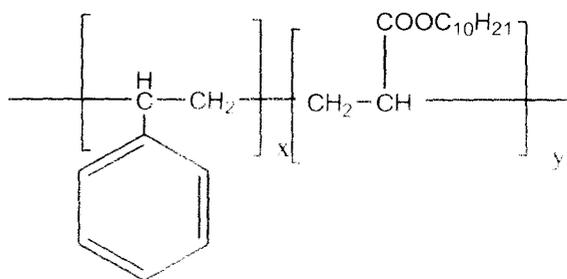
Section A comprises the **Preparation, Characterization, Compatibility Studies and Evaluation of Homopolymer of Decyl Acrylate and its Copolymer with Styrene along with their Blends as Lubricating Oil Additives**

Homopolymer of decyl acrylate (DA) and copolymer of decyl acrylate with styrene and polymer blends (mixture) with different percentage of these polymeric samples were prepared, characterized and evaluated as additives for lubricating oil. Viscometric studies have been conducted on the binary solutions (polymer-solvent) of homopolymer of decyl acrylate (DA), copolymer of DA as well as on their ternary solutions (polymer-polymer-solvent) having different concentrations of each polymer at 30°C in chloroform and toluene. The estimation of the compatibility degree of the above polymer pairs has been made by means of five criteria. Results show that in most of the cases polymer blends are compatible, except Ab_m data. This is probably due to non ideal behavior (hydrodynamic interaction) of polymers in ternary solutions. Data obtained in the solvents are not similar implying that polymer-polymer interactions and polymer-solvent interactions are both important for long chain polymers. The two solvents were chosen based on their ability to dissolve the two polymers and because of their differences in both structure and properties. The evaluation data indicates that compatible polymer mixtures act as much better viscosity index improvers (VII) and pour point depressants (PPD) than both the homopolymer and copolymer. With increasing

concentration of the copolymer in the blend, there is gradual increase in the additive performance.



Homopolymer of decyl acrylate



Copolymer of decyl acrylate with styrene

Section B comprises the **Viscometric Analysis of Homopolymer of Decyl Acrylate, its Copolymer with Styrene and their Polymer Mixture (Blends)**

Homopolymer of decyl acrylate (DA) and copolymer of decyl acrylate with styrene and their blends of different percentage were synthesized and characterized. The viscometric measurements of the synthesized homopolymer, copolymer and their blends were performed in two 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. The purpose of the viscometric study with the blends was to determine the solvent effect over the polymer-polymer-solvent (ternary) interaction in solution.

Chapter III Consists of experimental and References

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1. Homopolymer of Methyl Acrylate and its Copolymer with Styrene: Synthesis and Characterization, Pranab Ghosh, Tapan Das, **Debabrata Nandi**, Kinshuk Poddar and Gobinda Karmakar, *Journal of Polymer Materials*, **2010**, Vol. 27, No. 4, 323-334.
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3. Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate, Pranab Ghosh, Tapan Das and **Debabrata Nandi**, *American Journal of Polymer Science*, **2011**; 1(1), 1-5.
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5. 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*, **2010**, 59, 1008-1017.
6. 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*, **2009**, 13(1), 10-25.

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.
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5. Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate, **Debabrata Nandi**, Tapan Das, Mahua Upadhyay, Koushik Dey and Pranab Ghosh, proceeding of "13th CRSI National Symposium in Chemistry" 2-4 February 2011. KIIT University, Bhubaneshwar, India.

Abbreviations

1. ASTM – American Society for Testing and Materials
2. BPCL- Bharat Petroleum Corporation Limited
3. B1- Base Oil 1
4. B2- Base Oil 2
5. B3- Base Oil 3
6. BZP- Benzoyl peroxide
7. DA- Decyl acrylate
8. DC- Deb-Chatterjee
9. FM- Friction modifier
10. GE- Graphic extrapolation
11. GPC- Gas permeation chromatography
12. IOCL. Indian Oil Corporation Limited
13. IR- Infra red
14. KV- Kinematic viscosity
15. MA- Methyl acrylate
16. MMA- Methyl methacrylate
17. MHS- Mark-Houwink-Sakurada
18. M_n - Number average molecular weight
19. M_w - Weight average molecular weight
20. M_v - Viscosity molecular weight
21. NMR- Nuclear magnetic resonance
22. OCP- Olefin copolymer
23. OEM- Original equipment manufacturer
24. PAMA- Poly(alkyl methacrylates)
25. PDA- Polydecylacrylate
26. PMMA- Poly(methyl methacrylate)
27. PPD- Pour point depressant
28. PSSI- Permanent shear stability index
29. PVL- Permanent viscosity loss
30. PWI.- Percent weight loss

31. SB- Schulz- Blaschke
32. SC- Solomon- Ciute
33. SEC- Size exclusion chromatography
34. SPD- Single point determination
35. SSI- Shear stability index
36. S1- Source 1
37. S2- Source 2
38. TE- Thickening effect
39. TGA- Thermo gravimetric analysis
40. VI- Viscosity index
41. VII- Viscosity index improver
42. VM- Viscosity modifier
43. THF- Tetrahydrofuran
44. TVL- Temporary viscosity loss
45. M_n - Molecular weight calculated from values using Huggins equation
46. η_r - Relative viscosity
47. η_{sp} - Specific viscosity
48. $[\eta]$ - Intrinsic viscosity

LIST OF TABLES

| Table No. | Table Name | Page No. |
|------------------|---|-----------------|
| PART I | | |
| Table 1 | Composition of the monomers in the copolymer (prepared in toluene) in terms of mass fraction determined by PMR and FT-IR spectrometric method. | 22 |
| Table 2 | Percent yield of homo and copolymer prepared in different solvents and at different initiator concentrations (w/w) | 22 |
| Table 3 | Solubility behaviours of homo and copolymers | 23 |
| Table 4 | Intrinsic viscosity values of homopolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures | 24 |
| Table 5 | Intrinsic viscosity values of copolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures. | 24 |
| Table 6 | Intrinsic viscosity values of homopolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures. | 25 |
| Table 7 | Intrinsic viscosity values of copolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures | 25 |
| Table 8 | Intrinsic viscosity values of homopolymer prepared in toluene at different initiator concentrations and at three different temperatures | 26 |
| Table 9 | Intrinsic viscosity values of copolymer prepared in toluene at different initiator concentrations and at three different temperatures | 26 |
| Table 10 | Viscometric parameter values of the homopolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures | 27 |
| Table 11 | Viscometric parameter values of the copolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures | 27 |

| Table No. | Table Name | Page No. |
|------------------|---|-----------------|
| Table 12 | Viscometric parameter values of the homopolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures | 28 |
| Table 13 | Viscometric parameter values of the copolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures | 28 |
| Table 14 | Viscometric parameter values of the homopolymer prepared in toluene at different initiator concentrations and at three different temperatures | 29 |
| Table 15 | Viscometric parameter values of the copolymer prepared in toluene at different initiator concentrations and at three different temperatures | 29 |
| Table 16 | Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the homopolymer in tetrahydrofuran, | 30 |
| Table 17 | Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the copolymer in tetrahydrofuran | 30 |
| Table 18 | Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the homopolymer in 1, 4-dioxane | 31 |
| Table 19 | Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the copolymer in 1, 4-dioxane | 31 |
| Table 20 | Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the homopolymer in toluene | 32 |
| Table 21 | Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the copolymer in toluene | 32 |
| Table 22 | Determination of molecular weight of the homopolymer in tetrahydrofuran by Mark Houwinks equation | 33 |
| Table 23 | Determination of molecular weight of the copolymer in tetrahydrofuran by Mark Houwinks equation | 33 |
| Table 24 | Determination of molecular weight of the homopolymer in 1, 4-dioxane by Mark Houwinks equation | 34 |

| Table No. | Table Name | Page No. |
|------------------------------|--|-----------------|
| Table 25 | Determination of molecular weight of the copolymer in 1, 4-dioxane by Mark Houwinks equation | 34 |
| Table 26 | Determination of molecular weight of the homopolymer in toluene by Mark Houwinks equation | 35 |
| Table 27 | Determination of molecular weight of the copolymer in toluene by Mark Houwinks equation | 35 |
| Table 28 | Base oil properties | 36 |
| Table 29 | Pour point of homopolymer doped base oils (B1) | 36 |
| Table 30 | Pour point of copolymer doped base oils (B1) | 37 |
| Table 31 | Pour point of homopolymer doped base oils (B2) | 37 |
| Table 32 | Pour point of copolymer doped base oils (B2) | 38 |
| Table 33 | Viscosity index of homopolymer doped base oils (B1) | 38 |
| Table 34 | Viscosity index of copolymer doped base oils (B1) | 39 |
| Table 35 | Viscosity index of homopolymer doped base oils (B2) | 39 |
| Table 36 | Viscosity index of copolymer doped base oils (B2). | 40 |
| PART II | | |
| Chapter II, Section A | | |
| Table 1 | Composition of the monomers in the copolymers in terms of mass fraction determined by PMR and FT-IR spectrometric method | 72 |
| Table 2 | Molecular mass obtained by gel permeation chromatography and Thermal gravimetric analysis data for homo- and copolymers | 72 |
| Table 3 | Intrinsic viscosity values for all prepared homo and copolymer samples calculated by using different equation | 73 |
| Table 4 | Viscometric constants obtained for all prepared homo- and copolymer samples | 73 |
| Table 5 | Percentual differences ($\Delta = ([\eta]/[\eta]_h) - 1$) obtained for intrinsic viscosity values | 74 |

| Table No. | Table Name | Page No. |
|------------------------------|--|-----------------|
| Table 6 | Determination of molecular weight by Mark-Houwinks equation | 74 |
| Table 7 | Percentual differences obtained for viscometric molecular weight values | 75 |
| Section B | | |
| Table 1 | Composition of the monomers in the copolymers in terms of mass fraction determined by PMR and FT-IR spectrometric method | 81 |
| Table 2 | Physical parameters of Polymeric Samples | 82 |
| Table 3 | Thickening power and kinematic viscosity data | 82 |
| Table 4 | Base oil properties | 83 |
| Table 5 | Pour point of additive doped base oils | 84 |
| Section C | | |
| Table 1 | Base oil properties | 89 |
| Table 2 | Pour Point of additive doped base oils (B1) | 89 |
| Table 3 | Pour point of additive doped base oils (B2) | 90 |
| Table 4 | Pour point of additive doped base oils (B3) | 90 |
| Table 5 | Viscosity index of additive doped base oils (B1) | 91 |
| Table 6 | Viscosity index of additive doped base oils (B2) | 91 |
| Table 7 | Viscosity index of additive doped base oils (B3) | 92 |
| PART III | | |
| Chapter II, Section A | | |
| Table 1 | Composition of the monomers in the copolymer (prepared in toluene) in terms of mass fraction determined by PMR and FT-IR spectrometric method P-1 is homopolymer of decyl acrylate (DA); P-2 is the copolymer of DA with styrene | 127 |

| Table No. | Table Name | Page No. |
|------------------|--|-----------------|
| Table 2 | Interaction parameters and intrinsic viscosity data for the individual polymers in different solvents at 313K. | 127 |
| Table 3 | Experimental and theoretical viscometric parameters for the ternary mixtures of DA and its copolymer with styrene at different percentage in chloroform at 313K. | 128 |
| Table 4 | Experimental and theoretical viscometric parameters for the ternary mixtures of DA and its copolymer with styrene at different percentage in toluene at 313K. | 128 |
| Table 5 | Base oil properties | 129 |
| Table 6 | Pour point of additive doped base oils | 129 |
| Table 7 | Viscosity index of additive doped base oils | 130 |
| Section B | | |
| Table 1 | Intrinsic viscosity values for all prepared homopolymer, copolymer and polymer blends samples in toluene, | 135 |
| Table 2 | Intrinsic viscosity values for all prepared homopolymer, copolymer and polymer blends samples in chloroform | 135 |
| Table 3 | Viscometric constants obtained for all prepared homopolymer, copolymer and polymer blend samples in toluene | 136 |
| Table 4 | Viscometric constants obtained for all prepared homopolymer, copolymer and polymer blend samples in chloroform | 136 |
| Table 5 | Percentual differences ($\Delta = ([\eta]/[\eta]_h) - 1$) obtained for intrinsic viscosity values in Toluene | 137 |
| Table 6 | Percentual differences ($\Delta = ([\eta]/[\eta]_h) - 1$) obtained for intrinsic viscosity values in Chloroform | 137 |
| Table 7 | Determination of molecular weight (M_v) by Mark Houwinks equation $[\eta] = KM^a$ in toluene | 138 |
| Table 8 | Determination of molecular weight (M_v) by Mark Houwinks equation $[\eta] = KM^a$ in chloroform | 138 |

LIST OF FIGURES

| Figure No. | Figure Name | Page No. |
|------------------------------|---|----------|
| PART I | | |
| Figure 1 | FT-IR spectrum of homopolymer of methyl acrylate | 16 |
| Figure 2 | ¹ H NMR spectrum of homopolymer of methyl acrylate | 17 |
| Figure 3 | ¹³ C NMR spectrum of homopolymer of methyl acrylate | 18 |
| Figure 4 | FT-IR spectrum of copolymer of methyl acrylate with styrene | 19 |
| Figure 5 | ¹ H NMR spectrum of copolymer of methyl acrylate with styrene | 20 |
| Figure 6 | ¹³ C NMR spectrum of copolymer of methyl acrylate with styrene | 21 |
| PART II | | |
| Chapter II, Section A | | |
| Figure 1 | FT-IR spectrum of homopolymer of methyl methacrylate with styrene | 65 |
| Figure 2 | FT-IR spectrum of copolymer of methyl methacrylate with styrene | 66 |
| Figure 3 | ¹ H NMR spectrum of copolymer of methyl methacrylate with styrene | 67 |
| Figure 4 | FT-IR spectrum of copolymer of methyl methacrylate with 1-decene | 68 |
| Figure 5 | ¹ H NMR spectrum of copolymer of Methyl methacrylate with 1-decene | 69 |

| Figure No. | Figure Name | Page No. |
|-------------------|---|-----------------|
| Figure 6 | ¹³ C NMR spectrum of copolymer of Methyl methacrylate with 1-decene | 70 |
| Figure 7 | Plot of log C[η] vs log η _{sp} | 71 |
| Section B | | |
| Figure | Plot of % styrene in copolymer with PSSI | 81 |
| PART III | | |
| Figure 1 | FT-IR spectrum of polydecylacrylate | 120 |
| Figure 2 | ¹ H NMR spectrum of homopolymer of decyl acrylate | 121 |
| Figure 3 | FT-IR spectrum of copolymer of decyl acrylate with styrene | 122 |
| Figure 4 | ¹ H NMR spectrum of copolymer of decyl acrylate with styrene | 123 |
| Figure 5 | ¹³ C NMR spectrum of copolymer of decyl acrylate with styrene | 124 |
| Figure 6 | Plot of reduced viscosity, η _{sp} /C vs. concentration C in Chloroform | 125 |
| Figure 7 | Plot of reduced viscosity, η _{sp} /C vs. concentration C in Toluene | 126 |

CONTENTS

| | Page No. |
|---|----------|
| PART - I | |
| Synthesis, Characterization and Viscosity Analysis of Homo and copolymer of Methyl acrylate and Evaluation of their Viscosity index improver and Pour Point Depressant Properties in Lubricating Oils | 1 |
| Chapter-I | 2 |
| 1.1 A brief review of the present investigation | |
| Chapter II | 8 |
| 2.1 Section A: Synthesis, Characterization and Viscosity Analysis of Homo and Copolymer of Methyl Acrylate and Evaluation of their Pour Point Depressant (PPD) and Viscosity Index Improver (VII) Properties in different Base Stocks | 8 |
| 2.1.1 Introduction | 8 |
| 2.1.2 Results and Discussions | 10 |
| 2.1.3 Conclusions | 15 |
| Chapter III | 41 |
| 3.1 Experimental | 41 |
| 3.1.1 Materials used | 41 |
| 3.1.2 Purifications of Materials | 41 |
| 3.1.3 Polymerization | 41 |
| 3.1.4 Spectroscopic Measurements | 42 |
| 3.1.5 Viscometric measurements | 42 |
| 3.1.6 Evaluation of prepared polymer as pour point depressant in base oils | 42 |
| 3.1.7 Evaluation of prepared polymer as viscosity index improvers in base oils | 43 |
| 3.2 References | 43 |
| | 48 |

PART II

Synthesis, Characterization and Viscosity Studies of Homo polymer of Methyl Methacrylate, Copolymer of Methyl Methacrylate with Styrene and 1-Decene and Comparative Performance Evaluation of these Polymers as Pour Point Depressant (PPD) and Viscosity Index Improvers (VII) in Lubricating Oils.

| | |
|---|----|
| Chapter-I | 49 |
| 1.1 A brief review of the present investigation | |
| Chapter II | 57 |
| 2.1 Section A: Synthesis, Characterization and Viscosity Studies of Homopolymer of Methyl Methacrylate and its Copolymer with Styrene and 1-Decene. | 58 |
| 2.1.1 Introduction | 58 |
| 2.1.2 Results and Discussions | 60 |
| 2.1.3 Conclusion | 63 |
| 2.2 Section B: Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate and Evaluation of their Pour Point Depressant Properties in Lubricating (Lube) Oils. | 76 |
| 2.2.1 Introduction | 76 |
| 2.2.2 Results and Discussions | 78 |
| 2.2.3 Conclusion | 79 |
| 2.3 Section C: Comparative Performance Evaluation of Homopolymer of Methyl Methacrylate and Copolymer of Methyl Methacrylate with Styrene and 1-Decene as Pour Point Depressant and Viscosity Index Improver in three different Base Oils | 85 |
| 2.3.1 Introduction | 85 |
| 2.3.2 Results and Discussions | 86 |
| 2.3.3 Conclusion | 87 |
| Chapter III | 93 |

| | |
|--|----|
| 3.1 Experimental | 93 |
| 3.1.1 Materials used | 93 |
| 3.1.2 Purification of the materials | 93 |
| 3.1.3 Polymerization | 93 |
| 3.1.4 Spectroscopic Measurements | 94 |
| 3.1.5 Viscometric measurements | 94 |
| 3.1.6 Thermo gravimetric analysis | 94 |
| 3.1.7 determination of Shear Stability | 94 |
| 3.1.8 Evaluations of prepared polymers as pour point depressant in base oils | 95 |
| 3.1.9 Evaluations of prepared polymers as viscosity index improvers in base oils | 95 |
| 3.2 References | 95 |

PART III 101

Preparation, Characterization, Viscometric Analysis, Compatibility Studies and Evaluation of Homopolymer of Decyl Acrylate and its Copolymer with Styrene along with their Blends as Lubricating Oil Additives

| | |
|---|-----|
| Chapter-I | 102 |
| 1.1 A brief review of the present investigation | |
| Chapter II | 109 |
| 2.1 Section A: Preparation, Characterization, Compatibility Studies and Evaluation of Homopolymer of Decyl Acrylate and its Copolymer with Styrene along with their Blends as Lubricating Oil Additives | 110 |
| 2.1.1 Introduction | 110 |
| 2.1.2 Results and Discussions | 115 |
| 2.1.3 Conclusion | 119 |
| 2.2 Section B: Viscometric Analysis of Homopolymer of Decyl Acrylate, its Copolymer with Styrene and their Polymer Mixture (Blends). | 131 |
| 2.2.1 Introduction | 131 |

| | |
|---|-----|
| 2.2.2 Results and Discussions | 132 |
| 2.2.3 Conclusion | 134 |
| Chapter III | 139 |
| 3.1 Experimental | 139 |
| 3.1.1 Materials used | 139 |
| 3.1.2 Esterification of decyl acrylate (DA) from acrylic acid and decyl alcohol | 139 |
| 3.1.3 Purification of prepared ester | 139 |
| 3.1.4 Preparation of homo polymer of DA and its copolymer with styrene and their purification | 140 |
| 3.1.5 Spectroscopic Measurements | 141 |
| 3.1.6 Viscometric measurements | 141 |
| 3.1.7 Evaluation of prepared additive as pour point depressants (PPDs) in base oils | 142 |
| 3.1.8 Evaluation of prepared additive as viscosity index improvers (VIIs) in base oils | 143 |
| 3.2 References | 143 |

PART I

SYNTHESIS, CHARACTERIZATION AND VISCOSITY STUDIES OF HOMO AND COPOLYMER OF METHYL ACRYLATE AND EVALUATION OF THEIR VISCOSITY INDEX IMPROVER AND POUR POINT DEPRESSANT PROPERTIES IN LUBRICATING OILS

CHAPTER I

1.1 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

Lubricants are the materials which improve the smoothness of movement of one surface over another. Lubricants are usually liquids or semi-liquids. Lubricating oils (lube oil) are used to include all those classes of lubricating materials that are applied as fluids. The basic building block of lubricating oil is commonly known as base oil or base stock. The base oils 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. Base fluids mineral oil generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. These additives are compounds or mixtures when incorporated in base lubricating fluids, supplementing their natural characteristics and improving their field service performance in existing applications. In lubricating oils most commonly used functional additives are Viscosity index improvers (VII), Pour point depressants (PPD), Friction modifiers (FM), Anti-wear agents and extreme-pressure additives, Antioxidant additives, Anti-foam agents, Rust and corrosion inhibitors, Detergent and dispersant additives etc.

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) [1-7].

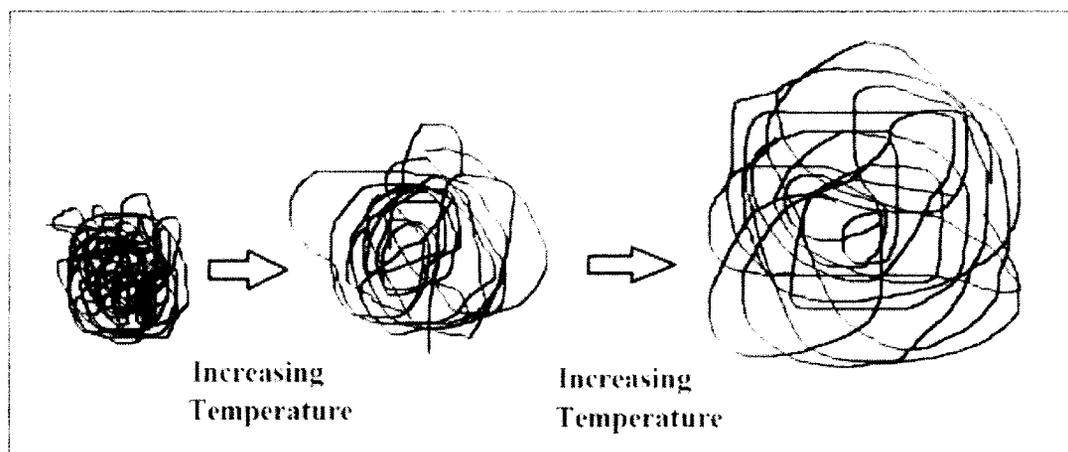
In accordance with the present invention, it will be very pertinent to include a brief introduction of multifunctional additives having both VII and PPD properties used in lube oil formulation, in this chapter.

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 both PPD and VII properties.

Viscosity index (VI) term to express the VII properties is an arbitrary number [8], which indicates the resistance of a lubricant to viscosity change with temperature.

Viscosity index improvers are added to lubricating oils to modify 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.

Performance of viscosity index improvers depends on the behaviour of the polymer molecules in the oil. Polymer solubility, molecular weight, and resistance to shear degradation are the most important parameters [9]. The polymer molecule in solution exists as random coil [10], which is swollen by the lube oil solvent (**Scheme I**). Polymer solubility generally increases with increasing temperature as the polymer molecules change from tight coils to an open configuration, which has a greater volume. This increase in volume causes increase of the viscosity of the oil, which offsets the normal reduction in viscosity with increasing temperature [11-12].



Scheme I

Increasing polymer molecular weight also increases the polymer volume in an oil solution [13]. Consequently, a higher molecular weight polymer will impart a higher viscosity index than a lower molecular weight polymer of the same type [14].

The pour point of lubricating oil is the lowest temperature at which it will pour or flow when it is chilled without disturbance under prescribed conditions [15]. Most mineral oils contain some dissolved wax, and as an oil is chilled, this wax begins to separate as crystal that interlock to form a rigid structure that traps the oil in small pockets in the structure [16]. When this wax crystal structure becomes sufficiently

complete, the oil will no longer flow under the conditions of the test. Low pour points may be achieved by intensively dewaxing the oil during refining. However, the deep dewaxing of oil fractions decreases its oxidation stability and increases the tendency toward formation of carbon deposits. Certain high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures [17-20]. The chemical additives are synonymously referred to as pour point depressants, flow improvers, paraffin inhibitors, or wax modifiers. Pour point depressants have no effect on the crystallization temperature or the number of crystals formed. Their most widely accepted mechanisms of action include adsorption, co-crystallization, nucleation, and improved wax solubility [20-22]. The effectiveness of a pour point depressant depends on the chemical composition and structural characteristics of the polymer and the structural characteristics of the polymer and the length of the alkyl side chains [13, 23-24]. Although the removal of the last traces of wax from oils is difficult and expensive, pour point depressants provide an economical means of facilitating the proper flow of the oil in an engine at low temperatures [25-27].

Many different types of pour point depressants have been used in the prior art [28]. 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 observation of the previous researchers in concord with the present line of investigation is being presented, in a selective manner, in the following paragraphs.

Although Polymethylacrylates (PMA) 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 VIIIs, considerable need and potential exists to develop polymers with improved performance.

In a recent communication A. A. A. Abdel Azim [29] 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 then 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 whereas their efficiency as PPD increases with decreasing the concentration of prepared polymer.

In a similar work [30] 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 [31] 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 No. 5834408 described preparation and evaluation of acrylate copolymers as a PPD in lube oil compositions.

U.S. Patent No. 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 No. 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 No. 4906702 discloses the olefin copolymer of unsaturated carboxylic acid ester as PPD for lube oil.

U.S. Patent No. 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 No. 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 No. 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 No 4032459 discloses lubricating composition containing hydrogenated butadiene-isoprene copolymers with PPD, VII properties.

U.S. Patent No. 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 No 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 perfluoro alkyl ethyl acrylate or methacrylate.

U.S. Patent No 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.

E. Patent No. 0236844 B1 teaches pour point improving agents derived from methyl methacrylate. This patent fails to teach the specific copolymers as viscosity index improvers for lubricating 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 VII properties or with a better PPD performances. But reports regarding the development of a multifunctional additives comprising VII – 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.

The present invention is directed to novel use of poly methyl acrylate and its copolymer with styrene as viscosity index improvers and pour point depressants for lubricating oils.

CHAPTER II

This chapter comprises **Synthesis, Characterization and Viscosity Analysis of Homo and copolymer of Methyl acrylate and Evaluation of their Viscosity index improver and Pour Point Depressant Properties in Different Base Stocks.**

2.1.1 Introduction

Acrylate based polymers are known to improve the viscometric and rheological properties of lubricant [32-35]. They also provide characteristic additional performances such as improved low temperature fluidity and dispersancy. In addition, this kind of additive is considered to be one of the most important classes of high performance additives due to their thermal stability and high temperature mechanical properties. Because of their good oil solubility, they provide adequate hydrodynamic lubrication at high temperatures and good starting pumping performance at low temperatures. They are also used extensively as a pour point depressant for crude and lubricating oil. However, a systematic study in relation to the suitability of this type of additive for their specific application is quite limited.

Therefore, a detailed investigation including the synthesis of a wide variety of acrylate based polymers as a function of monomer concentrations; concentration of initiator, solvent of polymerization and temperature of polymerization was felt necessary for a better understanding of their application in specific field. Herein we report the synthesis and characterization of homopolymer of methyl acrylate and its copolymer with styrene using different initiator concentration, different kinds of solvents and different feed ratios of the monomer. Physical characterization also included the viscometric analysis of the polymers.

Several mathematical equations [36-38] are available in the literature for determining the viscometric parameters of a dilute solution at determined temperatures by graphic extrapolation (GE). The most commonly used equations are eq. 1-4.

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

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

$$\text{Martin (M), } \ln\left(\frac{\eta_{sp}}{C}\right) = \ln[\eta]_m + k_m[\eta]_m C \quad (3)$$

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

Where $\eta_r = t/t_0$, 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 (SPD). This method has 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, practically in industrial laboratories. Most useful of them are Solomon-Ciuta (SC, eq 5) and Deb - Chatterjee (DC, eq 6) relations. [36-38]

$$[\eta] = \left[2(\eta_{sp} - \ln \eta_r)\right]^{1/2} / C \quad (5)$$

$$[\eta] = \left(3 \ln \eta_r + 3/2 \eta_{sp}^2 - 3 \eta_{sp}\right)^{1/3} / C \quad (6)$$

The use of these equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$ [39].

The viscosity of a solution is a function of molecular size, which is not the same as

molecular mass. 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 [40]. 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 the affinity between polymer and solvent, the lower is the K_h value. A range of K_h value 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 solvent [41-44]. At the same time, negative values for the Kraemer coefficient (k_k) indicate good solvents and positive values indicate poor ones.

Viscometry is the simplest technique used to study the macromolecules in solution and determine their molecular weight. According to Mark-Houwink-Sakurada (MHS eq 7), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = KM^a \quad (7)$$

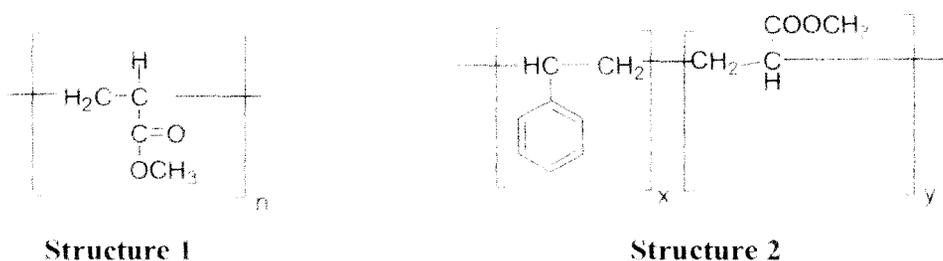
M is the viscosity average molecular weight and K and a are the Mark-Houwink constants. There are a specific set of Mark-Houwink constants for every polymer-solvent combination. So, these constant values are to be known for appropriate polymer-solvent combination in order to get an accurate measure of molecular weight. But it still gives a qualitative idea of whether molecular weight is high or low.

2.1.2 Results and discussions

Spectral analysis of one of the homopolymers and copolymers is presented as a representative sample of each of the type respectively.

IR spectra of the homopolymers showed a peak at 1732 cm^{-1} due to the stretching vibration of ester carbonyl group (**Figure 1**). The broad peak ranging from 1261 to 1164 cm^{-1} appeared owing to the ester C-O stretching vibration along with small peaks from 974 to 650 cm^{-1} (C-H bending) and a peak at 2954 cm^{-1} due to presence of stretching vibrations. In **Figure 2** the pick at 3.665 ppm indicated the presence of -OCH₂ group. The presence of the acrylate carbonyl group at 174.93 ppm was confirmed by ¹³C NMR of the homopolymer in **Figure 3**. The existence of copolymer was confirmed by IR and NMR analysis. Peaks at 760 cm^{-1} and 702 cm^{-1} were

attributed to the C-H bond of the phenyl group of styrene (**Figure 4**). In its ^1H NMR spectra (**Figure 5**) of the copolymer, apart from the appearance of CDCl_3 peak (7.256 ppm) presence of multiplets within the range 7.157 ppm to 7.654 ppm indicated the aromatic protons of styrene present in the copolymer skeleton and the presence of the $-\text{OCH}_2$ group from the acrylate at 3.421 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 3.421 ppm in the area of signal and due to phenyl protons, multiplets from 7.157 ppm to 7.654 ppm based on earlier report [45] as well as on the basis of our earlier paper [34], which was further verified through an analysis of FT-IR spectral data following a method discussed in our earlier paper [34]. The multiplets from 126 ppm to 133 ppm in ^{13}C NMR of copolymer (**Figure 6**) indicated the presence of phenylic carbons of styrene. From the above discussions the structure of the homopolymer of methyl acrylate and its copolymer with styrene may be represented by **Structure 1** and **Structure 2** respectively.



Among the three solvents used toluene showed better percentage yield of the polymer (**Table 2**). Considering the initiator concentration, it has been observed that yield of the polymer increases with increase in initiator concentration. In general the copolymer showed better percent yield in comparison to the homopolymer. All the polymers (homo and copolymer) showed poor solubility in n-hexane and methanol (**Table 3**). Among the other solvents studied, copolymer showed slightly better solubility than the homopolymer in acetone, DMF and ethanol. Both of them (homopolymer and copolymer) showed excellent solubility in tetrahydrofuran (THF), ether, toluene, DCM and in 1, 4-dioxane.

The polymers prepared in THF, showed a gradual increase in intrinsic viscosity (**Table 4** and **Table 5**) with rise in temperature irrespective of the initiator concentration. However, the copolymer did not show any appreciable change in

intrinsic viscosity with increase in temperature, although there is a gradual increase in intrinsic viscosity with the increase in initiator concentration.

The homopolymer, when prepared in 1, 4-dioxane (**Table 6** and **Table 7**), showed a gradual increase in intrinsic viscosity with rise in temperature for an initiator concentration of 0.1 and 0.3 %. However, there is a drop in intrinsic viscosity when the temperature is raised from 303 - 313K at 0.2% initiator concentration. However, when the temperature is raised to 323K the intrinsic viscosity is found to increase. Maximum values of intrinsic viscosity are observed at a 0.1% initiator concentration. For the copolymer the change in intrinsic viscosity with rise in temperature as well as with the increase in amount of initiator is not much significant.

A comparison of intrinsic viscosity (**Table 8** and **Table 9**) of the homopolymer in toluene showed that there is no correlation with the change in intrinsic viscosity with the change in temperature of the viscometric studies as well as with the concentration of initiator used during polymerization. Under the same condition the copolymer did not show any significant change in intrinsic viscosity with the change in initiator concentration or with the change in the temperature of the viscometric study.

The Viscometric constant values (**Table 10** and **Table 11**) obtained in THF indicated that copolymers showed better result than homopolymers. With increasing temperature viscometric constant values increases in case of homopolymers but decreases in case of copolymers.

In 1, 4-dioxane (**Table 12** and **Table 13**), the homopolymers gave better performance than copolymers.

Viscometric constant values (**Table 14** and **Table 15**) in toluene indicated that copolymers perform better than homopolymers. Deviation from relation $k_k + k_h = 0.5$ for the homopolymer may be attributed to the comparatively poor solubility of this polymer in toluene.

All viscometric constant values (**Table 10** to **Table 15**) obtained for the homopolymer and copolymers prepared in different solvents using different initiator concentrations indicated that irrespective of few cases all the polymers showed good solvation ($k_k + k_h$ value). However, the copolymer made in THF and toluene showed the best results as far as the solvation is concerned.

By comparing $[\eta]$ values of homopolymers and the copolymers determined

through graphic extrapolation using Kraemer, Martin and SB equations with the values determined by Huggins equation in graphic extrapolation in THF solvent (**Table 16** and **Table 17**), it can be noticed that the range (-12.17 to 6.86 for homopolymers, -4.51 to 2.23 for copolymers) was narrow when compared to the values obtained through a single point determination using SB, SC and DC equation (-13.18 to 14.18 for homopolymers, -9.79 to 4.76 for copolymers). Also comparing the values of homopolymers and copolymers the range were narrow in case of copolymers (-9.79 to 4.76) than homopolymers (-13.18 to 14.18).

The percentage differences ($\Delta \% = 100 \left(\frac{[\eta]}{[\eta]_h} - 100 \right)$ values (**Table 18** and **Table 19**) in 1, 4-dioxane showed that for both homopolymers and copolymers the range in graphic extrapolation method (-10.62 to 24.70 for homopolymers, -5.52 to 13.30 for copolymers) were narrow when compared to the values obtained through single point determination (-11.67 to 93.57 for homopolymers, -8.57 to 16.40 for copolymers). Again comparing all the values of homopolymers and copolymers the range were narrow in case of copolymers (-8.57 to 16.40) than homopolymers (-11.67 to 93.57).

similarly the percentage differences ($\Delta \% = 100 \left(\frac{[\eta]}{[\eta]_h} - 100 \right)$ values (**Table 20** and **Table 21**) in toluene showed that for both homopolymers and copolymers the range in graphic extrapolation method (-11.63 to 20.39 for homopolymers, -4.66 to 1.47 for copolymers) was narrow when compared to the values obtained through single point determination (-16.12 to 37.72 for homopolymers, -6.27 to 3.66 for copolymers). Comparing all the values of homopolymers and copolymers the range was very narrow in case of copolymers (-6.27 to 3.66) than homopolymers (-16.12 to 37.72).

A close observation of all the percentage differences values (**Table 16** to **Table 21**) in three different solvent indicated that, copolymers in toluene and THF showed better performance. This is due to the fact that toluene and THF both act as good solvents for copolymers. In case of homopolymers, as the data indicates THF act as the best solvent. Again copolymers gave better performance than homopolymers in all three solvents indicating greater solubility of copolymers and 1, 4-dioxane act as a poor solvent for these polymers. 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. **Table 16** to **Table 21** also

indicates that, the graphical extrapolation method seems to be more suitable in all three solvents rather than the single point determination for both homopolymers and copolymers and Mertin equation produced the lowest deviation values among the four when compared to those obtained from Huggins' equation.

As expected the trend of change in viscometric molecular weight (**Table 22** to **Table 27**) as determined by MH equation followed the same trend as was observed in case of their intrinsic viscosity values.

The data in **Table 28** indicates the properties of the base oils used for the evaluation of PPD and VII properties of the polymers.

Evaluation of the prepared polymers as pour point depressants (PPDs) in base oils.

Performance of homopolymers and copolymers as PPD has been tested and tabulated in **Table 29** to **Table 32**. The concentration range investigated was from 0.25 to 5 % (w/w) Data indicated that copolymer shows better efficiency than homopolymer. 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 [46]. Furthermore when the molecular weight of the additive and its concentration increases, solvation power of the solvent more obviously decreases and so does PPD [47]. Polymers prepared in toluene with higher initiator concentration (0.2% and 0.3%) and the polymers prepared in 1, 4-dioxane with highest initiator concentration (0.3%) performed better as PPD than others. Again, for all the polymers, performance increases with the decrease in concentration. This is may be because of the fact that with decreasing temperature the solvation power of a solvent decreases and vice versa. The performances of all the polymers were better in Base oil 1 (B1) than Base oil 2 (B2).

Evaluation of prepared polymers as viscosity index improvers (VIIs) in base oils.

The prepared copolymers were tested (**Table 33** to **Table 36**) for their effectiveness as viscosity index improvers in base oils (B1 and B2) and the results are expressed in terms of VI. The concentration range investigated was from 0.25 to 5 % (w/w). The effect of additive concentration on the viscosity index (VI) is studied and

the results are tabulated. Data from these tables indicated that for both base oils VI values of the homopolymer doped base oils are slightly higher (except homopolymer P^c- Dx) in comparison to the copolymers doped base oils. . The incorporation of styrene with methyl acrylate in copolymer decreases the molecular weight of copolymer and thus reduces its performance as VII. Homopolymers prepared in 1, 4-dioxane with 0.1% and 0.2% initiator concentration showed better performance than all other polymers in three different solvents. Furthermore, all over performance of polymers prepared in THF were better than polymers prepared in other solvents. This may be explained by grater hydrodynamic volume of the polymers due to preferable conformation of the polymers in THF. All the polymers showed better performance as VII in base oil B1 than B2

2.1.3 Conclusion

Percent yield of homopolymer and copolymer were highest in toluene. With increasing initiator concentration, the percent yield of all the polymers increased irrespective of the nature of the solvent.

Toluene, chloroform, 1, 4-dioxane, DCM are the best solvents for this homo and copolymer systems.

No similarity in intrinsic viscosity values was observed in between three solvents in which the polymers prepared. The copolymers showed lower intrinsic viscosity values than the homopolymers irrespective of the nature of the solvent.

The copolymers prepared in toluene and THF showed better solvation. Copolymers made in toluene showed better viscometric constant values than the homopolymers. Reverse was observed in case of polymers made in THF.

From the percentual differences values the graphic extrapolation method was proved to be better than the single point determination method.

Toluene and THF solvents are suitable for this polymer system, but 1, 4-dioxane is proved to be a poor solvent for this polymer system.

The copolymer performed better than the homopolymers as PPD. The PPD properties of polymers decreased with increasing concentration.

Performance of the homopolymers as VII was better than the copolymers. The efficiency of the polymers increases as VII with their increasing concentration. All the polymers performed better in B1 than B2.

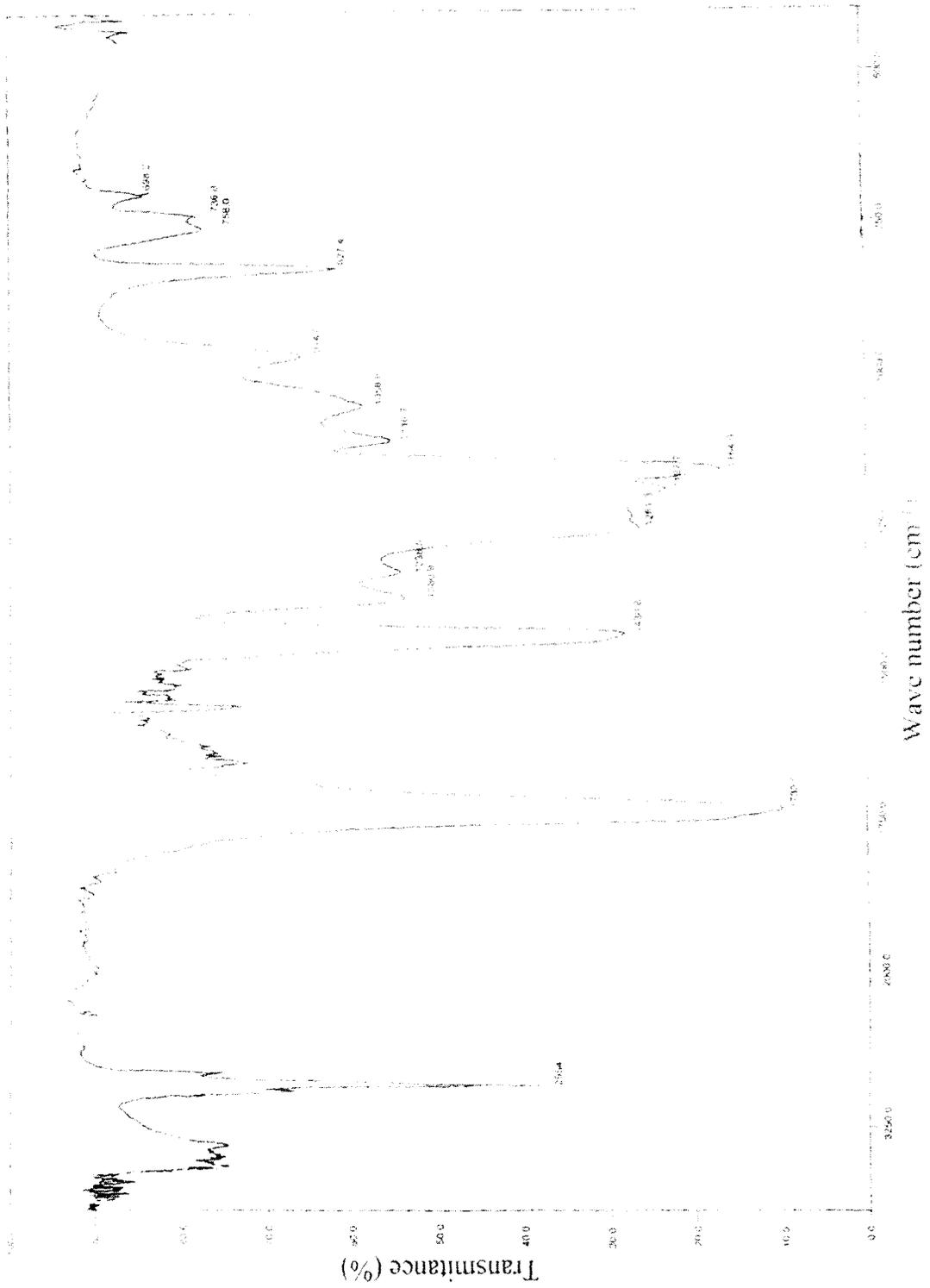


Figure 1: FT-IR spectrum of homopolymer of methyl acrylate

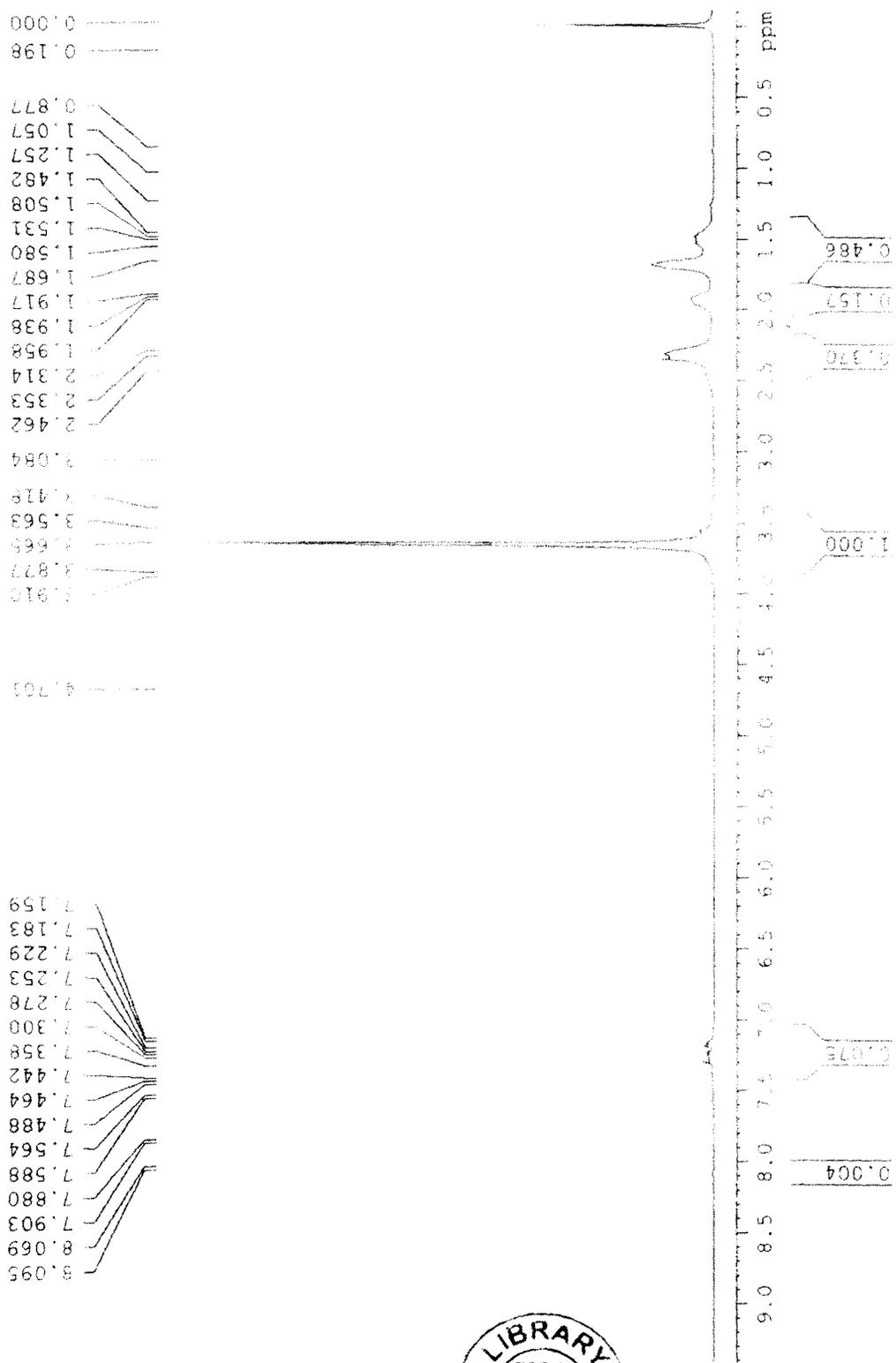


Figure 2: ¹H NMR spectrum of homopolymer of methyl acrylate



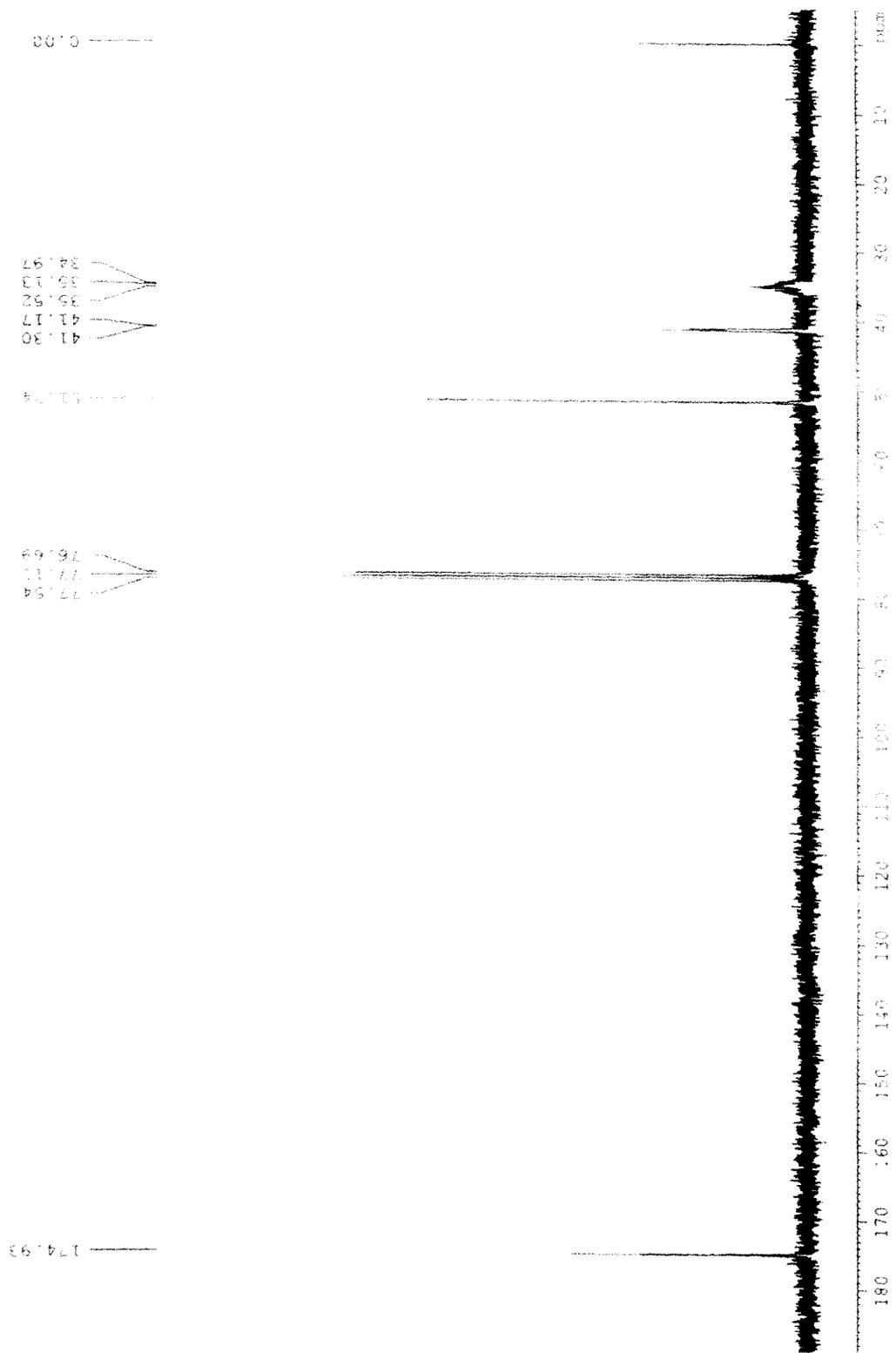


Figure 3: ^{13}C NMR spectrum of homopolymer of methyl acrylate

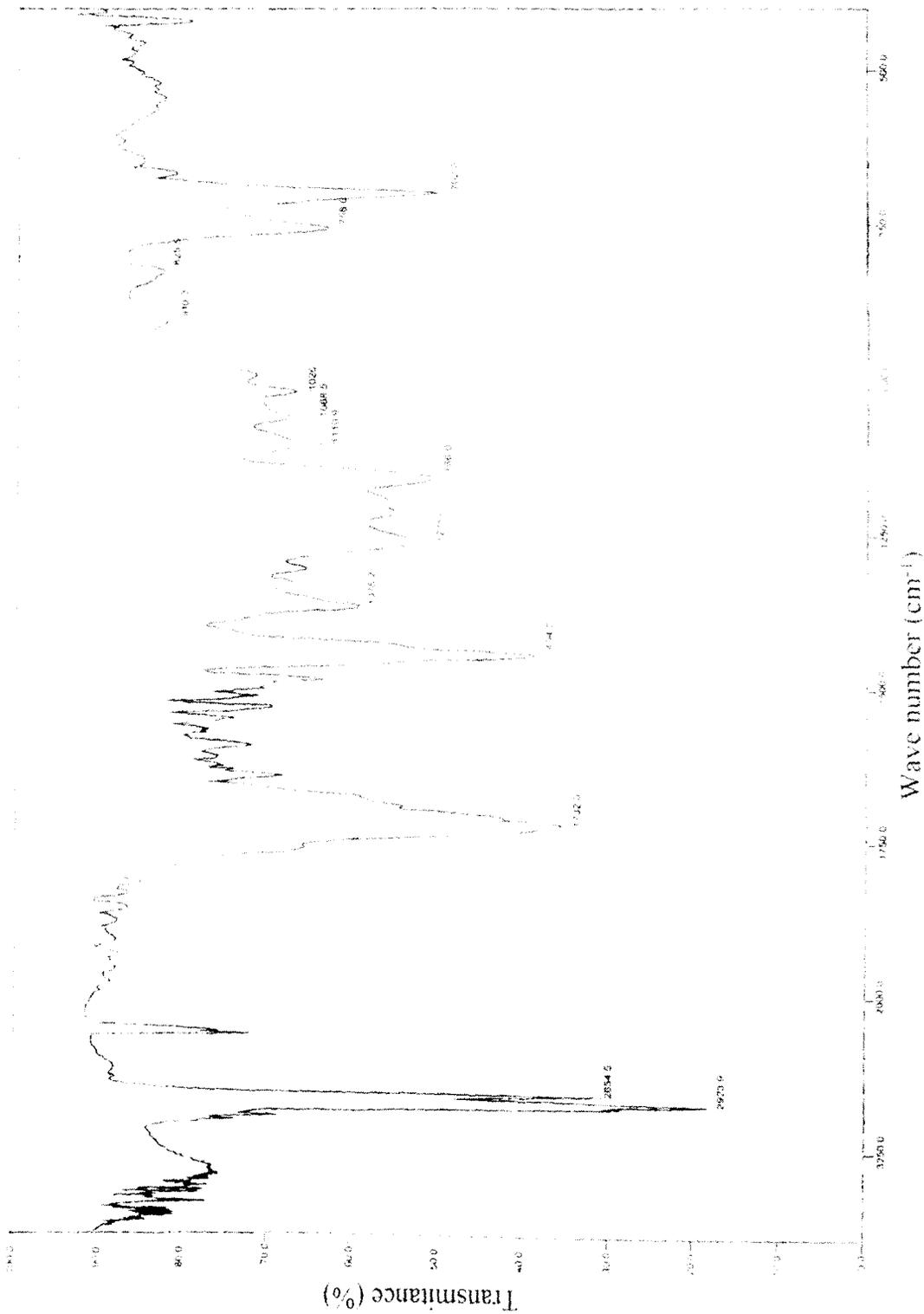


Figure 4: FT-IR spectrum of copolymer of methyl acrylate with styrene

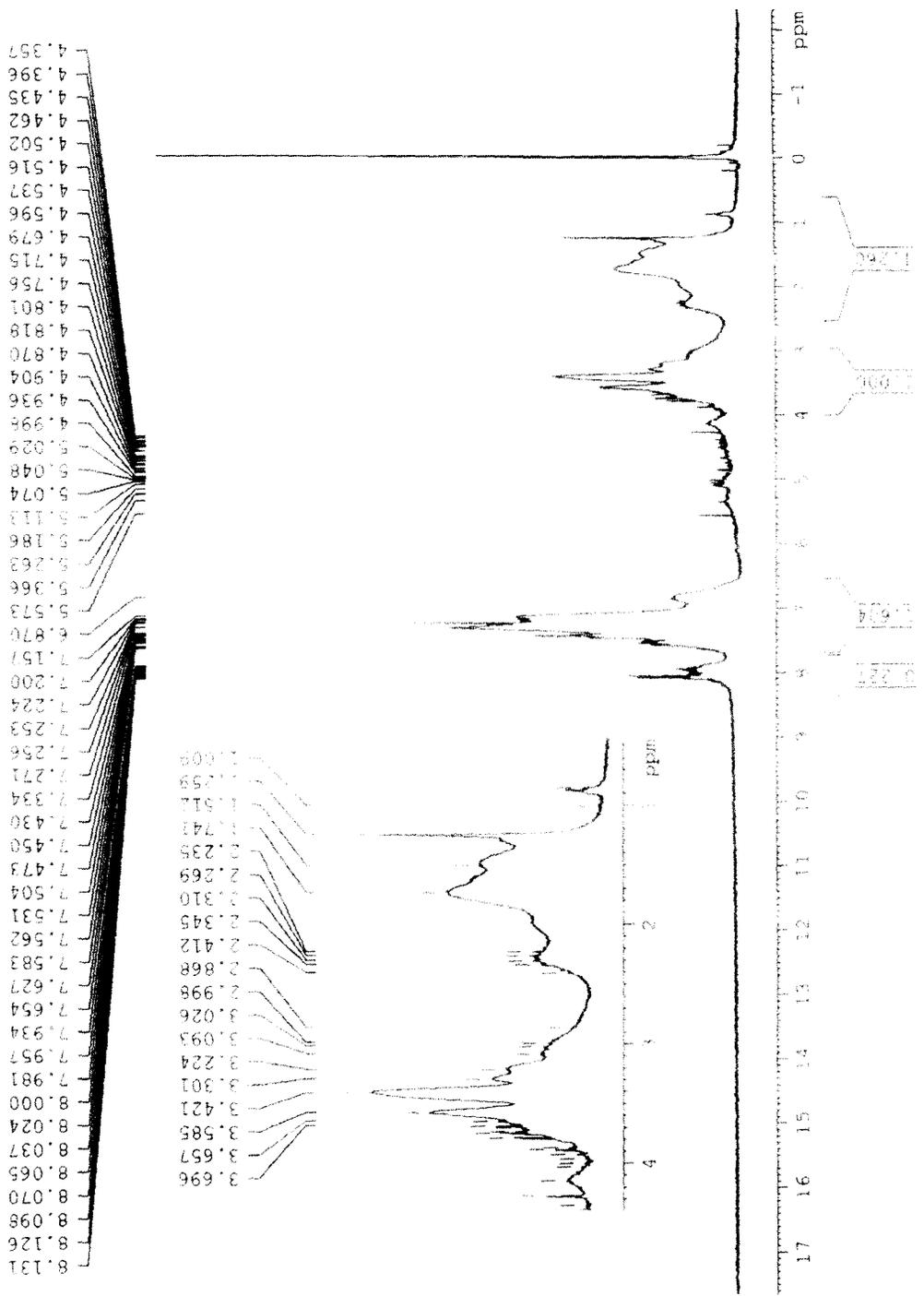


Figure 5: ^1H NMR spectrum of copolymer of methyl acrylate with styrene

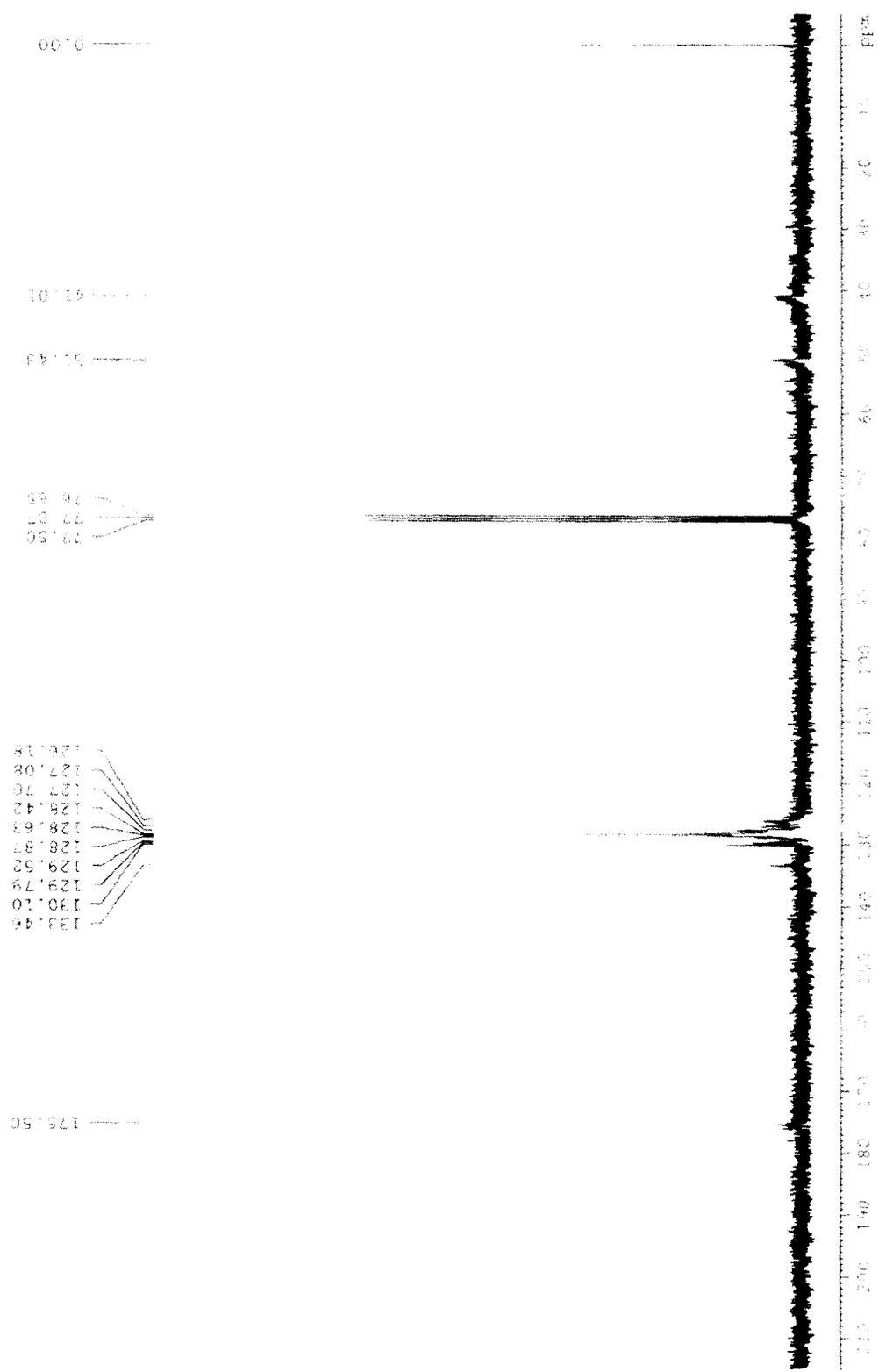


Figure 6: ^{13}C NMR spectrum of copolymer of methyl acrylate with styrene

Table 1. Composition of the monomers in the copolymer (prepared in toluene) in terms of mass fraction determined by PMR and FT-IR spectrometric method. P-1 is homopolymer of methyl acrylate (MA); P-2 is the copolymer of MA with 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 |
|----------------|---------------------------|---------|--|---|
| | MA | Styrene | | |
| P-1 | 1 | - | - | - |
| P-2 | 0.975 | 0.025 | 0.01 | 0.015 |

Table 2. Percent yield of homo and copolymer prepared in different solvents and at different initiator concentrations (w/w)

| Solvent | % of BZP (w/w) | % Yield | |
|-------------|----------------|-----------------|---------------|
| | | For Homopolymer | For Copolymer |
| THF | a. 0.1 | 20.20 | 27.10 |
| | b. 0.2 | 24.00 | 30.30 |
| | c. 0.3 | 26.30 | 31.80 |
| 1,4-Dioxane | a. 0.1 | 24.21 | 26.60 |
| | b. 0.2 | 28.30 | 28.00 |
| | c. 0.3 | 30.40 | 28.50 |
| Toluene | a. 0.1 | 30.00 | 34.00 |
| | b. 0.2 | 32.60 | 36.70 |
| | c. 0.3 | 35.30 | 37.25 |

Table 3. Solubility behaviours of homo and copolymers

| Solvents | P ^H -THF | P ^C -THF | P ^H -Dx | P ^C -Dx | P ^H -Tol | P ^C -Tol |
|-------------------|---------------------|---------------------|--------------------|--------------------|---------------------|---------------------|
| Acetone | PS | S | PS | S | PS | S |
| DMF | S | IS | S | IS | S | IS |
| DMSO | IS | IS | S | IS | S | IS |
| Hexane | IS | IS | IS | IS | IS | IS |
| Methanol | IS | IS | IS | IS | IS | IS |
| Ethanol | IS | IS | PS | PS | PS | PS |
| THF | S | S | S | S | S | S |
| CCl ₄ | PS | S | PS | S | PS | S |
| CHCl ₃ | S | S | S | S | S | S |
| Toluene | S | S | S | S | S | S |
| DCM | S | S | S | S | S | S |
| 1,4-dioxane | S | S | S | S | S | S |
| water | IS | IS | IS | IS | IS | IS |

H - homopolymer, C - Copolymer, S - Soluble, PS - Partially soluble, IS - Insoluble, THF - tetrahydrofuran, Tol - Toluene, Dx - 1, 4-dioxane

Table 4. Intrinsic viscosity values of homopolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures. g- extrapolation of graph, s- single point determination ($k_{sb}= 0.28$), x- single point determination. h, k, m, sb, sc and dc refers Huggin, Kraemer, Martin, Schulz- Blaschke, Solomon-Ciute and Deb-Chatterjee respectively

| Sample | $[\eta]_h^g$ | $[\eta]_k^g$ | $[\eta]_m^g$ | $[\eta]_{sb}^g$ | $[\eta]_{sb}^x$ | $[\eta]_{dc}^x$ | $[\eta]_{sc}^x$ |
|-----------------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -THF-1 | 15.64 | 15.62 | 15.780 | 16.01 | 16.606 | 15.464 | 15.954 |
| P ^a -THF-2 | 15.96 | 16.07 | 16.100 | 16.47 | 16.55 | 16.408 | 16.958 |
| P ^a -THF-3 | 18.455 | 17.804 | 18.502 | 18.49 | 17.18 | 17.030 | 16.609 |
| P ^b -THF-1 | 19.066 | 16.746 | 19.733 | 20.032 | 20.249 | 20.092 | 20.893 |
| P ^b -THF-2 | 19.512 | 19.513 | 19.929 | 20.28 | 19.888 | 19.735 | 20.551 |
| P ^b -THF-3 | 21.681 | 21.064 | 21.911 | 22.004 | 20.511 | 20.359 | 20.209 |
| P ^c -THF-1 | 13.383 | 14.189 | 14.013 | 14.302 | 15.278 | 15.147 | 15.634 |
| P ^c -THF-2 | 16.186 | 15.777 | 16.248 | 16.316 | 15.405 | 15.274 | 15.753 |
| P ^c -THF-3 | 18.789 | 18.622 | 18.795 | 18.759 | 16.867 | 16.719 | 17.305 |

a- 0.1 % BZP 1- 303 K Temperature THF - Tetrahydrofuran
b- 0.2% BZP 2- 313 K Temperature Tol- Toluene
c- 0.3 % BZP 3- 323 K Temperature Dx- 1, 4-dioxane

Table 5. Intrinsic viscosity values of copolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures.

| Sample | $[\eta]_h^g$ | $[\eta]_k^g$ | $[\eta]_m^g$ | $[\eta]_{sb}^g$ | $[\eta]_{sb}^x$ | $[\eta]_{dc}^x$ | $[\eta]_{sc}^x$ |
|-----------------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -THF-1 | 12.718 | 12.642 | 12.800 | 12.849 | 12.898 | 13.08 | 12.8 |
| P ^a -THF-2 | 12.605 | 12.426 | 12.650 | 12.688 | 12.272 | 12.436 | 12.164 |
| P ^a -THF-3 | 12.214 | 12.147 | 12.289 | 12.33 | 12.233 | 12.4 | 12.127 |
| P ^b -THF-1 | 13.185 | 13.171 | 13.307 | 13.422 | 13.303 | 13.508 | 13.182 |
| P ^b -THF-2 | 11.954 | 12.023 | 12.080 | 12.201 | 12.195 | 12.364 | 12.09 |
| P ^b -THF-3 | 14.452 | 13.801 | 14.448 | 14.447 | 13.155 | 13.36 | 13.038 |
| P ^c -THF-1 | 13.723 | 13.11 | 13.830 | 13.916 | 13.738 | 13.949 | 13.615 |
| P ^c -THF-2 | 14.732 | 14.505 | 14.802 | 14.886 | 14.634 | 14.903 | 14.508 |
| P ^c -THF-3 | 14.151 | 14.174 | 14.333 | 14.467 | 14.568 | 14.826 | 14.437 |

Table 6. Intrinsic viscosity values of homopolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures.

| Sample | $[\eta]_h^g$ | $[\eta]_k^g$ | $[\eta]_m^g$ | $[\eta]_{sb}^g$ | $[\eta]_{sb}^N$ | $[\eta]_{dc}^N$ | $[\eta]_{sc}^N$ |
|----------------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -Dx-1 | 22.71 | 23.737 | 24.046 | 24.851 | 24.727 | 24.614 | 26.828 |
| P ^a -Dx-2 | 25.547 | 25.643 | 26.459 | 26.626 | 26.296 | 26.218 | 27.612 |
| P ^a -Dx-3 | 28.255 | 27.724 | 29.186 | 29.932 | 27.782 | 27.737 | 29.291 |
| P ^b -Dx-1 | 21.973 | 21.323 | 22.220 | 22.433 | 21.277 | 21.124 | 21.983 |
| P ^b -Dx-2 | 17.007 | 18.416 | 18.411 | 16.387 | 19.411 | 19.256 | 20.026 |
| P ^b -Dx-3 | 23.548 | 22.984 | 23.969 | 23.646 | 23.280 | 23.201 | 24.207 |
| P ^c -Dx-1 | 12.607 | 15.500 | 14.448 | 15.722 | 21.245 | 21.095 | 24.404 |
| P ^c -Dx-2 | 18.133 | 19.452 | 19.311 | 20.157 | 21.181 | 20.80 | 21.660 |
| P ^c -Dx-3 | 26.748 | 23.909 | 26.818 | 27.077 | 24.196 | 23.629 | 24.755 |

Table 7. Intrinsic viscosity values of copolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures.

| Sample | $[\eta]_h^g$ | $[\eta]_k^g$ | $[\eta]_m^g$ | $[\eta]_{sb}^g$ | $[\eta]_{sb}^N$ | $[\eta]_{dc}^N$ | $[\eta]_{sc}^N$ |
|----------------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -Dx-1 | 11.357 | 10.731 | 11.381 | 11.39 | 10.467 | 10.524 | 10.384 |
| P ^a -Dx-2 | 10.322 | 10.322 | 10.382 | 10.438 | 10.923 | 10.888 | 10.833 |
| P ^a -Dx-3 | 8.3108 | 8.6861 | 8.5780 | 8.5543 | 9.474 | 9.574 | 9.400 |
| P ^b -Dx-1 | 11.562 | 11.369 | 11.589 | 11.682 | 11.33 | 11.365 | 11.130 |
| P ^b -Dx-2 | 10.274 | 10.307 | 10.348 | 10.423 | 10.354 | 10.449 | 10.271 |
| P ^b -Dx-3 | 11.774 | 11.385 | 11.589 | 11.852 | 11.338 | 11.486 | 11.242 |
| P ^c -Dx-1 | 9.9634 | 11.289 | 10.381 | 10.606 | 11.45 | 11.597 | 11.353 |
| P ^c -Dx-2 | 11.210 | 11.562 | 11.268 | 11.284 | 11.525 | 11.652 | 11.427 |
| P ^c -Dx-3 | 11.774 | 12.276 | 11.817 | 11.852 | 11.525 | 11.790 | 11.538 |

Table 8. Intrinsic viscosity values of homopolymer prepared in toluene at different initiator concentrations and at three different temperatures.

| Sample | $[\eta]_h^g$ | $[\eta]_k^g$ | $[\eta]_m^g$ | $[\eta]_{sb}^g$ | $[\eta]_{sb}^x$ | $[\eta]_{dc}^x$ | $[\eta]_{sc}^x$ |
|-----------------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -Tol-1 | 19.967 | 24.040 | 23.062 | 24.657 | 26.191 | 26.101 | 27.500 |
| P ^a -Tol-2 | 34.561 | 30.758 | 34.691 | 34.794 | 29.014 | 28.99 | 30.705 |
| P ^a -Tol-3 | 32.565 | 28.780 | 33.181 | 33.602 | 30.236 | 30.274 | 32.130 |
| P ^b -Tol-1 | 14.233 | 15.317 | 15.094 | 15.680 | 16.746 | 16.595 | 17.085 |
| P ^b -Tol-2 | 18.361 | 17.738 | 18.247 | 18.520 | 17.615 | 17.463 | 20.798 |
| P ^b -Tol-3 | 18.311 | 17.915 | 18.467 | 18.346 | 18.433 | 18.29 | 18.946 |
| P ^c -Tol-1 | 17.534 | 17.070 | 17.647 | 17.716 | 16.893 | 16.751 | 17.305 |
| P ^c -Tol-2 | 16.911 | 16.308 | 16.867 | 16.623 | 14.376 | 14.956 | 15.420 |
| P ^c -Tol-3 | 14.943 | 15.18 | 15.262 | 15.527 | 15.317 | 15.178 | 15.634 |

Table 9. Intrinsic viscosity values of copolymer prepared in toluene at different initiator concentrations and at three different temperatures.

| Sample | $[\eta]_h^g$ | $[\eta]_k^g$ | $[\eta]_m^g$ | $[\eta]_{sb}^g$ | $[\eta]_{sb}^x$ | $[\eta]_{dc}^x$ | $[\eta]_{sc}^x$ |
|-----------------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -Tol-1 | 11.377 | 10.847 | 11.395 | 11.423 | 11.108 | 11.253 | 11.019 |
| P ^a -Tol-2 | 10.755 | 10.738 | 10.814 | 10.867 | 10.727 | 10.860 | 10.646 |
| P ^a -Tol-3 | 10.701 | 10.847 | 10.738 | 10.777 | 10.416 | 10.507 | 10.309 |
| P ^b -Tol-1 | 12.222 | 11.969 | 12.238 | 12.239 | 11.60 | 11.652 | 11.501 |
| P ^b -Tol-2 | 10.603 | 10.422 | 10.597 | 10.588 | 10.164 | 10.267 | 10.083 |
| P ^b -Tol-3 | 11.236 | 11.060 | 11.246 | 11.233 | 10.886 | 10.934 | 10.795 |
| P ^c -Tol-1 | 11.302 | 11.249 | 11.402 | 11.422 | 11.219 | 11.365 | 11.130 |
| P ^c -Tol-2 | 10.080 | 10.144 | 10.169 | 10.229 | 10.354 | 10.449 | 10.271 |
| P ^c -Tol-3 | 11.397 | 11.118 | 11.402 | 11.343 | 10.789 | 10.888 | 10.683 |

Table 10. Viscometric parameter values of the homopolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures. k_h , k_k , k_m and k_{sb} are Huggins, Kraemer, Martin and Schulz-Blaschke coefficients, respectively

| Sample | k_h | k_k | k_m | k_{sb} | k_h+k_k |
|-----------------------|-------|--------------------|-------|----------|-----------|
| P ^a -THF-1 | 0.368 | 0.172 | 0.312 | 0.262 | 0.540 |
| P ^a -THF-2 | 0.409 | 0.124 | 0.344 | 0.277 | 0.533 |
| P ^a -THF-3 | 0.121 | 0.240 | 0.112 | 0.109 | 0.361 |
| P ^b -THF-1 | 0.455 | 0.186 | 0.332 | 0.273 | 0.641 |
| P ^b -THF-2 | 0.374 | 0.137 | 0.293 | 0.239 | 0.511 |
| P ^b -THF-3 | 0.237 | 0.177 | 0.200 | 0.181 | 0.414 |
| P ^c -THF-1 | 0.798 | 2×10^{-3} | 0.547 | 0.437 | 0.800 |
| P ^c -THF-2 | 0.190 | 0.211 | 0.172 | 0.157 | 0.401 |
| P ^c -THF-3 | 0.032 | 0.356 | 0.032 | 0.034 | 0.388 |

Table 11. Viscometric parameter values of the copolymer prepared in tetrahydrofuran at different initiator concentrations and at three different temperatures

| Sample | k_h | k_k | k_m | k_{sb} | k_h+k_k |
|-----------------------|-----------------------|-------|-----------------------|-----------------------|-----------|
| P ^a -THF-1 | 0.285 | 0.182 | 0.250 | 0.229 | 0.467 |
| P ^a -THF-2 | 0.232 | 0.202 | 0.210 | 0.195 | 0.434 |
| P ^a -THF-3 | 0.314 | 0.164 | 0.276 | 0.254 | 0.478 |
| P ^b -THF-1 | 0.362 | 0.141 | 0.310 | 0.270 | 0.503 |
| P ^b -THF-2 | 0.433 | 0.108 | 0.367 | 0.316 | 0.541 |
| P ^b -THF-3 | 1.28×10^{-3} | 0.330 | 8.79×10^{-4} | 1.95×10^{-3} | 0.333 |
| P ^c -THF-1 | 0.338 | 0.087 | 0.293 | 0.261 | 0.425 |
| P ^c -THF-2 | 0.257 | 0.184 | 0.229 | 0.206 | 0.441 |
| P ^c -THF-3 | 0.379 | 0.135 | 0.316 | 0.273 | 0.514 |

Table 12. Viscometric parameter values of the homopolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures.

| Sample | k_h | k_k | k_m | k_{sb} | k_h+k_k |
|----------------------|-------|--------|-------|----------|-----------|
| P ^a -Dx-1 | 0.558 | 0.0979 | 0.364 | 0.274 | 0.460 |
| P ^a -Dx-2 | 0.373 | 0.143 | 0.265 | 0.228 | 0.230 |
| P ^a -Dx-3 | 0.339 | 0.135 | 0.249 | 0.195 | 0.204 |
| P ^b -Dx-1 | 0.231 | 0.179 | 0.180 | 0.186 | 0.052 |
| P ^b -Dx-2 | 0.931 | 0.342 | 0.545 | 0.673 | 0.589 |
| P ^b -Dx-3 | 0.230 | 0.185 | 0.184 | 0.189 | 0.045 |
| P ^c -Dx-1 | 0.193 | 0.325 | 1.155 | 0.717 | 0.518 |
| P ^c -Dx-2 | 0.784 | 0.0298 | 0.500 | 0.360 | 0.814 |
| P ^c -Dx-3 | 0.124 | 0.176 | 0.113 | 0.098 | 0.300 |

Table 13. Viscometric parameter values of the copolymer prepared in 1, 4-dioxane at different initiator concentrations and at three different temperatures.

| Sample | k_h | k_k | k_m | k_{sb} | k_h+k_k |
|----------------------|-------|-------|---------|----------|-----------|
| P ^a -Dx-1 | 0.206 | 0.165 | 0.19100 | 0.183 | 0.371 |
| P ^a -Dx-2 | 0.373 | 0.135 | 0.329 | 0.296 | 0.508 |
| P ^a -Dx-3 | 1.140 | 0.246 | 0.841 | 0.712 | 1.386 |
| P ^b -Dx-1 | 0.190 | 0.227 | 0.176 | 0.152 | 0.417 |
| P ^b -Dx-2 | 0.425 | 0.107 | 0.371 | 0.327 | 0.532 |
| P ^b -Dx-3 | 0.245 | 0.229 | 0.176 | 0.206 | 0.474 |
| P ^c -Dx-1 | 1.023 | 0.097 | 0.72 | 0.574 | 1.12 |
| P ^c -Dx-2 | 0.329 | 0.196 | 0.29 | 0.269 | 0.525 |
| P ^c -Dx-3 | 0.216 | 0.284 | 0.221 | 0.206 | 0.50 |

Table 14. Viscometric parameter values of the homopolymer prepared in toluene at different initiator concentrations and at three different temperatures.

| Sample | k_h | k_k | k_m | k_{sb} | k_h+k_k |
|------------------------|-------|-------|-------|----------|-----------|
| P ^a -Tol-1 | 1.154 | 0.329 | 0.55 | 0.357 | 1.483 |
| P ^a -Tol -2 | 0.147 | 0.184 | 0.093 | 0.086 | 0.331 |
| P ^a -Tol-3 | 0.193 | 0.108 | 0.155 | 0.13 | 0.301 |
| P ^b -Tol-1 | 0.900 | 0.021 | 0.586 | 0.430 | 0.921 |
| P ^b -Tol-2 | 0.183 | 0.205 | 0.181 | 0.149 | 0.388 |
| P ^b -Tol-3 | 0.226 | 0.194 | 0.194 | 0.187 | 0.420 |
| P ^c -Tol-1 | 0.226 | 0.187 | 0.199 | 0.181 | 0.413 |
| P ^c -Tol-2 | 0.200 | 0.190 | 0.192 | 0.209 | 0.390 |
| P ^c -Tol-3 | 0.513 | 0.080 | 0.404 | 0.330 | 0.593 |

Table 15. Viscometric parameter values of the copolymer prepared in toluene at different initiator concentrations and at three different temperatures.

| Sample | k_h | k_k | k_m | k_{sb} | k_h+k_k |
|------------------------|-------|-------|-------|----------|-----------|
| P ^a -Tol-1 | 0.207 | 0.189 | 0.193 | 0.181 | 0.396 |
| P ^a -Tol -2 | 0.324 | 0.176 | 0.288 | 0.260 | 0.500 |
| P ^a -Tol-3 | 0.345 | 0.189 | 0.310 | 0.292 | 0.534 |
| P ^b -Tol-1 | 0.159 | 0.241 | 0.149 | 0.145 | 0.400 |
| P ^b -Tol-2 | 0.152 | 0.252 | 0.148 | 0.148 | 0.404 |
| P ^b -Tol-3 | 0.184 | 0.231 | 0.174 | 0.173 | 0.415 |
| P ^c -Tol-1 | 0.327 | 0.195 | 0.074 | 0.267 | 0.522 |
| P ^c -Tol-2 | 0.433 | 0.109 | 0.372 | 0.333 | 0.542 |
| P ^c -Tol-3 | 0.078 | 0.292 | 0.074 | 0.088 | 0.370 |

Table 16. Percentual differences ($\Delta\% = 100 ([\eta]/ [\eta]_h) - 100$) obtained for intrinsic viscosity values of the homopolymer in tetrahydrofuran, 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 ^a - THF -1 | -0.13 | 0.89 | 2.36 | 6.17 | -1.13 | 2 |
| P ^a - THF -2 | 0.68 | 0.87 | 3.19 | 3.69 | 2.80 | 6.25 |
| P ^a - THF -3 | -3.53 | 0.25 | 0.18 | -6.91 | -7.73 | -10.01 |
| P ^b - THF -1 | -12.17 | 3.49 | 5.06 | 6.20 | 5.38 | 9.58 |
| P ^b - THF -2 | 0.005 | 2.13 | 3.93 | 1.92 | 1.14 | 5.32 |
| P ^b - THF -3 | -2.85 | 1.06 | 1.48 | -5.40 | -6.10 | -6.79 |
| P ^c - THF -1 | 6.02 | 4.70 | 6.86 | 14.15 | -13.18 | 16.18 |
| P ^c - THF -2 | -2.53 | 0.38 | 0.80 | -4.84 | -5.64 | -2.68 |
| P ^c - THF -3 | -0.89 | 0.03 | -0.16 | -10.23 | -11.02 | -7.90 |

Table 17. Percentual differences ($\Delta\% = 100 ([\eta]/ [\eta]_h) - 100$) obtained for intrinsic viscosity values of the copolymer in tetrahydrofuran, Huggins equation taken as a reference.

| Sample | K ^a | M ^a | SB ^a | SB ^b | SC ^b | DC ^b |
|-------------------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| P ^a - THF -1 | -0.60 | 0.64 | 1.03 | 1.41 | 2.84 | 0.64 |
| P ^a - THF -2 | -1.50 | 0.35 | 0.65 | -2.65 | -1.35 | -3.50 |
| P ^a - THF -3 | -0.55 | 0.61 | 0.94 | 0.15 | 1.52 | -0.72 |
| P ^b - THF -1 | -0.11 | 0.92 | 1.79 | 0.89 | 2.44 | -0.03 |
| P ^b - THF -2 | 0.57 | 1.05 | 2.06 | 2.01 | 3.42 | 1.13 |
| P ^b - THF -3 | -4.51 | -0.03 | -0.04 | -8.98 | -7.56 | -9.79 |
| P ^c - THF -1 | -4.47 | 0.77 | 1.40 | 0.10 | 1.64 | -0.79 |
| P ^c - THF -2 | -1.55 | 0.47 | 1.04 | 0.67 | 1.16 | -1.53 |
| P ^c - THF -3 | 0.16 | 1.28 | 2.23 | 2.94 | 4.76 | 2.02 |

Table 18. Percentual differences ($\blacktriangle \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the homopolymer in 1, 4-dioxane.

| Sample | K ^a | M ^a | SB ^a | SB ^b | SC ^b | DC ^b |
|------------------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| P ^a - Dx -1 | 4.52 | 5.88 | 9.42 | 8.88 | 8.38 | 18.13 |
| P ^a - Dx -2 | 0.37 | 3.57 | 4.22 | 2.93 | 2.62 | 8.08 |
| P ^a - Dx -3 | -1.88 | 3.29 | 5.93 | -1.63 | -1.84 | 3.66 |
| P ^b - Dx -1 | -2.96 | 1.12 | 2.02 | -3.17 | -3.87 | 0.04 |
| P ^b - Dx -2 | 8.28 | 8.25 | -3.65 | 14.13 | 13.22 | 17.75 |
| P ^b - Dx -3 | -2.40 | 1.78 | 0.41 | -1.14 | -1.48 | 2.79 |
| P ^c - Dx -1 | 22.94 | 14.60 | 24.70 | 68.51 | 67.32 | 93.57 |
| P ^c - Dx -2 | 7.27 | 6.49 | 11.16 | 16.80 | 14.70 | 19.45 |
| P ^c - Dx -3 | -10.62 | 0.26 | 1.22 | -9.55 | -11.67 | 7.50 |

Table 19. Percentual differences ($\blacktriangle \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the copolymer in 1, 4-dioxane.

| Sample | K ^a | M ^a | SB ^a | SB ^b | SC ^b | DC ^b |
|------------------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| P ^a - Dx -1 | -5.52 | 0.21 | 0.29 | -7.84 | -7.34 | -8.57 |
| P ^a - Dx -2 | 0.00 | 0.58 | 1.21 | 5.82 | 5.48 | 4.95 |
| P ^a - Dx -3 | 4.52 | 3.22 | 2.93 | 14 | 15.21 | 13.11 |
| P ^b - Dx -1 | -1.67 | 0.23 | 1.03 | -2.01 | -1.72 | -3.74 |
| P ^b - Dx -2 | 0.32 | 0.72 | 1.46 | 0.78 | 1.71 | -0.02 |
| P ^b - Dx -3 | -3.31 | -1.58 | 0.66 | -3.71 | -2.45 | -4.52 |
| P ^c - Dx -1 | 13.30 | 4.19 | 6.45 | 14.92 | 16.40 | 13.95 |
| P ^c - Dx -2 | 2.81 | 0.51 | 0.66 | 2.80 | 3.94 | 1.93 |
| P ^c - Dx -3 | 4.28 | 0.36 | 0.66 | -2.12 | 0.13 | -2.00 |

Table 20. Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the homopolymer in toluene

| Sample | K ^a | M ^a | SB ^a | SB ^b | SC ^b | DC ^b |
|-----------------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -Tol-1 | 20.39 | 15.50 | 23.48 | 31.17 | 30.72 | 37.72 |
| P ^a -Tol-2 | -11.01 | 0.37 | 0.67 | -16.05 | -16.12 | -11.16 |
| P ^a -Tol-3 | -11.63 | 1.89 | 3.18 | -7.16 | -7.04 | -1.34 |
| P ^b -Tol-1 | 7.61 | 6.04 | 10.16 | 17.65 | 16.15 | 20.03 |
| P ^b -Tol-2 | -3.40 | -0.63 | 0.86 | -4.07 | -4.90 | 13.27 |
| P ^b -Tol-3 | 2.17 | 0.85 | 0.19 | 0.66 | -0.12 | 3.45 |
| P ^c -Tol-1 | -2.65 | 0.64 | 1.03 | -3.66 | -4.47 | -1.31 |
| P ^c -Tol-2 | -3.50 | 0.27 | 1.71 | -1.5 | -11.57 | -8.82 |
| P ^c -Tol-3 | 1.58 | 2.14 | 3.90 | 2.50 | 1.57 | 4.62 |

Table 21. Percentual differences ($\Delta \% = 100 ([\eta]/[\eta]_h) - 100$) obtained for intrinsic viscosity values of the copolymer in toluene

| Sample | K ^a | M ^a | SB ^a | SB ^b | SC ^b | DC ^b |
|-----------------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| P ^a -Tol-1 | -4.66 | 0.15 | 0.40 | -2.37 | -1.09 | -3.15 |
| P ^a -Tol-2 | -0.16 | 0.54 | 1.04 | -0.27 | 0.97 | -1.02 |
| P ^a -Tol-3 | 1.36 | 0.34 | 0.71 | -2.67 | -1.82 | -3.67 |
| P ^b -Tol-1 | -2.08 | 0.13 | 0.14 | -5.09 | -4.67 | -5.9 |
| P ^b -Tol-2 | -1.71 | -0.06 | -0.15 | -4.15 | -3.17 | -4.95 |
| P ^b -Tol-3 | -1.57 | 0.08 | -0.03 | -3.12 | -2.69 | -3.39 |
| P ^c -Tol-1 | -0.47 | 0.88 | -1.06 | -0.74 | 0.55 | 1.53 |
| P ^c -Tol-2 | 0.63 | 0.88 | 1.47 | 2.71 | 3.66 | 1.89 |
| P ^c -Tol-3 | -2.45 | 0.04 | -0.48 | -5.44 | -4.47 | -6.27 |

Table 22. Determination of molecular weight of the homopolymer in tetrahydrofuran by Mark Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$

| Sample | M_h^g | M_k^g | M_m^g | M_{sb}^g | M_{sb}^x | M_{sc}^x | M_{dc}^x |
|-----------------------|---------|---------|---------|------------|------------|------------|------------|
| P ^a -THF-1 | 94214 | 94048 | 95380 | 97302 | 102334 | 92755 | 96833 |
| P ^a -THF-2 | 96884 | 97806 | 98058 | 101179 | 101858 | 100655 | 105312 |
| P ^a -THF-3 | 118375 | 112654 | 118791 | 118684 | 107244 | 105955 | 102359 |
| P ^b -THF-1 | 123814 | 103526 | 129828 | 132549 | 134534 | 133097 | 140471 |
| P ^b -THF-2 | 127827 | 127836 | 131610 | 134818 | 131237 | 129846 | 137309 |
| P ^b -THF-3 | 147830 | 142059 | 149998 | 150876 | 136941 | 135543 | 143410 |
| P ^c -THF-1 | 75991 | 82375 | 80969 | 83281 | 91220 | 90143 | 94165 |
| P ^c -THF-2 | 98781 | 95355 | 99303 | 99877 | 92267 | 91187 | 95155 |
| P ^c -THF-3 | 121340 | 119855 | 121393 | 121073 | 104559 | 103295 | 108322 |

Table 23. Determination of molecular weight of the copolymer in tetrahydrofuran by Mark Houwinks equation $[\eta] = KM^d$ where, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$

| Sample | M_h^g | M_k^g | M_m^g | M_{sb}^g | M_{sb}^x | M_{sc}^x | M_{dc}^x |
|-----------------------|---------|---------|---------|------------|------------|------------|------------|
| P ^a -THF-1 | 70832 | 70249 | 71463 | 71840 | 72219 | 73628 | 71463 |
| P ^a -THF-2 | 69965 | 68599 | 70310 | 70607 | 67429 | 68705 | 66612 |
| P ^a -THF-3 | 66990 | 66483 | 67565 | 67869 | 67133 | 68401 | 66355 |
| P ^b -THF-1 | 74444 | 74335 | 75396 | 76296 | 75365 | 76971 | 74421 |
| P ^b -THF-2 | 65031 | 65549 | 65978 | 66891 | 66846 | 68127 | 66053 |
| P ^b -THF-3 | 84488 | 79284 | 84478 | 84472 | 74211 | 75811 | 73317 |
| P ^c -THF-1 | 78666 | 73861 | 80196 | 79514 | 78785 | 80459 | 77814 |
| P ^c -THF-2 | 86754 | 84916 | 87323 | 87844 | 85959 | 88146 | 84940 |
| P ^c -THF-3 | 82070 | 81982 | 83530 | 84609 | 85425 | 87518 | 84367 |

Table 24. Determination of molecular weight of the homopolymer in 1, 4-dioxane by Mark Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$

| Sample | M_h^g | M_k^g | M_m^g | M_{sb}^g | M_{sb}^x | M_{sc}^x | M_{dc}^x |
|----------------------|---------|---------|---------|------------|------------|------------|------------|
| P ^a -Dx-1 | 157594 | 167508 | 170523 | 178446 | 177219 | 176103 | 198318 |
| P ^a -Dx-2 | 184476 | 186338 | 194565 | 196261 | 192914 | 192125 | 206356 |
| P ^a -Dx-3 | 213013 | 207511 | 222754 | 230645 | 208110 | 207645 | 223860 |
| P ^b -Dx-1 | 150583 | 144474 | 170523 | 178446 | 177219 | 142617 | 150678 |
| P ^b -Dx-2 | 105758 | 118030 | 194565 | 196261 | 192914 | 125519 | 132494 |
| P ^b -Dx-3 | 165671 | 160223 | 222754 | 230645 | 126915 | 162313 | 172099 |
| P ^c -Dx-1 | 69981 | 93053 | 84456 | 94896 | 143745 | 142347 | 170464 |
| P ^c -Dx-2 | 115535 | 127285 | 126014 | 133691 | 143148 | 139609 | 147633 |
| P ^c -Dx-3 | 197503 | 169184 | 198216 | 200861 | 171992 | 166457 | 177496 |

Table 25. Determination of molecular weight of the copolymer in 1, 4-dioxane by Mark Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$

| Sample | M_h^g | M_k^g | M_m^g | M_{sb}^g | M_{sb}^x | M_{sc}^x | M_{dc}^x |
|----------------------|---------|---------|---------|------------|------------|------------|------------|
| P ^a -Dx-1 | 60594 | 56036 | 60830 | 60837 | 54143 | 54550 | 53552 |
| P ^a -Dx-2 | 53111 | 53111 | 53538 | 53936 | 57423 | 57170 | 56772 |
| P ^a -Dx-3 | 39388 | 41862 | 41145 | 40989 | 47188 | 47877 | 46681 |
| P ^b -Dx-1 | 62108 | 60682 | 62308 | 62999 | 60395 | 60653 | 58930 |
| P ^b -Dx-2 | 52771 | 53005 | 53296 | 53830 | 53339 | 54015 | 52750 |
| P ^b -Dx-3 | 63684 | 60800 | 62308 | 64267 | 60454 | 61545 | 52544 |
| P ^c -Dx-1 | 50583 | 60094 | 53531 | 55137 | 61279 | 62367 | 60564 |
| P ^c -Dx-2 | 59515 | 62108 | 59940 | 60057 | 61834 | 62776 | 61110 |
| P ^c -Dx-3 | 63684 | 67459 | 64005 | 64267 | 61834 | 63803 | 61930 |

Table 26. Determination of molecular weight of the homopolymer in toluene by Mark Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$

| Sample | M_h^g | M_k^g | M_m^g | M_{sb}^g | M_{sb}^x | M_{sc}^x | M_{dc}^x |
|-----------------------|---------|---------|---------|------------|------------|------------|------------|
| P ^a -Tol-1 | 131902 | 170464 | 84456 | 175669 | 191852 | 190944 | 205202 |
| P ^a -Tol-2 | 281132 | 239470 | 282705 | 28386 | 220946 | 220694 | 23890 |
| P ^a -Tol-3 | 259089 | 218492 | 265873 | 270537 | 233883 | 234288 | 254327 |
| P ^b -Tol-1 | 82727 | 91541 | 89708 | 94547 | 103526 | 102240 | 106427 |
| P ^b -Tol-2 | 117544 | 112078 | 116538 | 118950 | 111016 | 109689 | 139590 |
| P ^b -Tol-3 | 117103 | 113624 | 118481 | 117419 | 118180 | 116917 | 122741 |
| P ^c -Tol-1 | 110348 | 106298 | 111286 | 111887 | 10478 | 103568 | 108322 |
| P ^c -Tol-2 | 104935 | 99809 | 104559 | 102478 | 83876 | 88579 | 92391 |
| P ^c -Tol-3 | 88472 | 90414 | 91088 | 93277 | 91541 | 96850 | 94165 |

Table 27. Determination of molecular weight of the copolymer in toluene by Mark Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387 \text{ dl}\cdot\text{g}^{-1}$ and $a = 0.725$

| Sample | M_h^g | M_k^g | M_m^g | M_{sb}^g | M_{sb}^x | M_{sc}^x | M_{dc}^x |
|-----------------------|---------|---------|---------|------------|------------|------------|------------|
| P ^a -Tol-1 | 60741 | 56873 | 60874 | 61080 | 58796 | 59830 | 50973 |
| P ^a -Tol-2 | 56209 | 56086 | 56634 | 57018 | 56007 | 56967 | 55424 |
| P ^a -Tol-3 | 55820 | 56873 | 56086 | 56367 | 53780 | 54429 | 53019 |
| P ^b -Tol-1 | 52403 | 65143 | 67171 | 67179 | 62389 | 62776 | 61656 |
| P ^b -Tol-2 | 55116 | 53822 | 55073 | 55008 | 51993 | 52729 | 51423 |
| P ^b -Tol-3 | 59705 | 58419 | 59779 | 59683 | 57155 | 57503 | 56497 |
| P ^c -Tol-1 | 60190 | 59801 | 60925 | 61073 | 59581 | 60653 | 58930 |
| P ^c -Tol-2 | 51402 | 51852 | 52029 | 52452 | 53339 | 54015 | 52750 |
| P ^c -Tol-3 | 60888 | 58842 | 60925 | 60491 | 56389 | 57170 | 55690 |

Table 28: Base oil properties

| Base oil properties | Base oils | |
|--|-----------|--------|
| | B1 | B2 |
| Density (g.cm ⁻³) at 40 ⁰ C | 0.8458 | 0.8792 |
| Viscosity at 40 ⁰ C in cSt | 13.691 | 27.07 |
| Viscosity at 100 ⁰ C in cSt | 2.817 | 4.520 |
| Cloud point, ⁰ C | -8 | -10 |
| Pour point, ⁰ C | -3 | -6 |
| Viscosity Index | 85 | 96 |

Table 29. Pour point of homopolymer doped base oils (B1)

| PPD Sample | Pour Point (⁰ C) of base oils containing different %(w/w) of PPD | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | -12 | -12 | -9 | -9 | -9 | -6 |
| P ^b -Tol | -15 | -15 | -12 | -12 | -12 | -12 |
| P ^c -Tol | -12 | -12 | -9 | -9 | -6 | -6 |
| P ^a - THF | -12 | -12 | -12 | -12 | -9 | -9 |
| P ^b - THF | -9 | -12 | -9 | -9 | -6 | -6 |
| P ^c - THF | -12 | -12 | -12 | -12 | -9 | -9 |
| P ^a - Dx | -9 | -12 | -9 | -9 | -6 | -6 |
| P ^b - Dx | -15 | -12 | -12 | -12 | -12 | -9 |
| P ^c - Dx | -15 | -15 | -12 | -12 | -12 | -9 |

Table 30. Pour point of copolymer doped base oils (B1).

| PPD Sample | Pour Point ($^{\circ}\text{C}$) of base oils containing different %(w/w) of PPD | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | -18 | -15 | -12 | -12 | -12 | -9 |
| P ^b -Tol | -21 | -21 | -18 | -18 | -18 | -15 |
| P ^c -Tol | -18 | -18 | -15 | -15 | -12 | -12 |
| P ^a - THF | -18 | -18 | -15 | -15 | -15 | -12 |
| P ^b - THF | -15 | -15 | -15 | 15 | -15 | -12 |
| P ^c - THF | -18 | -18 | -15 | -15 | -15 | -12 |
| P ^a - Dx | -15 | -15 | -15 | -15 | -12 | -12 |
| P ^b - Dx | -18 | -18 | -15 | -15 | -15 | -12 |
| P ^c - Dx | -18 | -18 | -15 | 15 | -15 | -12 |

Table 31. Pour point of homopolymer doped base oils (B2).

| PPD Sample | Pour Point ($^{\circ}\text{C}$) of base oils containing different %(w/w) of PPD | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | -12 | -12 | -12 | -12 | -12 | -9 |
| P ^b -Tol | -18 | -18 | -15 | -15 | -15 | -12 |
| P ^c -Tol | -18 | -15 | -15 | -12 | -12 | -9 |
| P ^a - THF | -15 | -15 | -15 | -12 | -12 | -9 |
| P ^b - THF | -12 | -12 | -15 | -12 | -12 | -9 |
| P ^c - THF | -18 | -15 | -15 | -12 | -12 | -12 |
| P ^a - Dx | -12 | -12 | -12 | -9 | -9 | -9 |
| P ^b - Dx | -12 | -12 | -12 | -12 | -9 | -9 |
| P ^c - Dx | -18 | -18 | -15 | 15 | -15 | -12 |

Table 32. Pour point of copolymer doped base oils (B2).

| PPD Sample | Pour Point (°C) of base oils containing different %(w/w) of PPD | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | -21 | -18 | -18 | -15 | -15 | -12 |
| P ^b -Tol | -21 | -24 | -21 | -18 | -18 | -15 |
| P ^c -Tol | -21 | -21 | -18 | -15 | -15 | -15 |
| P ^a - THF | -18 | -18 | -18 | -15 | -15 | -12 |
| P ^b - THF | -18 | -18 | -18 | -15 | -15 | -12 |
| P ^c - THF | -21 | -21 | -18 | -18 | -15 | -15 |
| P ^a - Dx | -18 | -18 | -18 | -15 | -12 | -12 |
| P ^b - Dx | -18 | -18 | -18 | -18 | -15 | -15 |
| P ^c - Dx | -21 | -21 | -21 | -18 | -18 | -15 |

Table 33. Viscosity index of homopolymer doped base oils (B1).

| VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | 89 | 96 | 106 | 112 | 123 | 135 |
| P ^b -Tol | 90 | 97 | 104 | 111 | 119 | 129 |
| P ^c -Tol | 90 | 96 | 105 | 113 | 122 | 132 |
| P ^a - THF | 90 | 97 | 106 | 116 | 125 | 135 |
| P ^b - THF | 91 | 97 | 105 | 115 | 126 | 137 |
| P ^c - THF | 90 | 96 | 106 | 115 | 125 | 136 |
| P ^a - Dx | 91 | 97 | 108 | 117 | 128 | 140 |
| P ^b - Dx | 91 | 98 | 107 | 116 | 127 | 139 |
| P ^c - Dx | 89 | 94 | 100 | 106 | 113 | 120 |

Table 34. Viscosity index of copolymer doped base oils (B1)

| VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | 88 | 92 | 100 | 108 | 115 | 127 |
| P ^b -Tol | 87 | 91 | 96 | 102 | 108 | 115 |
| P ^c -Tol | 88 | 94 | 102 | 107 | 113 | 122 |
| P ^a - THF | 89 | 96 | 103 | 109 | 116 | 130 |
| P ^b - THF | 90 | 94 | 103 | 110 | 118 | 131 |
| P ^c - THF | 90 | 96 | 104 | 110 | 120 | 133 |
| P ^a - Dx | 88 | 92 | 98 | 105 | 111 | 119 |
| P ^b - Dx | 90 | 94 | 101 | 107 | 114 | 123 |
| P ^c - Dx | 86 | 90 | 95 | 100 | 106 | 116 |

Table 35. Viscosity index of homopolymer doped base oils (B2).

| VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | 99 | 104 | 110 | 115 | 121 | 130 |
| P ^b -Tol | 98 | 102 | 106 | 111 | 117 | 126 |
| P ^c -Tol | 98 | 103 | 107 | 112 | 119 | 129 |
| P ^a - THF | 97 | 101 | 105 | 111 | 116 | 127 |
| P ^b - THF | 98 | 101 | 106 | 112 | 118 | 129 |
| P ^c - THF | 99 | 102 | 107 | 113 | 119 | 129 |
| P ^a - Dx | 98 | 99 | 103 | 108 | 122 | 133 |
| P ^b - Dx | 99 | 104 | 110 | 115 | 122 | 132 |
| P ^c - Dx | 96 | 98 | 101 | 104 | 109 | 118 |

Table 36. Viscosity index of copolymer doped base oils (B2).

| VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | | |
|----------------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| P ^a -Tol | 97 | 100 | 104 | 110 | 116 | 123 |
| P ^b -Tol | 96 | 98 | 102 | 107 | 113 | 119 |
| P ^c -Tol | 96 | 98 | 101 | 105 | 110 | 117 |
| P ^a - THF | 98 | 101 | 104 | 109 | 115 | 124 |
| P ^b - THF | 98 | 101 | 106 | 112 | 118 | 126 |
| P ^c - THF | 99 | 102 | 107 | 113 | 119 | 129 |
| P ^d - Dx | 97 | 99 | 103 | 108 | 113 | 119 |
| P ^b - Dx | 97 | 100 | 104 | 109 | 115 | 122 |
| P ⁱ - Dx | 96 | 98 | 101 | 104 | 107 | 112 |

CHAPTER III

3.1 Experimental

3.1.1 Materials used

Methyl acrylate and styrene were purchased from Merck India Ltd. Solvents like tetrahydrofuran (THF), 1, 4-dioxane, and toluene were procured from S.D. Fine Chem., India Ltd. and benzoyl peroxide (BZP) from LOBA Chemicals. Base oils were collected from Indian Oil Corporation Ltd., Dhakuria, Kolkata.

3.1.2 Purification of the materials

Methyl acrylate (MA) 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 used as initiator after recrystallization from CHCl_3 -MeOH mixture, THF, 1, 4-Dioxane, and toluene were purified by distillation after being refluxed for 2 h in presence of sodium

3.1.3 Polymerization

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 to add styrene drop wise. In the flask was placed desired mass of MA and initiator (BZP) followed by the desired mass of styrene, added drop wise for 2 h in the presence of different solvents (toluene, tetrahydrofuran and 1, 4-dioxane). The reaction temperature was maintained at 353K 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 homopolymer of MA was 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 300 MHz FT-NMR Spectrophotometer using 5 mm BBO probe. CDCl_3 was used as solvent and TMS as reference material.

3.1.5 Viscometric measurements.

Viscometric properties were determined at 303 K, 313 K and 323 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values, $K' = 0.00268 \text{ cm}^2 \text{ sec}^{-2}$, $L = -19.83 \text{ cm}^3$ 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 for at least seven 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 $K = 0.00387 \text{ dl.g}^{-1}$ and $a = 0.725$ [37, 38] were employed.

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

The prepared additives were evaluated as pour point depressant using base oils (B1 and B2) 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 were 0.25%, 0.50%, 1%, 2%, 3% and 5 % (w/w). The experimental data were noted by taking an average of three experimental results under identical conditions.

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

The various blends were prepared by using two different types of base stocks (B1 and B2). Viscosity index of these oils were calculated by ASTM D 2270-87 method using viscosity index calculator. The kinematic viscosities 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 0.25%, 0.50%, 1%, 2%, 3% and 5 % (w/w).

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PART II

**SYNTHESIS, CHARACTERIZATION, VISCOSITY ANALYSIS OF
HOMOPOLYMER OF METHYL METHACRYLATE AND COPOLYMERS
OF METHYL METHACRYLATE WITH STYRENE AND 1-DECENE AND
COMPARATIVE PERFORMANCE EVALUATION OF THESE POLYMERS
AS POUR POINT DEPRESSANT (PPD) AND VISCOSITY INDEX
IMPROVERS (VII) IN LUBRICATING OILS.**

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).

One important feature of an additive is that it should be effective in small quantities. Another important feature is that the additive must not produce unwanted by-products with its use in lubricating oil. An additive should also ideally perform more than one function so that fewer different additives have to be blended into the lubricating oil. Effectiveness in all viscosities and being liquid for ease of use are also desirable attributes in an additive.

A challenge for oil formulators is to find polymers that may improve high temperature viscosity performance as well as low temperature performance such as cold engine starting performance. These attributes, among others, can cause performance tradeoffs with respect to given polymer additives wherein an improvement in one way can be offset by reduced performance in another. Additionally, there is always a commercial incentive to have the polymer be effective at the lowest reasonable concentrations in order to minimize the cost of a given engine oil product or additive.

An enormous research has been devoted to the synthesis, technology and applications of different lube oil additives. Technology has successfully concerned itself with the development of lubricating oil additives which improve the viscosity

index of lubricating oils and additionally have good thickening, dispersing, and detergents effects together with a good protective effect against wear. Further critical points are the effect on the pour point as well as the shear stability of the lubricating oil additives. At the same time, mixtures thereof with mineral oils must give stable systems.

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. With respect to many applications of lubricating oils, it is desirable that viscosity changes of lubricating oil be relatively small within the temperature change of use and with particular respect to the engine from cold starting up to hot running conditions. Lubricating oil and hydraulic fluids showing smaller changes in viscosity with temperature are desired for many applications. Such oils permit easy starting of cold mechanisms and assure both rapid circulation of the oil to moving parts and an adequate viscosity at maximum operating temperature [1].

A brief introduction of PPD and VII has already been presented in **Chapter I** of **Part I**.

The most extensively used flow improvers (PPD) for fuel oils are ethylene-vinyl acetate copolymers [2-4], the alkyl ester of unsaturated carboxylic acid-olefin copolymers [5-6], and the maleic anhydride alkyl ester of unsaturated carboxylic acid copolymers [7-8].

On the other hand some of the polymers generally used commercially as VII, and known to possess certain inherent advantages and disadvantages in performance, are- (i) Poly isobutylene (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) (PAMA).

Polymethacrylate (PMA) viscosity index improvers (VII's) are well known in the lubricating industry. Many attempts have been made to produce PMA VII's that have the desired balance of high temperature and low temperature viscometrics, as well as the required shear stability for a given application.

Polymethacrylates have been known for a long time as lubricating oil additives and are used on a large technical scale. In the last few years the more economical polyolefins have found increasing significance for the same purposes.

Both classes of products show advantages and disadvantages: polymethacrylates are characterized by a good effect from the point of view of the viscosity-temperature relationship of the oil improved therewith, and, when used in sufficiently high concentration, show an outstanding protective effect against wear. Further, they lower the pour point of lubricating oil. On the other hand, the treating costs for these products are comparatively high. This concept is to be understood as meaning the costs required for achieving a desired effect. Polyolefins bring about the same thickening of oil as do polymethacrylates, even already in clearly smaller concentrations, but polyolefins do not improve the pour point. In order to achieve an improvement in the pour point, lubricating oil additives comprising polyolefins must have added there to special pour point improvers such as chlorination products of wax and naphthalene, polyalkylmethacrylates, copolymers of alkylaminoalkylmethacrylates, and polyalkylacrylates. Nevertheless, the decrease in the pour point by the addition of pour point improvers encounters difficulties with certain polyolefins, particularly those which tend to form associates.

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. Patent 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. Patent 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. Patent 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.

I. M. El-Gamel [4] 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 [9] Rasha has reported a novel PPD based on maleic anhydride -acrylates terpolymers.

N. S. Ahmed et al [10] 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 531556 A disclosed a method for making a lubricating oil multifunctional additive which comprises a polyalkyl methacrylates and hydrogenated block copolymers comprising a conjugated diene having 4 to 6 carbon atoms and styrene.

U.S. Patent no. 3,598,736 disclosed the addition of small amounts of oil soluble copolymers of poly(methacrylates) (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. 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.

The invention in U.S. patent 3,252,949 relates to highly syndiotactic oil-soluble methacrylate polymers having superior viscosity index improving properties when incorporated in mineral and synthetic oils (functional fluids) and to compositions of these polymers in functional fluids. These polymers also have dispersancy properties by incorporating a minor amount of appropriate co-monomer during polymerisation to give the polymer dispersancy properties or by treatment after the formation of the polymer.

Conventional methacrylate polymers useful as viscosity index improvers in functional fluids are described in U.S. patent 2,091,627. These polymers are made by free radical polymerization at about 70⁰ F or above.

U.S. Patent No. 4,089,794 discloses ethylene copolymers derived from ethylene and one or more C₃ to C₈ alphaolefin solution grafted with an ethylenically-unsaturated carboxylic acid material followed by a reaction with a polyfunctional material reactive with carboxyl groups, such as a polyamine, a polyol, or a hydroxyamine which reaction product is useful as a sludge and varnish control additive in lubricating oils.

U.S. Patent No. 4,357,250 discloses a reaction product of a copolymer and an olefin carboxylic acid via the "ene" reaction followed by a reaction with a monoaminepolyamine mixture

U.S. Patent No. 4,382,007 discloses a dispersant-VI improver prepared by reacting a polyamine-derived dispersant with an oxidized ethylene-propylene polymer or an ethylene-propylene diene terpolymer.

U.S. Patent No. 4,320,019 discloses a multipurpose lubricating additive prepared by the reaction of an interpolymer of ethylene and a C3-C8 alpha-monoolefin with an olefinic carboxylic acid acylating agent to form an acylating reaction intermediate which is then reacted with an amine.

U.S. Patent No. 4,144,181 discloses polymer additives for fuels and lubricants comprising a grafted ethylene copolymer reacted with a polyamine, polyol or hydroxyamine and finally reacted with an alkaryl sulfonic acid.

U.S. Patent No. 5,932,525 teaches multi-grade lubricating oils comprising a low saturate base stock, less than three mass percent of an ash less dispersant and a viscosity modifier.

U.S. Patent No. 5,427,702 discloses mixed ethylene alphaolefin copolymer multifunctional viscosity modifiers.

U.S. Patent No. 4,863,623 teaches multifunctional olefin copolymer VI improvers.

W.O. Patent No. 2007042560 A1 discloses a multifunctional lubricating oil composition having a polymethacrylate additive.

W.O. Patent No. 2013055481 A1 discloses multifunctional polyalphaolefin high efficiency engine oil composition for lube oils.

W.O. Patent No. 2013055483 A1 discloses preparation of mixed polyalphaolefin high efficiency engine oil additive composition for lube oils.

U.S. Patent No. 20100292424 A1 discloses an improved process which employs mixed alpha-olefins as feed over activated metallocene catalyst systems to provide essentially random liquid polymers particularly useful in lubricant components or as functional fluids.

U.S. Patent No. 8293689 B2 provides a lubricating composition containing an oil of lubricating viscosity and methacrylate polymer with pendant groups. The invention further provides for a method of controlling viscosity index by supplying to an oil of lubricating viscosity the polymer with pendant groups.

U.S. Patent No. 8163683 B2 discloses a pour point depressant for lubricants comprising: a mixture of an alkyl(meth)acrylate polymer (A) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_A) of 12.5 to 13.8, and an alkyl(meth)acrylate polymer (B) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_B) of 13.9 to 15.5.

Thus from above literature survey it has been observed that either with methacrylate (or acrylate) polymers/copolymers or olefin polymers/copolymers, one could not hold the both PPD and VII properties satisfactorily. So there are still a limitation with the development of multifunctional additives comprising both PPD and VII properties.

The idea of combining products of both classes of polymers, in order thereby to produce lubricating oil additives with improved properties, was obvious. Industry awaits the preparation of lubricating oil additives in a liquid (oil-based) form and with the highest possible absolute polymer content.

In the present work multifunctional additives were prepared via the preparation of methyl methacrylate (MMA) homopolymer, methyl methacrylate - styrene copolymers and methyl methacrylate - 1-decene copolymers with different

percentage. Comparative characterization of these polymers and their evaluation as viscosity index improvers and pour point depressants were also carried out.

These compositions have the advantage of providing a better compromise between the various effects required of a viscosity additive: solubility, thickening power, selectivity, shearing strength and pour point.

CHAPTER II

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

Section A Comprises **Synthesis, Characterization and Viscosity Studies of Homo polymer of Methyl Methacrylate and its Copolymers with Styrene and 1-Decene.**

Section B Comprises **Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate and Evaluation of their Pour Point Depressant properties in Lubricating (Lube) Oils.**

Section C Comprises **Comparative Performance Evaluation of Homopolymer of Methyl Methacrylate and Copolymers of Methyl Methacrylate with Styrene and 1-Decene as Pour Point Depressant and Viscosity Index Improver in three different Base Oils.**

2.1 Section A: Synthesis, Characterization and Viscosity Studies of Homo polymer of Methyl Methacrylate and its Copolymer with Styrene and 1-Decene.

2.1.1 Introduction

Polymers of alkyl methacrylate used as additives in lubricant composition for improving the viscometric and rheological properties of the lubricant [11-14]. They also looked upon to provide additional performance characteristics such as improved low temperature fluidity and dispersancy. Although polyalkylmethacrylates (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 polyalkylmethacrylates, 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 and 1-decene 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 work the results of our investigation towards the synthesis, characterization and viscometric measurement of copolymers of MMA with styrene and 1-decene in compare to homo polymer of MMA will be discussed. Four copolymers of MMA were prepared by varying the mass fractions of styrene and 1-decene in the monomer mixture from 5 % to 10 % 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 [13]. 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), FT-IR and FT-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 [15], 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 [16-17] and almost nil for polymers used as lube oil additives, present research also include viscometric study of the copolymers as well as the homopolymer.

Viscometry is the simplest technique used to study the macromolecules in solution and determine their molecular weight. For the determination of molecular weights of the polymers here again we used Mark - Houwink – Sakurada relation as earlier (**Chapter II of Part I**) which relates the intrinsic viscosity with the molecular weight of the polymer in a solvent.

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. As we discussed earlier in chapter II of part I, 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 method [16-19]. We used Huggins, Kraemer, Martin and Schulz-Blaschke equations in this work and for determining the intrinsic viscosity in dilute polymer solution from a single point determination we used Solomon- Ciute (SC) and Deb– Chatterjee (DC) relations [16-20].

All the equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$ [19], where k_h and k_k are the Huggins coefficient and Kraemer coefficient respectively.

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.

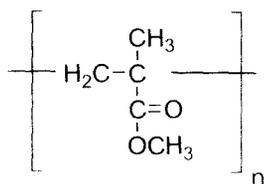
Since, viscometry provides very important data about the interaction of additive in base fluid and hence conformation of polymeric system [15] in the base stock, the process of polymerization in the presence of a suitable solvent has been attracting considerable interest [21-22].

Since the behaviour 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.

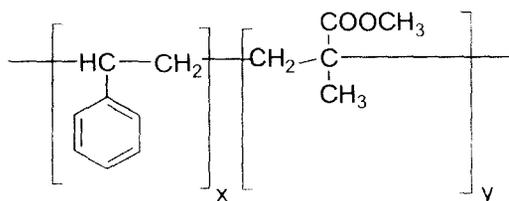
In this work viscometric parameters (intrinsic viscosity and the value of constants) of toluene solution for sample of poly methyl methacrylate and its copolymer were obtained by graphic extrapolation and single point determination. The viscosity average molecular weight determined by using different equations, were 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 discussions

IR spectra of the homo polymer of MMA (**Figure 1**) 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 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 with styrene was confirmed by IR (**Figure 2**) and NMR (**Figure 3**) analysis. Carbonyl stretching vibration at 1732 cm^{-1} of the homo polymer shifted to 1728 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 (**Figure 3**) of the copolymer, apart from the appearance of CDCl_3 pick (7.26 ppm) presence of multiplates within the range 6.91 ppm to 7.31 ppm indicated the aromatic protons of styrene present in the copolymer skeleton and the presence of 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 [23] as well as on the basis of our earlier paper [13], which was further verified through an analysis of FT-IR spectral data following a method as also discussed in our earlier paper [13]. From the above discussion structure of the homopolymer of MMA and its copolymer with styrene may be presented by **Structure 1** and **Structure 2** respectively.



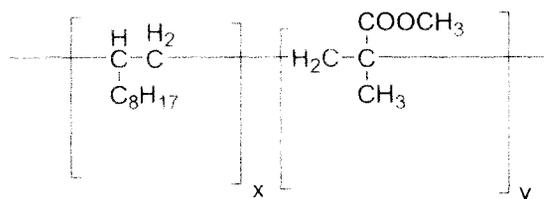
Structure 1



Structure 2

The formation of copolymer of MMA with 1-decene is also confirmed by IR

and NMR analysis. Carbonyl stretching vibration at 1732 cm^{-1} of the homopolymer (MMA) shifted to 1729 cm^{-1} in the copolymer. ^1H NMR spectra the copolymer indicated the absence of any vinylic protons and showed the presence of ester methyls at 3.60 ppm. The extent of incorporation of 1-decene in polymer chain was determined by two independent method based on FT-IR, ^1H NMR and ^{13}C NMR data. The structure of the copolymer of MMA with 1-decene may be represented as **Structure 3**.



Structure 3

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 in both cases than the homopolymer (except Poly-5).

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 the samples (**Figure 7**) indicated that measurements were performed in Newtonian flow [24-25].

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 [16-20]. The same is used here also.

Table 3 presents intrinsic viscosity values related to all equation for the sample analysed. 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 co polymers 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 PMMA itself. But in case of copolymers with 1-Decene, intrinsic viscosity values gradually decreases with

increase in mass fraction of 1-decene. However, beyond a concentration of 2.5 % of styrene hydrodynamic volume of it 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 [26-27].

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 co polymers. For the homo polymer and copolymer, $[\eta]_{int}$ value obtained by Huggins and Kramer's equation were identical.

Both homopolymer and copolymers in toluene medium is indicating towards poor solvation (**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 [15]. 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 4**), but found similar as reported elsewhere [25]. Maximum deviation for the homo polymer of MMA may be attributed to the comparatively poor solubility of the polymer in toluene.

Styrene copolymers showed slightly better solubility amongst all the polymers in toluene solvent.

A comparison on the basis of calculated percentual differences ($\blacktriangle \% = 100 ([\eta] / [\eta]_h) - 100$) of $[\eta]$ values, taking Huggins equation as a reference indicated that with the $[\eta]$ values (**Table 3**) determined through graphic extrapolation using Kraemer, Martin and SB equations, the range of $\blacktriangle \%$ (-0.66 to 26.31 %, Table 5) was narrow in comparison to the values (10.43 to 41.40 %), when $[\eta]$ is obtained through single point method using SB, SC and DC equation. Between the two types of copolymers MMA-Styrene and MMA - 1-decene, similar comparison indicated that the range was narrow in case of 1-decene (5.3 to 25.30) than the styrene copolymers (-0.66 to 41.60). However, the percentual differences ($\blacktriangle = ([\eta]/[\eta]_h) - 1$) obtained in the case of homo polymer are always higher (except one in each case) than the co

polymers, irrespective of the method of determination (**Table 5**).

This may be because of the fact that, the homopolymer PMMA, with lowest molecular mass (M_n 45000 g.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 3**) 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. The Martin equation produced the lowest deviation value among the four when compared to those obtained from the Huggins equation. **Table 6** presents the value of viscometric molecular weights obtained for homo polymer and co polymers analyzed. The trend is similar as was observed in case of GPC molecular weight and is in line with their respective intrinsic viscosity values. However, as expected, a difference was observed in the values of molecular weight obtained by GPC and viscometric method. This is probably due to the differences in analysis conditions, like solvents, temperature techniques and standard employed [28].

Comparison between viscosity molecular weight (M_v) and number average molecular weight obtained by GPC, indicated that graphical extrapolation values are more close to that of the GPC values rather than the single point determination values. The percentual difference, $\Delta = (M/M_h) - 1$, obtained for viscometric molecular weight values are showed in (Table 7) taking M_v determined by Huggins equation (M_h) as a reference. Martin equation showed the smallest Δ % values.

2.1.3 Conclusion

Incorporation of 1-decene in to MMA is greater than styrene under identical condition of copolymerization.

Molecular mass of (GPC and Viscometry) of 1-decene copolymer is always less than styrene copolymer.

In general, copolymers showed greater thermal stability than the homopolymer.

Incorporation of styrene raises the thermal stability of MMA more than 1-decene

does.

In general, increased styrene concentration in the feed is directly proportional to intrinsic viscosity of the copolymer solution but reverse is observed in case of MMA - 1-decene copolymer.

Intrinsic viscosity values obtained by using Huggins and Kramer's equations are found to be identical for both homo and copolymers.

Homo and copolymers showed a tendency towards the formation of micelle or spherical structure in toluene medium.

MMA - styrene copolymer showed better solubility in comparison to homopolymer and MMA - 1-decene copolymer in toluene.

Amongst the single point determination method, SB equation found to be most suitable for the copolymer system analysed, whereas for the homopolymer, PMMA, graphical extrapolation method seems to be most suitable in toluene.

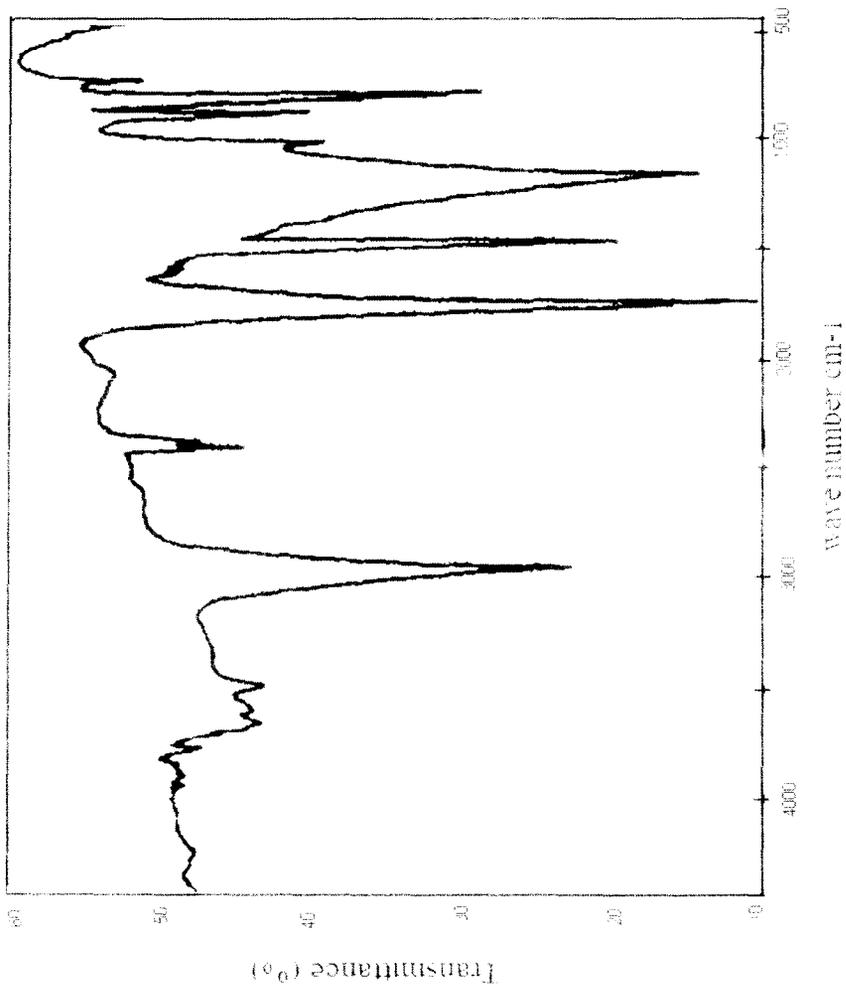


Figure 1: FT-IR spectrum of homopolymer of methyl methacrylate

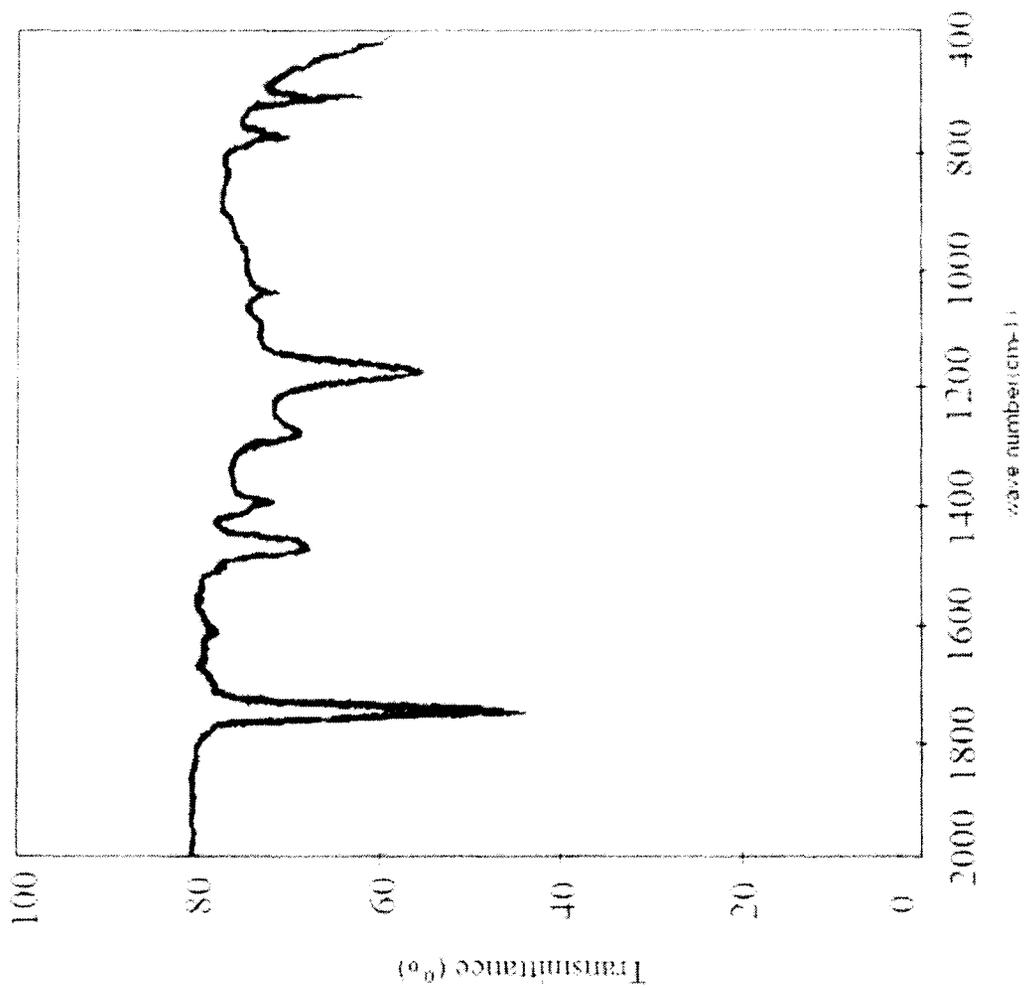


Figure 2: FT-IR spectrum of copolymer of methyl methacrylate with styrene

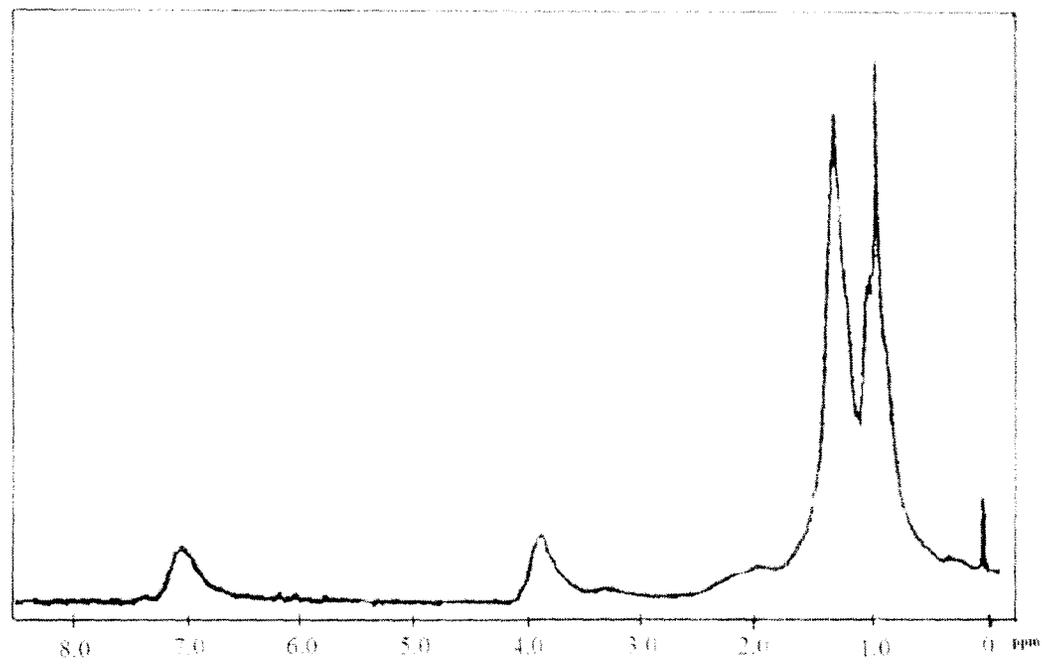


Figure 3: ^1H NMR spectrum of copolymer of methyl methacrylate with styrene

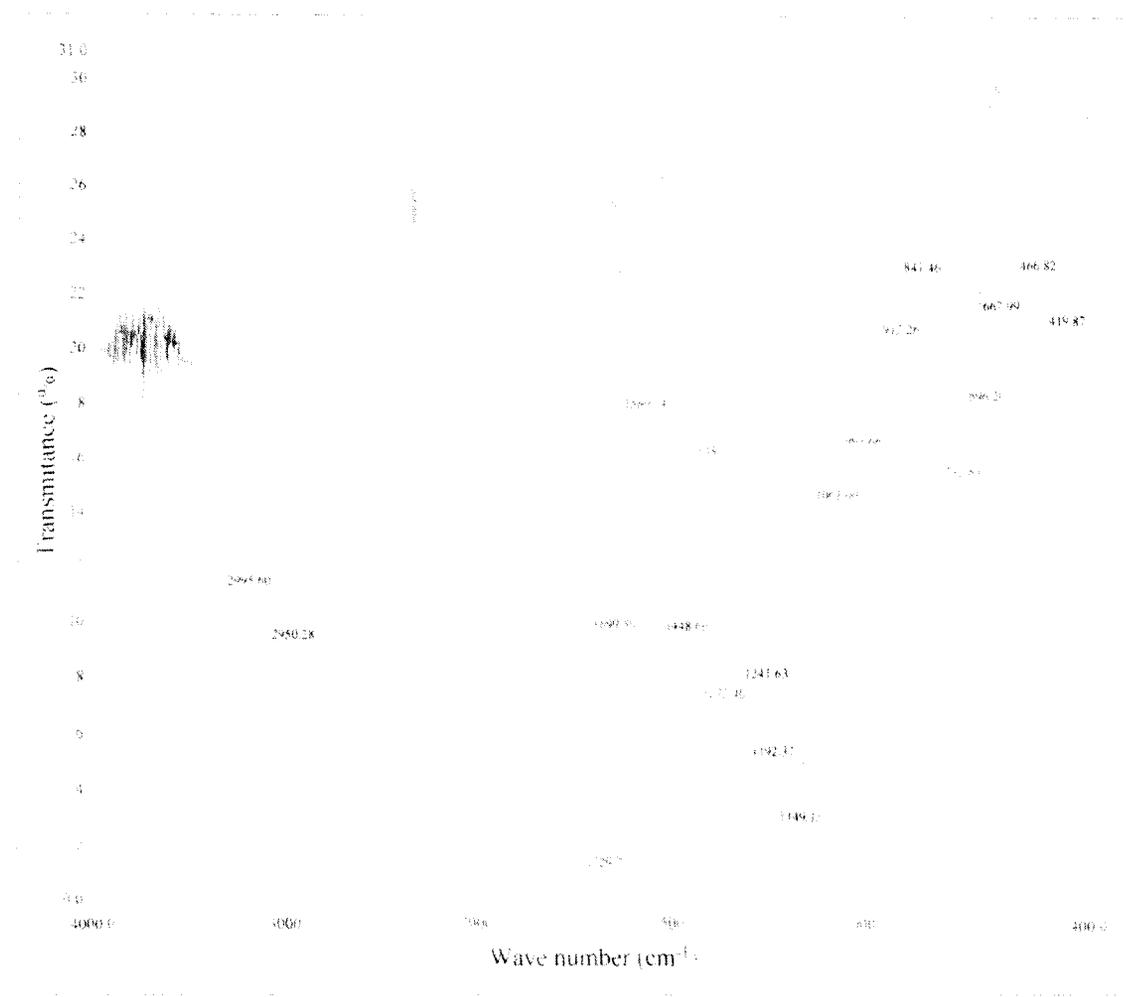


Figure 4: FT-IR spectrum of copolymer of methyl methacrylate with 1-decene

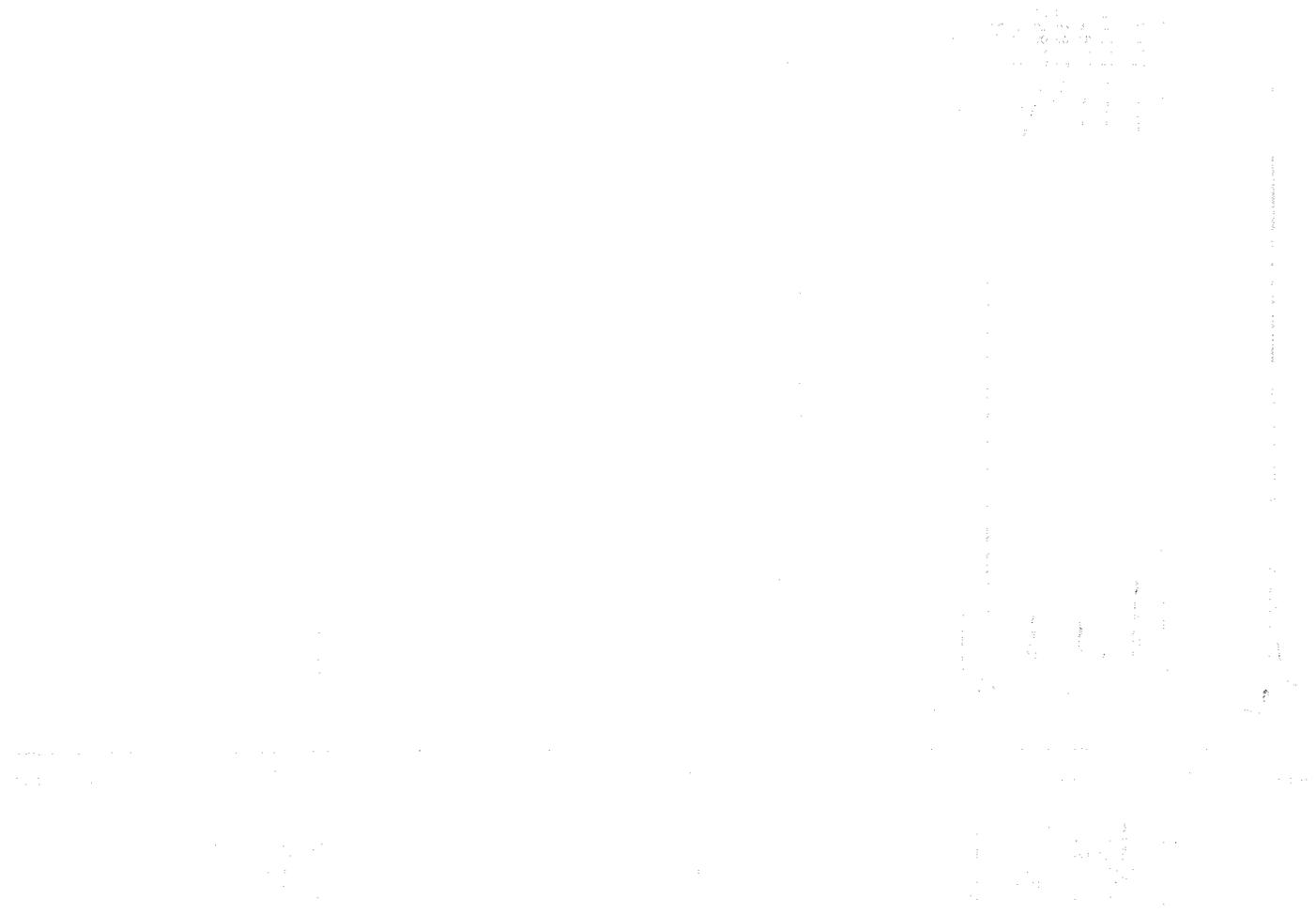


Figure 5: ^1H NMR spectrum of copolymer of Methyl methacrylate with 1-decene

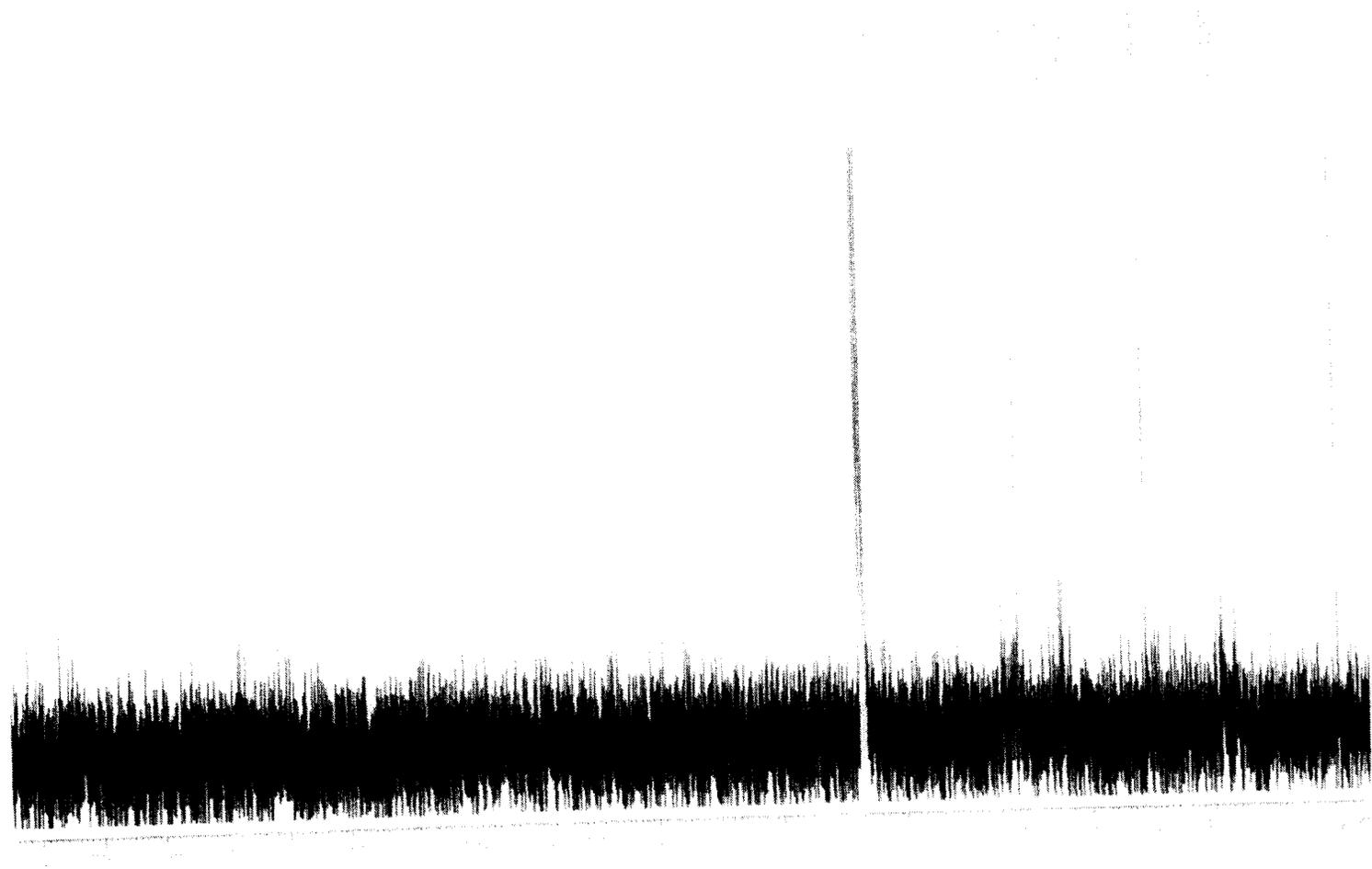


Figure 6: ^{13}C NMR spectrum of copolymer of Methyl methacrylate with 1-decene

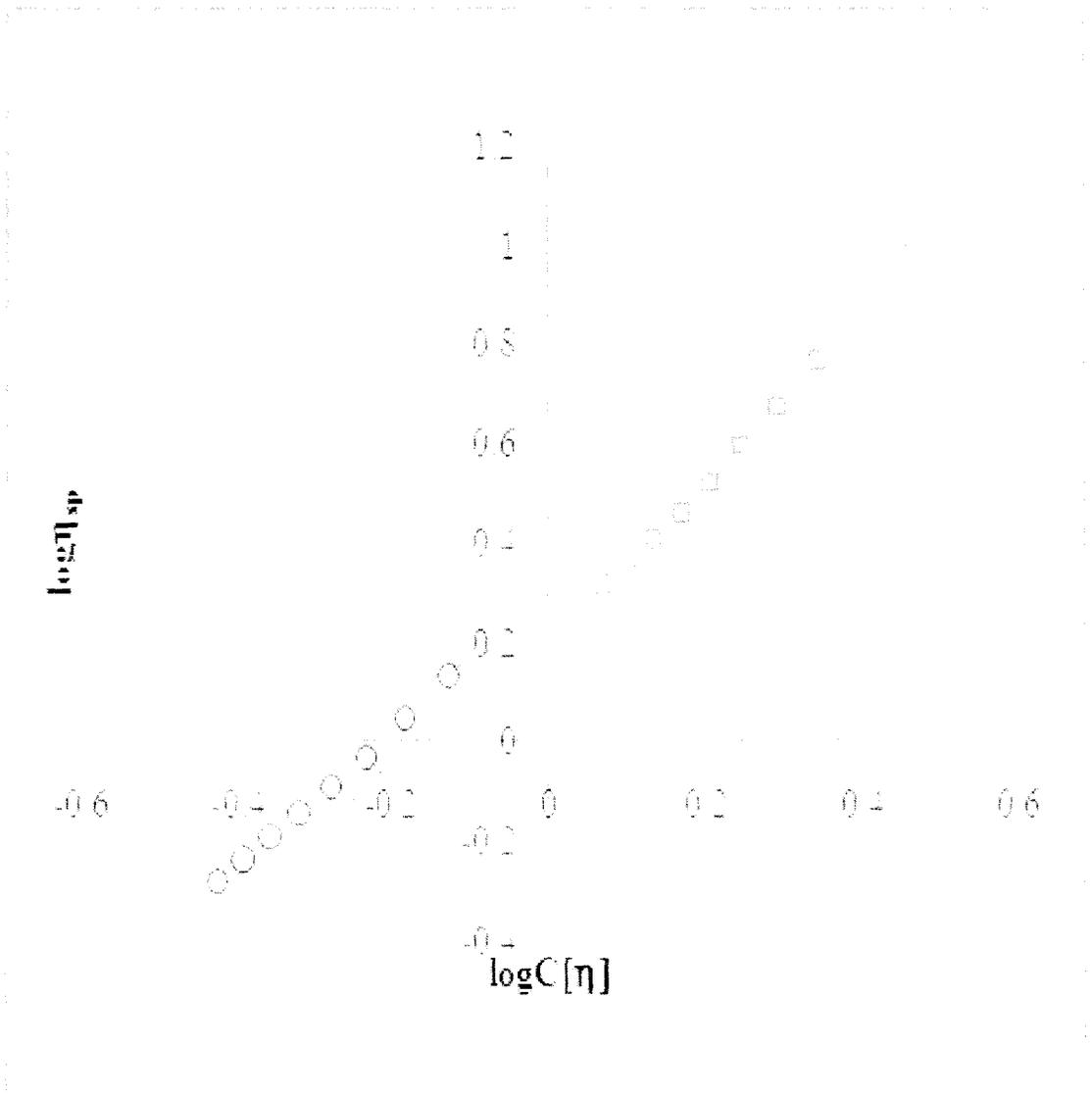


Figure 7: Plot of $\log C[\eta]$ vs $\log \eta_{sp}$: \diamond , Poly-1; \square , Poly-2; Δ , Poly-3; \times , Poly-4, \circ , Poly-5

Table 1. Composition of the monomers in the copolymers in terms of mass fraction determined by PMR and FT-IR spectrometric method. Poly-1 is homopolymer of methyl methacrylate (MMA); Poly-2 and Poly-3 are the copolymer of MMA with different mass fractions of styrene and Poly-4 and Poly-5 are the copolymer of MMA with different mass fractions of 1-decene

| 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-2 and poly-3) / 1-decene (poly-4 and poly-5) | | |
| Poly-1 | 1 | - | - | - |
| Poly-2 | 0.95 | 0.05 | 0.02 | 0.023 |
| Poly-3 | 0.90 | 0.10 | 0.04 | 0.045 |
| Poly-4 | 0.95 | 0.05 | 0.028 | 0.03 |
| Poly-5 | 0.90 | 0.10 | 0.049 | 0.051 |

Table 2. Molecular mass obtained by gel permeation chromatography and Thermal gravimetric analysis data for homo- and copolymers. M_n is number average molecular weight and M_w is weight average molecular weight. a - percent weight loss

| Polymer sample | $M_n \times 10^{-4}$ | $M_w \times 10^{-4}$ | TGA data | |
|----------------|----------------------|----------------------|------------------|------------------|
| | | | Decom. Temp., °C | PWL ^a |
| Poly-1 | 4.5 | 16 | 230/280 | 26/77 |
| Poly-2 | 8.5 | 19 | 295/356 | 29/71 |
| Poly-3 | 14.5 | 25 | 320/375 | 48/52 |
| Poly-4 | 1.8 | 5.6 | 240/280 | 35/75 |
| Poly-5 | 4.8 | 10.6 | 205/265 | 30/70 |

Table 3. Intrinsic viscosity values for all prepared homo and copolymer samples calculated by using different equation. a- extrapolation of graph, b- single point determination ($k_{sb}= 0.28$), c- single point determination

| 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 | 13.5 | 14 | 14.78 | 15.61 | 15.39 | 15.81 | 17.68 |
| Poly-3 | 15.12 | 15.02 | 16.88 | 18.2 | 16.694 | 18.17 | 21.41 |
| Poly-4 | 5.59 | 5.89 | 6.27 | 6.28 | 6.25 | 6.25 | 6.549 |
| Poly-5 | 4.02 | 4.48 | 4.39 | 4.63 | 4.86 | 4.86 | 5.040 |

Table 4. Viscometric constants obtained for all prepared homo- and copolymer samples. K_h , k_k , k_m and k_{sb} are 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 | 0.639 | 0.0006 | 0.337 | 0.247 | 0.640 |
| Poly-3 | 0.678 | 0.038 | 0.356 | 0.227 | 0.716 |
| Poly-4 | 0.657 | 0.046 | 0.343 | 0.289 | 0.703 |
| Poly-5 | 1.058 | -0.026 | 0.611 | 0.42 | 1.032 |

Table 5. Percentual differences ($\Delta = ([\eta]/[\eta]_h) - 1$) 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 | 3.70 | 9.48 | 15.55 | 14.01 | 17.11 | 30.96 |
| Poly-3 | -0.66 | 11.64 | 20.37 | 10.41 | 20.15 | 41.60 |
| Poly-4 | 5.30 | 12.08 | 12.24 | 12.34 | 11.71 | 17.05 |
| Poly-5 | 11.64 | 9.20 | 15.31 | 21.98 | 21.01 | 25.30 |

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 | $M_h^a \times 10^{-4}$ | $M_k^a \times 10^{-4}$ | $M_m^a \times 10^{-4}$ | $M_{sb}^a \times 10^{-4}$ | $M_{sb}^b \times 10^{-4}$ | $M_{sc}^b \times 10^{-4}$ | $M_{dc}^b \times 10^{-4}$ |
|--------|------------------------|------------------------|------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| Poly-1 | 3.54 | 4.65 | 3.58 | 4.88 | 4.97 | 5.05 | 5.59 |
| Poly-2 | 7.67 | 8.09 | 8.71 | 9.99 | 9.22 | 9.56 | 11.16 |
| Poly-3 | 8.99 | 8.91 | 10.47 | 11.62 | 10.31 | 11.58 | 14.54 |
| Poly-4 | 2.28 | 2.44 | 2.66 | 2.67 | 2.67 | 2.65 | 2.83 |
| Poly-5 | 1.44 | 1.68 | 1.63 | 1.75 | 2.77 | 1.87 | 1.97 |

Table 7. Percentual differences obtained for viscometric molecular weight values $\Delta = (M/M_h) - 1$, 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 | 50.14 | 13.30 | 29.80 | 19.80 | 24.34 | 45.12 |
| Poly-3 | -0.91 | 16.40 | 29.10 | 14.60 | 28.80 | 61.00 |
| Poly-4 | 7.30 | 16.90 | 17.20 | 17.40 | 16.40 | 24.10 |
| Poly-5 | 16.40 | 12.90 | 21.60 | 21.80 | 30.00 | 36.40 |

2.2 Section B Shear Stability and Thickening Properties of Homo and Copolymer of Methyl Methacrylate and Evaluation of their Pour Point Depressant properties in Lubricating (Lube) Oils.

2.2.1 Introduction

Polymer containing fluids exhibit less reduction in viscosity with increase in temperature than the corresponding base fluids containing no polymer. The hydrodynamic volume of the polymer in the fluid increases with increase in temperature thereby resulting in an increase in viscosity, which greatly compensates the opposing effect of commonly observed reduction in viscosity of a fluid with rise in temperature. In the fields of lubricants, the degree of susceptibility of viscosity of a fluid to temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI). A higher VI value signifies a lesser effect of temperature on viscosity. Polymers employed as additives in lubricants to enhance the VI (i.e. to minimize the temperature dependency of viscosity) are called as viscosity index improvers (VII) or viscosity modifiers (VM) [13,29-30] and corresponding VII - treated lubricants are categorized as multigrade oils as opposed to monograde oils which contain no VI improvers. Several kinds of polymers, such as poly methyl methacrylate (PMMA), olefin copolymer (OCP) and hydrogenated styrene-diene copolymer (SDP) are generally used as VMs in lubricating oil compositions.

Shear stability of the VM is one of the important criteria that determine its suitability in a lubricant formulation. The shear stability of the doped additive has strong influence on multigrade engine oil's ability to retain its viscosity under shearing conditions, experienced by the lubricant while in use. The loss of viscosity of a lubricant under shear can be two kinds, namely a temporary viscosity loss (TVL) or a permanent viscosity loss (PVL) [31-33]. The PVL values are more frequently expressed in terms of permanent shear stability index (PSSI) [34-35] using the equations,

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

$$\text{PSSI} = (V_i - V_s) / (V_i - V_0) \times 100$$

Where V refers to kinematic viscosity (KV), $V_0 =$ KV of the solvent before addition of polymer, $V_1 =$ initial KV of the solvent with polymer, $V_s =$ KV of the solvent after shearing. A detailed study of the literature indicated that only a few investigations have so far been carried out on the effects of lubricant compositional parameters such as polymer type, polymer concentration, base oil viscosity, etc. on the shear stability performance of multigrade lubricants. Polymers of alkyl methacrylate used as additives in lubricant composition for improving the viscometric and rheological properties of the lubricant [11, 14, 36-37]. 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 co polymer compounded oil to the action of heat. Since homopolymer of styrene is insoluble in lube oil they are introduced in the composition of oil soluble polymer by copolymerization which may be useful as a PPD / VM (Viscosity modifier) for petroleum and synthetic oil.

Thus, as a part of our ongoing studies on lube oil additives [13,28], studies were undertaken in this area with a view to arriving at possible generalization on the effects of different level of concentration, of the copolymer of MMA - styrene on shear stability as well as on the pour point depressant performance of the additives. In this investigation, shear stabilities of the homopolymer of MMA and four of its copolymer with styrene (2.5 to 10%, w/w) taken in toluene were determined in terms of kinematic viscosity and as per the standard ASTM method. The prepared additives were also evaluated as pour point depressant using base oils collected from two different sources through the standard ASTM test method. The observations have been correlated with the homopolymer towards arriving at possible generalization on this effect.

Oil thickening property of the polymer, which is a direct measure of percent

increase in the viscosity of the base stocks for addition of its unit amount of weight has also been investigated and reported here. This property can also be taken as the extent of interaction of the polymer with the base stock, greater the thickening property; greater is the extent of interaction [13]. Fuel economy may also be predicted by the thickening power of a lube oil additive.

All the polymers were synthesized by following the method as reported earlier [29] and characterized on the basis of spectral analysis (IR, NMR), thermo gravimetric analysis (TGA) and viscometric method.

The shear stability of the polymer solutions in toluene was determined in terms of kinematic viscosity and as per the standard ASTM method. During the investigation, the type and concentration of the VMs, effect of styrene incorporation in the copolymer, effect of intrinsic viscosity / polymer molecular weight on their PSSI were evaluated and the results are being reported here.

2.2.2 Results and Discussions

Spectroscopic Analysis

The spectroscopic data of MMA and its copolymer with styrene has been thoroughly discussed in the **section I** of this chapter

Effect of Styrene Incorporation

The comparison of SSI results (**Table 2**) indicated that PSSI values of copolymer are greater than homopolymer. It is also observed that PSSI of copolymer gradually increases with increase in styrene concentration in the feed of copolymerization mixture. A comparison of SSI among the copolymers studied, shows that there is a linear relationship between SSI and % of styrene in the copolymer. These suggest that styrene incorporation in the acrylate chain has a strong influence on the viscosity of the polymer – solvent blend (**Figure 1**).

Effect of Polymer Molecular Weight / Intrinsic Viscosity

It is observed that SSI values of the copolymers (except P-2) are higher compare to the homopolymer (**Table 2**) and there is a gradual increase of these values of the copolymer with the increase in styrene concentration in the feed of

copolymerization mixture. It is also observed maximum SSI value is obtained for the copolymer with maximum styrene concentration in the feed. This may be explained on the basis of molecular weight of the polymer. The higher and narrow mol weight distribution can provide relatively a higher molecular mass to undergo degradation with increase in polymer concentration than in the case of poly(methyl methacrylate) or copolymer with relatively lower mol weight. The intrinsic viscosity data (**Table 2**) also indicated higher molecular size for the copolymer compared to PMMA. It is reported that styrene copolymers exhibited aggregated structure in solvents [15,16]. This phenomenon is expected to play a significant role in determining the shear stability of copolymer with styrene.

Evaluation of Thickening Property in Toluene Solvent

Thickening behaviour of the polymers in toluene solvent has been determined and the results are presented in **Table 3**. The data generated (**Table 3**) for the entire polymer solutions have been compared. It revealed that although thickening performance of the polymers, both the homopolymer and copolymers, is higher at a higher concentration but the data could not yield any correlation of thickening properties among the homo and copolymers as well as among the co-polymers with different extent of styrene concentrations in them. This is consistent with our earlier observation [13].

Performance of the Homo and Copolymers as PPD in Base Oils

Base oil (lube oil) of three different viscosity grades (B1, B2 and B3) were used to study the PPD performance of the copolymers in comparison to the homopolymer. Properties of base oils were tabulated in **Table 4** and pour point of the different levels of additive doped lube oils were tested and tabulated in **Table 5**. 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.

2.2.3 Conclusion

The study indicated that the PSSI values of copolymer are greater than

homopolymer and increased gradually with the increase in styrene concentration in the feed of copolymerization mixture. PPD performance of the additive doped base oils also followed the similar trend.

These suggest that styrene incorporation in the acrylate chain has a strong influence on the shear stability and PPD of the polyacrylate type of additives.

Molecular weight of the acrylate-styrene copolymer is directly proportional to their shear stability. Incorporation of styrene raises the molecular size of the copolymer, as is evident from the intrinsic viscosity data.

There is no correlation of thickening properties among the homo and copolymers as well as among the copolymers with different extent of styrene concentrations in them.

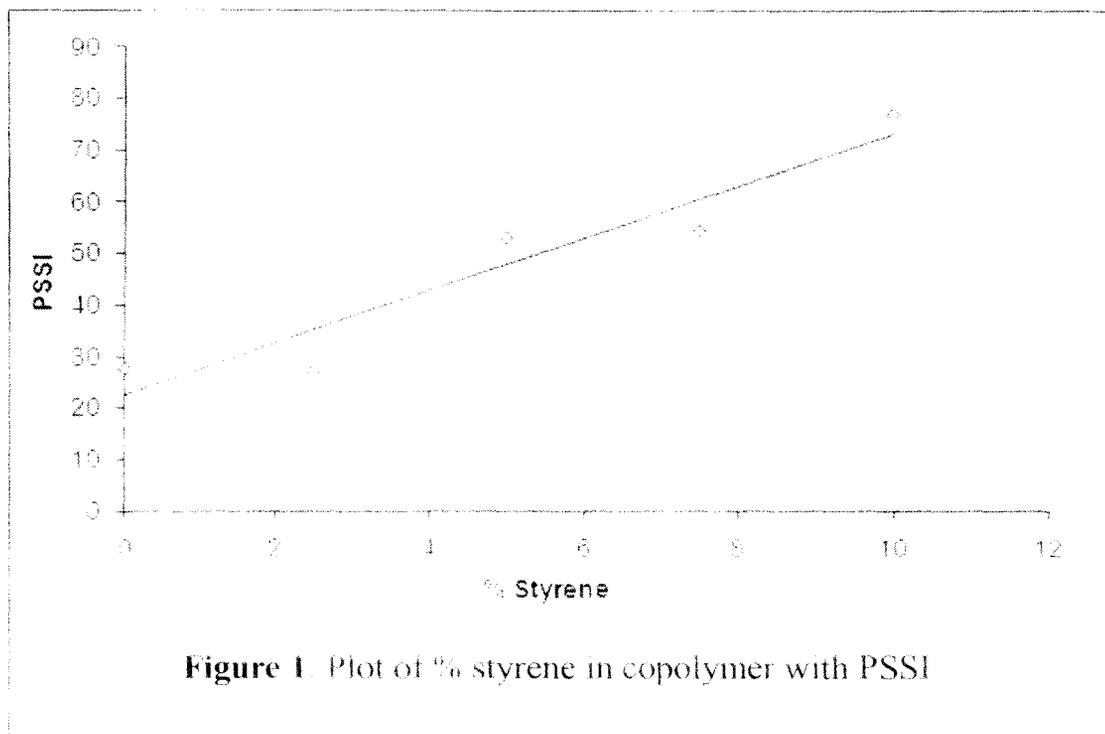


Table 1. Composition of the monomers in the copolymers in terms of mass fraction determined by PMR and FT-IR spectrophotometric method. P-1 is homopolymer of Methyl methacrylate (MMA); P-2 to P-5 are the copolymer of MMA with different mass fractions of styrene

| Polymer sample | Mass fraction in the feed | | Mass fraction of MMA/styrene in copolymer | |
|----------------|---------------------------|---------|---|--------------|
| | MMA | Styrene | PMR method | FT-IR Method |
| P-1 | 1 | - | - | - |
| P-2 | 0.975 | 0.025 | 0.012 | 0.013 |
| P-3 | 0.950 | 0.050 | 0.024 | 0.025 |
| P-4 | 0.925 | 0.075 | 0.038 | 0.033 |
| P-5 | 0.900 | 0.100 | 0.049 | 0.051 |

Table 2. Physical parameters of Polymeric Samples

| Sample | $[\eta]_h$ | $M_h \times 10^{-4}$ | PVL | PSSI |
|--------|------------|----------------------|-------|-------|
| P-1 | 7.69 | 3.54 | 25.93 | 27.65 |
| P-2 | 6.32 | 2.70 | 51.02 | 26.98 |
| P-3 | 13.5 | 7.69 | 49.43 | 53.00 |
| P-4 | 14.4 | 8.41 | 74.44 | 54.38 |
| P-5 | 15.12 | 8.99 | 25.66 | 77.00 |

Table 3. Thickening power and kinematic viscosity data

| Sample | Conc.(g.cm ⁻¹) | Kinematic Viscosity | Increase in viscosity | Thickening |
|---------|----------------------------|---------------------|-----------------------|------------|
| Solvent | - | 0.451 | - | - |
| P-1 | 0.0605 | 0.783 | 0.332 | 2.00 |
| | 0.0454 | 0.695 | 0.224 | 1.10 |
| P-2 | 0.0605 | 0.806 | 0.355 | 2.15 |
| | 0.0454 | 0.629 | 0.178 | 0.808 |
| P-3 | 0.0605 | 0.886 | 0.435 | 2.63 |
| | 0.0454 | 0.779 | 0.328 | 1.49 |
| P-4 | 0.0605 | 0.788 | 0.337 | 2.04 |
| | 0.0454 | 0.689 | 0.238 | 1.08 |
| P-5 | 0.0605 | 0.893 | 0.442 | 2.67 |
| | 0.0454 | 0.770 | 0.319 | 1.45 |

Table 4. Base oil properties

| Base oil properties | Base oil | | | | | |
|--|----------|------|-------|-------|--------|--------|
| | 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 | -6 | -6 |
| Pour point, ⁰ C | 3 | -3 | -6 | -6 | 0 | 0 |

Table 5. Pour point of additive doped base oils

| Base Oil | PPD Sample | Pour Point ($^{\circ}\text{C}$) of base oils containing different %(w/w) of PPD | | | | | |
|----------|------------|---|-----|------|-----|------|-----|
| | | 0.025 | | 0.05 | | 0.10 | |
| | | A | B | A | B | A | B |
| B1 | P-1 | -9 | -9 | -9 | -9 | -9 | -9 |
| | P-2 | -12 | -12 | -15 | -15 | -15 | -15 |
| | P-3 | -12 | -15 | -18 | -18 | -18 | -18 |
| | P-4 | -15 | -15 | -15 | -18 | -21 | -21 |
| | P-5 | -12 | -12 | -18 | -18 | -18 | -21 |
| B2 | P-1 | -9 | -9 | -12 | -9 | -12 | -12 |
| | P-2 | -15 | -15 | -15 | -15 | -15 | -15 |
| | P-3 | -18 | -18 | -18 | -18 | -18 | -18 |
| | P-4 | -18 | -21 | -18 | -21 | -18 | -18 |
| | P-5 | -21 | -24 | -21 | -18 | -24 | -21 |
| B3 | P-1 | -6 | -6 | -9 | -12 | -12 | -12 |
| | P-2 | -12 | -12 | -12 | -15 | -15 | -15 |
| | P-3 | -15 | -15 | -15 | -18 | -18 | -18 |
| | P-4 | -18 | -15 | -15 | -15 | -15 | -18 |
| | P-5 | -18 | -18 | -15 | -18 | -21 | -18 |

Section C: Comparative Performance Evaluation of Homopolymer of Methyl Methacrylate and Copolymer of Methyl Methacrylate with Styrene and 1-Decene as Pour Point Depressant and Viscosity Index Improver in three different Base Oils.

2.3.1 Introduction

Lubricating oil additives are chemical compounds added to base oils to impart specific properties to the oils. Some additives impart new and useful properties to the lubricant, and others enhance properties already present. These materials are normally more chemically reactive than the base oil. The amounts of additives are being used at various concentrations, from a few parts per million to over 30% [38]. A great deal of research is being done at present into the synthesis, technology, and applications of different lube oil additives [39-40]. Although additives of many diverse types have been developed to meet special lubrication needs, their principal functions are relatively few in number.

A challenge for oil formulators is to find polymers that may both improve high temperature viscosity performance as well as improve low temperature performance such as cold engine starting performance. These attributes, among others, can cause performance tradeoffs with respect to given polymer additives wherein an improvement in one way can be offset by reduced performance in another. Additionally, there is always a commercial incentive to have the polymer be effective at the lowest reasonable concentrations in order to minimize the cost of a given engine oil product or additive. So the importance of multifunctional additives having both Viscosity index improver (VII) and Pour point depressant (PPD) properties is still increasing.

Viscosity index improvers are long chain, high molecular weight polymers that function by increasing the relative viscosity of oils 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 that 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 [41].

Pour point depressants are used to improve the low temperature characteristics of the base oils. Certain high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures. Pour point depressants act through surface adsorption on the wax crystals. The resulting surface layer of pour point depressant inhibits the growth of the wax crystals and their capacity to adsorb oil and form gels. In the absence of long interlocking crystals or swollen particles, oil can move freely through any solid wax particles that are present [42].

Some viscosity index improver compositions are chosen so as to incorporate pour point depressancy in addition to the basic viscosity control properties.

In the present work we prepared multifunctional additives via the preparation of methyl methacrylate copolymers with styrene and 1-decene in different percentage. Then we comparatively studied the efficiency of the prepared compounds as viscosity index improvers and pour point depressants for lube oil.

The current work provides the comparative study of the efficiency of copolymer of methyl methacrylate with styrene and copolymer of methyl methacrylate with 1-decene (both in two different percentages) along with its homopolymer as VII and PPD properties. The preparation, characterisation and viscometric analysis of these polymers were discussed earlier in **chapter II** in this part.

2.3.2 Results and Discussions

Comparative evaluation of PPD properties of homopolymer and copolymers in different base oils

The effectiveness of a pour point depressant depends on the chemical composition and structural characteristics of the polymer and the length of the alkyl side chains [43] and molecular weight of the polymer [30].

Pour points of the different levels of additive-doped lube oils (B1 and B2 and B3) were tested and tabulated in **Table 2**, **Table 3** and **Table 4**. The values indicate that all the copolymer performed better as PPD than the MMA homopolymer. In case of copolymers with 1-decene, it is easily explainable by their greater hydrodynamic

volume and lower molecular weight. In case of copolymers with styrene although they have higher molecular weight, copolymers showed better performance than the homopolymer. This is probably due to the incorporation of styrene ring structure which increases the adsorption of wax crystals to the additive. The prepared MMA copolymers with 1-decene samples showed more efficiency as PPD than the MMA copolymers with styrene. The efficiency increases with the decrease in concentration of the additive in base oil. This may be explained on the basis that, when the molecular weight of the additive and its concentration increases, solvation power decreases and so does PPD [30].

Comparative evaluation of VII properties of homopolymer and copolymers in different base oils

It is clear from the VI data, as evaluated in the present investigation (Table 5, Table 6 and Table 7), that irrespective of the polymer (homo and copolymer) and nature of the base oil VI values increase with the increase in additive concentration in the base oils studied. A critical observation of the VI values indicated that slight better performance is obtained for the copolymers of MMA with styrene than copolymers with 1-decene. 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 the temperature of the mixture. The increase in concentration of the polymer leads to an increase in the total volume of polymer micelles in the oil solution, thus exerting greater thickening effect and so as to VI [10, 30]. It is also noticed that all copolymers show better VII properties than the homopolymer. Although copolymers with 1-decene has lower molecular weight, they performed better than the homopolymer as VII due to much greater thickening effect of 1-decene compared to MMA which counterbalances the lower molecular weight of copolymers.

2.3.3 Conclusion

All the copolymer performed better as PPD than the MMA homopolymer. The prepared copolymers with 1-decene samples showed better efficiency as PPD than the

copolymers with styrene. The PPD values decreases with the increase in additive concentration in the base oils studied.

All the copolymers showed better performance than the homopolymer as VII. Copolymers of styrene performed better than copolymers of 1-decene as VII. The VI values of all polymers decreases with the increase in additive concentration in the base oils studied. All the polymers showed best efficiency in base oil B1 and efficiency in base oil B3 were very poor.

Table 1. Base oil properties

| Base oil properties | Base oils | | |
|--|-----------|--------|---------|
| | B1 | B2 | B3 |
| Density (g.cm ⁻³) at 40 ⁰ C | .848 | .885 | .931 |
| Viscosity at 40 ⁰ C in cSt | 16.979 | 31.062 | 102.104 |
| Viscosity at 100 ⁰ C in cSt | 3.227 | 4.927 | 10.97 |
| Cloud point, ⁰ C | -8 | -10 | -6 |
| Pour point, ⁰ C | -3 | -6 | -3 |
| Viscosity Index | 84 | 95 | 99 |

Table 2. Pour Point of additive doped base oils (B1)

| PPD Sample | Pour Point (⁰ C) of base oils containing different %(w/w) of PPD | | | | | |
|------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| Poly-1 | -12 | -9 | -9 | -9 | -9 | -9 |
| Poly-2 | -21 | -18 | -18 | -18 | -15 | -15 |
| Poly-3 | -18 | -15 | -15 | -15 | -15 | -12 |
| Poly-4 | -21 | -21 | -15 | -15 | -15 | -15 |
| Poly-5 | -24 | -24 | -24 | -21 | -21 | -18 |

Where, Poly-1 is homopolymer of methacrylate (MMA); Poly-2 and Poly-3 are the copolymer of MMA with different mass fractions of styrene and Poly 4 and Poly-5 are the copolymer of MMA with different mass fractions of 1-decene.

Table 3. Pour point of additive doped base oils (B2).

| PPD Sample | Pour Point ($^{\circ}\text{C}$) of base oils containing different %(w/w) of PPD | | | | | |
|------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| Poly-1 | -12 | -12 | -12 | -9 | -9 | -9 |
| Poly-2 | -21 | -18 | -18 | -15 | -18 | -15 |
| Poly-3 | -18 | -18 | -15 | -15 | -12 | -12 |
| Poly-4 | -21 | -21 | -18 | -18 | -15 | -15 |
| Poly-5 | -24 | -24 | -21 | -21 | -21 | -18 |

Table 4. Pour point of additive doped base oils (B3).

| PPD Sample | Pour Point ($^{\circ}\text{C}$) of base oils containing different %(w/w) of PPD | | | | | |
|------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| Poly-1 | -9 | -9 | -9 | -6 | -6 | -6 |
| Poly-2 | -15 | -12 | -12 | -12 | -9 | -9 |
| Poly-3 | -12 | -12 | -9 | -9 | -9 | -6 |
| Poly-4 | -15 | -15 | -15 | -12 | -12 | -12 |
| Poly-5 | -18 | -15 | -15 | -15 | -12 | -12 |

Table 5. Viscosity index of additive doped base oils (B1)

| VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | | |
|---------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| Poly-1 | 87 | 91 | 97 | 106 | 113 | 121 |
| Poly-2 | 92 | 101 | 109 | 117 | 127 | 137 |
| Poly-3 | 89 | 100 | 110 | 119 | 130 | 141 |
| Poly-4 | 91 | 97 | 107 | 116 | 126 | 137 |
| Poly-5 | 90 | 95 | 104 | 113 | 123 | 132 |

Table 6. Viscosity index of additive doped base oils (B2)

| VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | | |
|---------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| Poly-1 | 98 | 102 | 107 | 112 | 118 | 126 |
| Poly-2 | 99 | 105 | 109 | 116 | 126 | 137 |
| Poly-3 | 100 | 106 | 112 | 119 | 129 | 140 |
| Poly-4 | 99 | 105 | 110 | 117 | 125 | 135 |
| Poly-5 | 98 | 103 | 109 | 116 | 124 | 133 |

Table 7. Viscosity index of additive doped base oils (B3)

| VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | | |
|---------------|---|------|-----|-----|-----|-----|
| | 0.25 | 0.50 | 1 | 2 | 3 | 5 |
| Poly-1 | 99 | 103 | 106 | 110 | 114 | 118 |
| Poly-2 | 99 | 104 | 108 | 114 | 121 | 129 |
| Poly-3 | 100 | 104 | 110 | 117 | 125 | 133 |
| Poly-4 | 99 | 103 | 108 | 113 | 121 | 128 |
| Poly-5 | 99 | 104 | 109 | 113 | 117 | 125 |

CHAPTER III

3.1 Experimental

3.1.1 Materials used

Methyl methacrylate was purchased from Merck India Ltd. Styrene and 1-decene was purchased from SIGMA-ALDRICH, Co. Toluene was procured from S.D. Fine Chem., India Ltd. and benzoyl peroxide (BZP) from LOBA Chemicals. Base oils were collected from different sources Indian Oil Corporation Ltd., Dhakuria, Kolkata and BPCL India, 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 used as initiator after recrystallization from CHCl_3 -MeOH mixture. Toluene was purified by distillation after being refluxed for 2 h in presence of sodium.

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 353K 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 MMA and copolymer with 1-decene 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 and on Perkin Elmer FT-IR 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 spectrophotometer and Varian 200MHz spectrophotometer using 5mm 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 [15].

3.1.5 Viscometric measurements

Viscometric properties were determined at 313 K 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. 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 0.2 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl/g}$ (deciliter/g) and $a = 0.725$ [44, 45] were employed.

3.1.6 Thermo gravimetric analysis (TGA)

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

3.1.7 Shear Stability

Tests were conducted as per ASTM D- 3945 method and kinematic viscosity of fresh toluene and sheared polymer solution in toluene was determined by ASTM D- 445 and D-4741 procedure respectively.

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

The prepared additives were evaluated as pour point depressant using base oils (B1 and B2) 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 were 0.25%, 0.50%, 1%, 2%, 3%, and 5% (w/w) The experimental data were noted by taking an average of three experimental results under identical conditions.

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

The various blends were prepared by using two different types of base stocks (B1 and B2) Viscosity index of these oils were calculated by ASTM D2270-87 method using viscosity index calculator. The kinematic viscosity of the polymer doped base oils was determined at 313K and 373K. Range of concentration of the additives (in lube oils) used to study the effect of concentration on VI of the lube oil, were 0.25%, 0.50%, 1%, 2%, 3%, and 5% (w/w).

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Part III

**Preparation, Characterization, Viscometric Analysis, Compatibility
Studies and Evaluation of Homopolymer of Decyl Acrylate and its
Copolymer with Styrene along with their Blends as Lubricating Oil
Additives**

CHAPTER I

1.2 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

In recent years, in view of the reduction of petroleum resources and environmental problems such as global warming, an improvement of fuel efficiency of automobiles which is aimed at reducing CO₂ emissions is required. A significant effect with low cost can be expected from lowering fuel consumption by lubricating oils, as compared to physical modification of the lubricated machinery. Therefore, the requirement for improving fuel efficiency by lubricating oils is growing.

Lubricating oils contain additives that help the lubricating oil to have a certain viscosity at a given temperature. In general, the viscosity of lubrication oils and fluids is inversely dependent upon temperature. When the temperature of a lubrication fluid is increased, the viscosity generally decreases, and when the temperature is decreased, the viscosity generally increases. For internal combustion engines, for example, it is desirable to have a lower viscosity at low temperatures to facilitate engine starting during cold weather, and a higher viscosity at higher ambient temperatures when lubrication properties typically decline.

Lubricating oil compositions for internal combustion engines typically include polymeric additives for improving the viscosity index of the lubricating composition, that is, modifying the relationship between temperature and the viscosity of the oil composition to reduce the temperature dependence of the viscosity, to lower the "pour point" of the composition, that is, to allow the composition to remain fluid at reduced temperature, and to provide "dispersant" properties, that is, to allow sludge particles to remain suspended in the oil composition.

Accordingly, the viscosity modifier to be blended with lubricating oil which is required to have particularly excellent low-temperature properties is desired to exhibit an excellent effect of improving viscosity index and not to inhibit the function of the pour point depressant.

Polymethacrylates (PMAs) and polyacrylates (PAs) having monomeric chain length C₈ to C₂₀ are characterized by a good effect with respect to the viscosity-temperature behaviour of the oils to which they are added as improvers, and when

used in sufficiently high concentration they also show an outstanding protective effect against wear. Their pour-point lowering effect should also be stressed.

For a given class of polymers, with higher molecular weight and concentration, the viscosity of lubricating oil containing the PAs or PMAs is higher. However, higher molecular weight polymers exhibit a greater tendency to break down under the shear and high temperature conditions normally found in engine operation, frequently resulting in the loss of viscosity.

Another important characteristic required for a viscosity index improver is viscosity at low temperatures, which relates to the ease of engine cranking during start-up in cold climates. Homopolymer of PAs cannot exhibit a negligible viscosity contribution at low temperatures while providing a large viscosity contribution at engine operating temperatures. The high molecular weight and high concentration of PAs facilitate their power as VII but at the same time inhibit their power as PPD. Another disadvantage for PAs and PMAs is the treating costs for these products are comparatively high. This concept is to be understood as meaning the costs required for achieving a desired effect.

To overcome these problems copolymer of PAs with different olifinic and vinylic monomers (styrene, maleic anhydride, 1-decene etc.) has been introduced by many groups of inventors [1-3]. The treating costs for the copolymers are comparatively low due to incorporation of low cost olifinic and vinylic monomers. Although the copolymer performance as PPD quite satisfactorily, they performed poorly as VII. This is due to the lower molecular weight of the copolymers. To achieve the desired performance of the copolymers as VII, they must be added very high concentration in lube oil. However, the higher concentration of the copolymers adversely affects their performance as PPD. The need for higher concentration of the copolymers also makes their treating cost comparatively high.

Accordingly, in formulating lubricating oils to satisfy the varying conditions desired, it has generally been the practice to select those polymers which provide, at the lowest cost, the best overall balance of properties including viscosity index improvers (VIIs) and pour point depressants (PPDs).

The idea of combining the homopolymers and copolymers of the same class of PAs, in order thereby to produce lubricating oil additives with improved properties, was obvious. Industry awaits the preparation of lubricating oil additives in a liquid (oil-based) form and with the highest possible absolute polymer content.

It has now been found that lubricating oil additives having outstanding properties are obtained if two different polymers of different or same kind combined to form a polymer mixture or polymer blend [4-5].

Polymers to be combined in blends are generally selected to complement each other in one or more of the following properties: cost, processability, mechanical properties, chemical resistance, weatherability, flammability resistance, thermal performance and a variety of other properties. Blends are typically viewed as cost saving devices, whereby an expensive polymer may be combined with a less costly polymer to provide adequate performance at a significantly reduced price to the consumer. The blend can offer a set of properties that are not possible with either of the polymers comprising the blend.

Polymer blends may comprise miscible polymers, immiscible polymers, or a combination of miscible and immiscible polymers. Blends comprising immiscible polymers have two or more phases and such blends may be compatible or incompatible. Incompatible blends of immiscible polymers can suffer from phase separation as demonstrated by delamination or the formation of skin-core layered structures during polymer processing operations, especially injection molding. The term, "delamination," as used when referring to such materials, describes visually observed separation of a surface layer giving a flaking or onion skin effect. Incompatibility may also result in poor mechanical properties and marginal surface appearance (streaking, pearlescence, etc.). Compatible blends of immiscible polymers typically do not show any delamination and can result in acceptable end-use properties [6].

Miscible polymer blends, on the other hand, may offer desirable end-use properties and the advantage of tailoring product properties intermediate of the individual components across the miscible composition range. Miscible blends do not suffer from delamination and generally have consistent physical properties.

So while a miscible blend of two polymers is generally desirable it can be difficult to achieve. Blends of two polymers of a same or similar class might be expected to have a better chance of miscibility. However, polymers from the same class are frequently immiscible and form multiphasic compositions. Thus, polymer miscibility is difficult to predict, even within the same class of polymers.

For the foregoing reasons there remains an unmet need for non-delaminated polymer blends, i.e., blends free of delamination, which are either miscible blends or

immiscible, but nonetheless compatible, blends. More particularly, there remains an unmet need to develop blends having high heat resistance, and methods of forming such polymer blends.

To achieve good mechanical properties in polymer/polymer blends, some degree of compatibility between the respective components is desirable. This may occur, even in incompatible blends that develop two separate phases, by the presence of interactions between chain segments and some degree of intermolecular mixing. By simply varying the concentration of the constituents of an incompatible blend, a compatible blend with a unique set of properties can be obtained.

Some previous work involving polymer blend additives for lube oil are enlisted below:

U.S. Patent No. 4,622,031 discloses concentrated blends of a nitrogen-containing PMA, an OCP and a "compatibilizer" graft copolymer having PMA branches grafted onto an OCP backbone, each dissolved in a hydrocarbon fluid. The compatibilizer copolymer stabilizes the thermodynamically incompatible PMA and OCP additives to discourage separation of the blend into discrete phases.

U.S. Patent No. 5,188,770 discloses a concentrated emulsion including a poly(alkyl methacrylate) copolymer and an olefin copolymer wherein alkyl methacrylate monomers are polymerized in an oil compatible liquid vehicle in the presence of an olefin polymer, hydrogenated isoprene, a hydrogenated butadiene-styrene copolymer, hydrogenated polyisoprene or hydrogenated polybutadiene.

W.O. Patent No. 2002083825 A1 is directed to lubricating oil compositions comprising polyolefins and polyacrylates. These lubricating oil compositions display good low temperature and shear performance in driveline lubricants and provide improved efficiency without sacrificing durability under severe loading conditions. The invention is also directed to polymeric compositions comprising mixtures of the polyolefins and polyacrylates.

U.S. Patent No. 4,194,057, discloses viscosity index improving compositions containing a combination of a certain class of relatively low molecular weight vinyl aromatic/conjugated diene diblock copolymers and ethylene α -olefin copolymer. The patent describes the specified class of vinyl aromatic/conjugated diene diblock copolymer as being relatively insoluble in oil and that blending with ethylene α -olefin copolymer improves solubility and allows for the formation of polymer concentrates.

U.S. Patent No. 4,194,057, discloses viscosity index improving compositions

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W.O. Patent No. 96/17041, discloses certain blends of star-branched styrene-isoprene polymers and ethylene α -olefin copolymers. The publication describes the addition of an amount of the ethylene α -olefin copolymer to the star-branched styrene-isoprene polymer as being effective to improve the dimensional stability of the star branched polymer so that the star branched polymer can be formed as a stable, solid bale.

In U.S. Patent No. 5,747,433, Luciani et al., discloses a composition of about 2 to about 20 percent (of a hydrogenated diene/vinyl aromatic block copolymer and a selected non-ionic surface active agent, in a medium of oil of lubricating viscosity, which exhibits reduced viscosity compared with comparable compositions without the surface active agent.

E. Patent No. 1,178,102, discloses a lubricating oil composition of a lubricating base oil and a copolymer of ethylene and an α -olefin of 3 to 20 carbon atoms, having an ethylene content of 40-77% by weight and other characterizing parameters. Pour point depressants can also be present, such as copolymers of α olefins and styrene.

E. Patent No. 0,214,786 describes middle distillate additives comprising maleic anhydride and straight-chain 1-olefins, which are esterified with fatty alcohols by a polymer-analogous reaction, for improving the cold flow properties of middle distillates.

E. Patent No. 0,320,766 describes polymer blends comprising a copolymer (A1) of 10-60% by weight of vinyl acetate or a copolymer (A2) of 15-50% by weight of vinyl acetate, 0.5-20% by weight of C₆-C₂₄- α -olefin and 15.5-70% by weight of ethylene and a copolymer (B) of 10-90% by weight of C₆-C₂₄- α -olefin and 10-90% by weight of N-C₆-C₂₂-alkylmaleimide, the mixing ratio of the copolymers (A1) or (A2) to (B) being from 100:1 to 1:1. These polymer blends are used as flow improvers in middle distillates.

E. Patent No. 2154230 A1 discloses an additive composition comprising at least two viscosity index improvers containing copolymers of PMAs and PAs, and in

particular to lubricant additive compositions that provide improved viscosity index properties for meeting crankcase oil performance specifications when using relatively low levels of Group III and/or Group IV base oils.

U.S. Patent No. 20100120641 A1 discloses a pour point depressant for lubricants that has an effect of lowering pour points of both solvent refined base oils and high viscosity index base oils. A pour point depressant for lubricants comprising: a mixture of an alkyl(meth)acrylate polymer (A) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_A) of 12.5 to 13.8, and an alkyl(meth)acrylate polymer (B) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_B) of 13.9 to 15.5.

U.S. Patent No. 6,746,993 discloses a viscosity index improver defined as a polymer with a solubility parameter of 8.6-9.4, a crystallisation temperature of -15°C . or less and a steric hindrance factor of 0 to 13. The polymer comprises alkyl alkenyl ethers and C_{7-16} alkyl methacrylates, of which some may be β -branched. The viscosity index improver is suitable for gear oils, hydraulic fluids, automatic transmissions and engine oils.

U.S. Patent No. 5,763,374 discloses lubricating oil compositions containing a copolymer composed of 20-70% of alkyl acrylates and 30-80% alkyl methacrylates. The lubricating oil may be used as a gear oil or an engine lubricant.

U.S. Patent Application 2004/0077509 discloses a viscosity index improver polymer suitable for gear oils, transmissions, traction oils, hydraulic oil and engine oils. Further the polymer provides an improved shear stability and low temperature viscosity. The polymer is composed of (meth)acrylates derived from branched alcohols. The branched ester groups contain C_{18-36} alkyl groups, with the proviso that the group does not contain a methylene group containing more than 16 carbon atoms. The polymer further contains 5-90% of either a C_{8-17} alkyl (meth)acrylate or C_{18-24} alkyl (meth)acrylate; and 5-50% of a hydroxy, or amide or carboxyl containing monomer. The monomer with branched ester groups may be present at 5 to 90%, or to 70% or 20 to 60%.

U.S. Patent No. 7189682 B2 discloses a composition of the following components: an oil of lubricating viscosity; a polymethacrylate viscosity modifier; an ester of a maleic acid/styrene copolymer; and optionally, an additive package that imparts to the fluid the capacity to meet bench and dynamometer tests specified by an

equipment manufacturer, is suitable for use as a functional fluid such as a tractor hydraulic fluid, under a wide variety of climatic conditions.

Thus from the above literature survey it has been observed that reports regarding the development of a multifunctional polymer blend additives comprising both VII and PPD properties are still limited. Again works involving polymer blends of the same class, particularly homopolymer of PA with its copolymer of styrene as VII and PPD for lube oil are limited and has not been thoroughly investigated before.

It is the object of the present invention to provide a lubricant oil additive which improves the viscosity index of lubricating oil compositions and also is cost effective. Another object of the present invention is to provide a lubricating oil composition which has good low temperature properties.

This work is directed to the processes for preparing the mixture, to additive concentrates and to lubricating oil compositions. The overall effect of blending a low molecular weight, low vinyl content, crystalline acrylate copolymer with a higher molecular weight, acrylate homopolymer is to produce a polymeric viscosity improver composition for lubricating oils which has good thickening efficiency at high temperatures, and good low temperature properties without the problems of gelation. The result is a viscosity improver composition of decyl acrylate homopolymer with the outstanding low temperature properties of the decyl acrylate - styrene copolymers without the problems associated with them.

CHAPTER II

This chapter divided into two sections: **Section A** and **Section B**

Section A comprises the **Preparation, Characterization, Compatibility Studies and Evaluation of Homopolymer of Decyl Acrylate and its Copolymer with Styrene along with their Blends as Lubricating Oil Additives**

Section B comprises the **Viscometric Analysis of Homopolymer of Decyl Acrylate, its Copolymer with Styrene and their Polymer Mixture (Blends).**

2.1 Section A: Preparation, Characterization, Compatibility Studies and Evaluation of Homopolymer of Decyl Acrylate and its Copolymer with Styrene along with their Blends as Lubricating Oil Additives

2.1.1 Introduction

Rheological properties of mineral lubricating oils, particularly their viscosity index and pour point, are being considerably improved by the addition of certain polymers in low concentrations having controlled and defined structural characteristics [5, 7]. The most efficient and most commonly used polymers as viscosity index improvers and pour point depressants for lubricating oils are polymer of statistical olefins, long chain acrylates and methacrylates and their copolymers with different olefins (usually styrene, maleic acid anhydride, 1-decene etc.) [4,5]. Recently because of their field application, exploration of polymeric additive mixtures as viscosity modifiers and pour point depressant for lubricating oils has intensified since they have shown some complimentary and even synergistic effects in solvents [4, 5]. However, due to the physico-chemical differences many of the polymers are incompatible, they generate separate phases readily, particularly in solutions. Polymer-polymer compatibility has been extensively studied by several techniques, such as differential scanning calorimetry, dynamic mechanical measurements, neutron scattering, inverse gas chromatography, electron microscopy, light scattering and others, most of them are experimentally demanding and time-consuming techniques. For these reasons, an alternative, simple and reliable method to analyze polymer-polymer miscibility in solution is the viscometric technique.

When two different polymers are dissolved in a solvent, they interact (polymer–polymer interaction) with each other. These interactions are mainly of two types, hydrodynamic and thermodynamic. These two interactions, together, influence the compatibility (attraction or repulsion) of the polymer mixture. If the polymers attract each other, called as compatible, the effective hydrodynamic volume of the compatible polymer blend is higher than the sum of the two individual polymers in solution.

On the contrary, when there is repulsion between the polymers, called as incompatible, the effective hydrodynamic volume of the polymer blend is lower than the sum of the two individual polymers in solution. Again with variation of

percentage of each polymer, the compatibility of the polymer mixtures varies, for the interaction between them depends on the individual hydrodynamic volume of the polymers and on the polymer–solvent interaction [8-10]. Together with polymer–polymer interaction, polymer-solvent interaction also plays an important role on the compatibility of polymer mixture in ternary system [8-10]. When two different polymers are dissolved in a common solvent, the hydrodynamic volume and configuration of the polymers get affected greatly. Hence, the compatibility parameter values of the polymer mixtures will be different in different solvents.

According to literature, the compatible or miscible polymer mixtures show better performance as VII and PPD than the individual homo polymers and even copolymers [11-13].

Most base oil contains some paraffinic wax. In cold temperature the wax crystallizes to form a rigid structure that traps the oil in small pockets in the structure [14]. With sufficient formation of these crystal structures the oil will no longer be capable to flow. To overcome this problem certain high molecular weight polymers are used in base oil as PPD. With their presence in small amount, the polymer inhibits the formation of wax crystals by adsorption followed by cocrystallization to redirect the wax crystal structures in small sizes and thus increases the solubility of crystals in base oil [3]. The effectiveness of polymers as PPD depends on the chemical composition and structural characteristics of the polymers [15-17]. The higher the hydrodynamic volume of a polymer in base oils better is the performance as PPD.

Viscosity index improvers (VII) are those which modify the rate of change of viscosity of base oil with temperature. Certain high molecular weight polymers used as VII increase the base oil viscosity considerably amount at high temperature but at low temperature they increase the base oil viscosity a little. With rising temperature the viscosity of base oil decreases but its solubility power increases. At low temperature the polymer molecules remain as tight coil in base oil but with increasing temperature the hydrodynamic volume of polymer molecules increases which counterbalances the normal reduction of viscosity of base oil with temperature [18]. When the concentration of a polymer increases in base oil, total volume of polymer micelles also increases which will impart a higher viscosity index than a low concentration of the same polymer [19]. In the same manner a high concentration of a compatible polymer blend will contribute a higher viscosity index to the base oil than a low concentration of the same polymer blend.

The compatibility and evaluation of PDA with its copolymer with styrene has not been thoroughly investigated before. The present investigation comprises the preparation of PDA and copolymer of PDA with styrene followed by a comparative study on the viscosity behavior of PDA, its copolymer with styrene and mixtures of PDA with its copolymer in two different solvents, toluene and chloroform by following five criteria: (1) Viscosity interaction parameter Δb_m , which is used from the equations developed by both Krigbaum and Wall, and their modified forms by Williamson and Wright [20-22]; (2) Viscosity interaction parameter $\Delta b_m'$, as was first introduced by Campos et al [23]; (3) Viscosity interaction parameter α , as was developed by Sun et al. [24]; (4) Viscosity difference parameter $\Delta[\eta]_m$, treated as an excess property for compatibility of polymer mixtures and (5) Change of slope of the curve in the plot of reduced viscosity against concentration in ternary system. The fifth compatibility criterion, change of slope of the curve in the plot of reduced viscosity against concentration in ternary system as was proposed by Yang Haiyang *et al.* [8, 25]. Homopolymer and copolymers of PDA has been characterized by Thermo gravimetric analysis, IR and NMR spectra. At the end we have evaluated these polymers and their polymer blends as PPD and VII in two different base stocks from same source [26].

Theory

Many groups of workers [21-25, 27] have investigated the miscibility of polymer blends by carrying out viscosity measurements of the corresponding ternary (polymer-polymer-solvent) systems. These methods rely on different assumptions. We choose some of these methods to characterize our polymers and polymer blends.

2.1 According to the Huggins' equation [20], the value of intrinsic viscosity changes with the the concentration C of a single solute solution (binary system) as:

$$\eta_{sp} = [\eta]C + bC^2 \quad (1)$$

Equation (1) can be rewritten as:

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

Where $[\eta]$ is the intrinsic viscosity and b is the polymer–polymer interactions term at finite concentrations related to the Huggins coefficient k_{H1} , by the equation:

$$b = k_{H1}[\eta]^2 \quad (3)$$

Consequently in ternary systems (polymer 2-polymer 3-solvent) an analogue

of equation (2) as proposed by Krigbaum [21] can be obtained in the form

$$\eta_{\text{spm}}/C = [\eta]_m + b_m C \quad (4)$$

where the subscript 'm' denotes "mixture". For a ternary system containing a solvent (component 1) and two polymers (components 2 and 3), we have:

$$C = C_2 + C_3$$

And $w_2 = C_2/C$ and $w_3 = C_3/C$, Where w_2 and w_3 are the weight fractions of polymer 2 and polymer 3 respectively. Theoretically intrinsic viscosity of a ternary solution, η_m could be deduced as:

$$[\eta]_m^{\text{theo}} = [\eta]_2 w_2 + [\eta]_3 w_3 \quad (5)$$

Now, interaction parameter b_m for ternary solutions can be deduced as:

$$b_m = b_{22} w_2^2 + 2b_{23} w_2 w_3 + b_{33} w_3^2 \quad (6)$$

Or,

$$b_m^{\text{theo}} = b_{22} w_2^2 + b_{33} w_3^2 + 2b_{23}^{\text{theo}} w_2 w_3 \quad (7)$$

And,

$$b_m^{\text{exp}} = b_{22} w_2^2 + b_{33} w_3^2 + 2b_{23}^{\text{exp}} w_2 w_3 \quad (8)$$

Krigbaum and Wall [21] had defined b_{23}^{theo} for ideal mixture as:

$$b_{23}^{\text{theo}} = (b_{22} b_{33})^{1/2} \quad (9)$$

So, equation (10) can be rewritten as:

$$b_m^{\text{theo}} = b_{22} w_2^2 + b_{33} w_3^2 + 2(b_{22} b_{33})^{1/2} w_2 w_3 \quad (10)$$

The first criteria interaction parameter Δb_m , determines the intermolecular interaction between polymer 2 and polymer 3 in ternary solutions could be determined as:

$$\Delta b_m = b_{23}^{\text{exp}} - b_{23}^{\text{theo}} \quad (11)$$

Where b_{23}^{exp} is obtained from the slope of equation (4) and b_{23}^{theo} is obtained by equation (10).

That is why we have evaluated the Δb_m as:

$$\Delta b_m = b_{23}^{\text{exp}} - (b_{22} b_{33})^{1/2} \quad (12)$$

Both b_{22} and b_{33} are easily determined from the binary systems formed by polymers 2 or 3 in the solvents, respectively, through Eq. (2).

The criterion, Δb_m for compatibility in polymer mixtures in ternary solutions is based on the comparison between experimental (b_{23}^{exp}) and theoretical or ideal (b_{23}^{theo}) values of b_{23} [21, 22]. The values of $b_{23}^{\text{exp}} > b_{23}^{\text{theo}}$ or $\Delta b_m > 0$ indicates that

polymers are compatible in polymer mixtures or attractive molecular interaction exist between polymers and values of $b_{23}^{\text{exp}} < b_{23}^{\text{theo}}$ or $\Delta b_m < 0$ indicates incompatibility between polymers or repulsive molecular interaction.

2.2 The second compatibility criterion, Δb_m^f is the difference between b_m^{exp} and a new viscometric interaction parameter, b_m^{theo} such as:

$$\Delta b_m^f = b_m^{\text{exp}} - b_m^{\text{theo}} \quad (13)$$

Where b_m^{exp} data obtained experimentally but according to Campos et al [23], b_m^{theo} is determined as:

$$b_m^{\text{theo}} = b_{22}w_2^2 + b_{33}w_3^2 \quad (14)$$

When $b_m^{\text{exp}} < b_m^{\text{theo}}$ or $\Delta b_m^f > 0$, the polymers are compatible. When $b_m^{\text{exp}} > b_m^{\text{theo}}$ or $\Delta b_m^f < 0$, the polymers are incompatible.

2.3 The third compatibility parameter, α , proposed by Sun et al. [24] for the determination of polymer miscibility as follows:

$$\alpha = K_m - K_{22}[\eta]^2w_2^2 + 2(K_{22}K_{33})^{1/2}[\eta]_2[\eta]_3w_2w_3 + K_{33}[\eta]^2w_3^2 / ([\eta]_2w_2 + [\eta]_3w_3)^2 \quad (15)$$

Where, K_{22} , K_{33} , and K_m are the Huggins's constants for the individual polymers PDA, copolymer of PDA and their blend, respectively. They have also suggested that the polymers will be compatible when $\alpha \geq 0$ and incompatible when $\alpha < 0$.

2.4 The fourth compatibility parameter, $\Delta[\eta]_m$ is based on the difference between the experimental and theoretical or ideal values of $[\eta]_m$ as:

$$\Delta[\eta]_m = [\eta]_m^{\text{exp}} - [\eta]_m^{\text{theo}} \quad (16)$$

Where $[\eta]_m^{\text{exp}}$ determined from the intercept of plots of Eq. (4) and $[\eta]_m^{\text{theo}}$ calculated with Eq. (5) using the data from the binary systems.

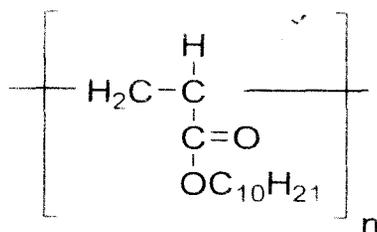
The values of $[\eta]_m^{\text{exp}} < [\eta]_m^{\text{theo}}$ or $\Delta[\eta]_m < 0$ indicates compatibility between polymers whereas $[\eta]_m^{\text{exp}} > [\eta]_m^{\text{theo}}$ or $\Delta[\eta]_m > 0$ indicates incompatibility between polymers

2.5 The fifth compatibility criterion, change of slope of the curve in the plot of reduced viscosity against concentration in ternary system was proposed by Yang Haiyang *et al.* [8, 25]. They proposed as in ternary system there exist either attraction or repulsion between polymers which changes effective hydrodynamic volume of the molecules and thus influences on the viscosity of ternary solutions. If attraction

existing between polymers (compatible), then mutual hydrodynamic volume of polymers increases which will lead to the positive deviation of curve. On the other hand, repulsion between the polymers (incompatible) leads to the decrease of their mutual hydrodynamic volume which is indicated by decrease in slope of the curve. So the change of slope in the plot of η_{sp} / C vs C in a ternary system can be used as a criterion to determine polymer-polymer compatibility.

2.1.2 Results and Discussions

IR spectra of the homopolymer (**Figure 1**) showed a peak at 1732 cm^{-1} due to the stretching vibration of ester carbonyl group. The broad peak ranging from (1261 to 1069) cm^{-1} appeared owing to the ester C-O stretching vibration; the absorption bands at 977 and 711 cm^{-1} were due to the bending vibration of C-H bonds and from 3100 to 2900 cm^{-1} were due to the stretching vibrations. Thus from the FT-IR and ^1H NMR spectral data (**Figure 2**) structure of this polymer may be represented by **Structure 1**



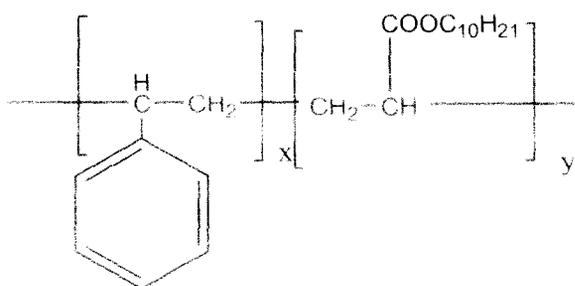
Structure 1: Homopolymer of Decyl acrylate

The existence of the copolymer was confirmed by FT-IR (**Figure 3**) and NMR analysis. The peak at 1732 cm^{-1} appeared due to the stretching vibration of ester carbonyl group and the absorption bands at 758 and 702 cm^{-1} were due to C-H bonds of the phenyl group of styrene.

In the ^1H NMR spectra (**Figure 4**) of the copolymer, a broad multiplet centered at 8.07 ppm indicated the presence of aromatic protons of 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 extent of incorporation of styrene in the polymer chain (**Table 1**) 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 [26].

The proton decoupled ^{13}C NMR spectrum (**Figure 5**) of the above sample of copolymer was in complete agreement with the original **structure 2**.



Structure 2: copolymer of Decyl acrylate with styrene

Table 2 present the interaction parameter values and viscosity values of binary systems in toluene and chloroform. Intrinsic viscosity value of the homopolymer is higher than copolymer irrespective of the nature of the solvent. 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. Higher values of interaction parameter (b_{ij}) indicate poorer solubility of the polymer. Hence, b_{ij} values from **Table 2** clearly indicate chloroform to be better solvent compared to toluene.

Table 3 and **Table 4** present the first four compatibility parameter values of ternary solutions with different percentage of polymer blends in toluene and chloroform respectively. In both solvents the theoretical interaction constant b_{23}^{theo} values for polymer blends are higher than experimental values (resulting negative Δb_m values) except for P_3 in toluene. According to this criterion there are repulsive intermolecular interaction existing between the polymers in ternary solutions. Here b_{23}^{theo} values determined from b_{22} and b_{33} values for binary mixtures. But the

hydrodynamic volume of polymers in ternary solution must be different from their binary solution because in ternary solution polymer-polymer interaction changes the effective hydrodynamic volume of the polymers. Again, in a ternary solution, interaction involves are both polymer-polymer interaction and polymer solvent interaction. Thus solvent has an influence on b_m^{exp} values of polymer blends.

According to our second compatibility criterion ($\Delta b_m'$), the polymer blends are compatible showing positive $\Delta b_m'$ values in both toluene and chloroform solutions except P_3 in toluene. This is due to higher solubility of PDA in chloroform.

In solutions of toluene, the theoretical $[\eta]_m$ values are lower than experimental values resulting negative $\Delta[\eta]_m$ values for all blends. In solutions of chloroform, at low (3:1) and equal (1:1) percentage of copolymer, theoretical $[\eta]_m$ values are lower than experimental values resulting negative $\Delta[\eta]_m$ values indicating incompatibility of polymers in ternary solutions, but at higher (1:3) percentage of copolymer theoretical $[\eta]_m$ values are lower than experimental values resulting negative $\Delta[\eta]_m$ values which indicates compatibility of polymers in polymer blends. This is due to the fact that, here chloroform is act as better solvent than toluene and for this reason the polymer-solvent interaction is more effective than polymer-polymer interaction. In other words, due to prominent solvent effect (i. e., good solvation) the experimental $[\eta]_m$ value increases with increasing hydrodynamic volume of polymer mixture and shows negative $\Delta[\eta]_m$ value. Again, literature survey indicates that solubility parameters of PDA and copolymer of DA with styrene are closer to chloroform than with toluene [27-31] but the polymers are in the solubility range of both solvents. Certain drop in $[\eta]_m$ value for P_5 in chloroform is due to the dissimilar structure of chloroform and the copolymer with styrene.

The fourth compatibility parameter, α , gives, positive value for all three polymer blends in toluene. So polymer mixtures are compatible in toluene solutions. In chloroform, $\alpha > 0$ for P_5 polymer blends indicating compatibility. But in case of polymer blends P_3 and P_4 , $\alpha < 0$ which indicating incompatibility.

This can also be shown in the graphical presentation (**Figure 5** and **Figure 6**) that the fifth parameter, change of slope of the curve in the plot of reduced viscosity against concentration in ternary system gives linear graph for binary systems. But in cases of ternary systems certain positive deviation in slope of the curve has been observed. So according to the fifth parameter all polymer blends in both solvents are

compatible.

Table 5 demonstrates the base oils properties.

Evaluation of polymers and polymer blends as PPD in different base oils

Performance of homopolymer, copolymer and polymer blends as PPD has been tested and tabularized in **Table 6**. Data indicates that in case of individual polymers, copolymer shows better efficiency than homopolymer. 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 [32]. The polymer blends give better performance against individual polymers and with increasing copolymer percentage, the performance of polymer blends increasing. This is because in compatible polymer blends the effective hydrodynamic volume of the polymers further increases from individual presence of polymers in solution due to mutual attraction of the polymers. The enhanced effective hydrodynamic volume of polymer blends more efficiently adsorbed wax crystals and cocrystallize with them in base oil to slow up the growth of the wax crystals and their capacity to adsorb oil and form gels. Thus compatible polymer blends of PDA and its copolymer contributes additional decrease in pour point of base oil. Again, with decreasing concentration of additives their performance increases. This may be explained on the basis that, with decreasing temperature the solvation power of a solvent decreases and *vice versa*. When the molecular weight of the additive and its concentration increases, solvation power of the solvent more obviously decreases and so does PPD [33].

Evaluation of polymers and polymer blends as VII in different base oils

The data in **Table 7** indicates that with increasing concentration of additives, the VI of the base oils increases. With rising temperature the solvation power of base oil increases but its viscosity decreases. Due to increasing solvation power the polymer molecules swell or in other words, its hydrodynamic volume increases. The enlarged hydrodynamic volume counterbalances the reduction in viscosity of lube oil and thus diminishes the changes of viscosity of additive doped base oil [3]. The polymer blends give better performance as VII than individual presence in lube oil

and their performance increases with increasing copolymer percentage. Further enlargement of effective hydrodynamic volume of polymer blends due to compatibility, the polymer blends additionally counterbalance the reduction in viscosity of the lube oil with increasing temperature and thus diminishes the change of viscosity of additive doped base oil more effectively. The copolymer gives poor results as VII than the homopolymer. The incorporation of styrene with decyl acrylate in copolymer decreases the molecular weight of copolymer and thus reduces its performance as VII. All the polymers and polymer blends give better performance as VII in base oil B1 than B2.

2.1.3 Conclusion

Though with the homopolymer of decyl acrylate (DA) and the copolymer of DA with styrene are efficient as VII and PPD, the homopolymer performed better as VII than the copolymer. On the contrary, the copolymer performed better as PPD than the homopolymer.

The polymer blends are compatible in chloroform and toluene and also in two different base oils. The compatibility of polymer mixtures was better in toluene than that in chloroform. The compatibility of polymer mixtures increases with increasing copolymer percentage.

The efficiency of all polymer blends as PPD and VII were much better than individual homo and copolymers due to compatibility. The polymer blends with higher copolymer percentage performed better as PPD and VII.

With increasing concentration, the efficiency of the polymer blends as VII increases but their effectiveness as PPD decreases.

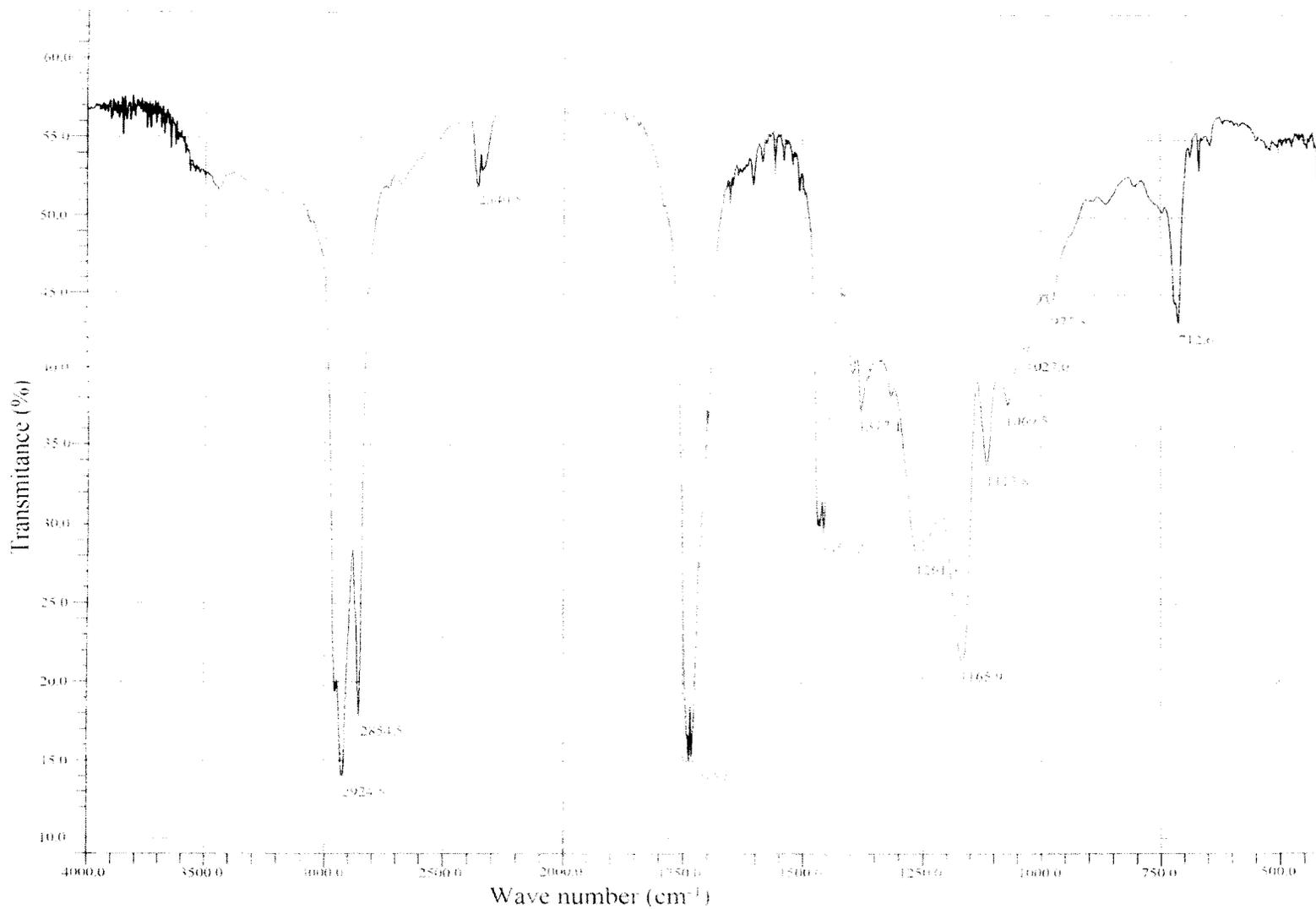


Figure 1: FT-IR spectrum of homopolymer of decyl acrylate

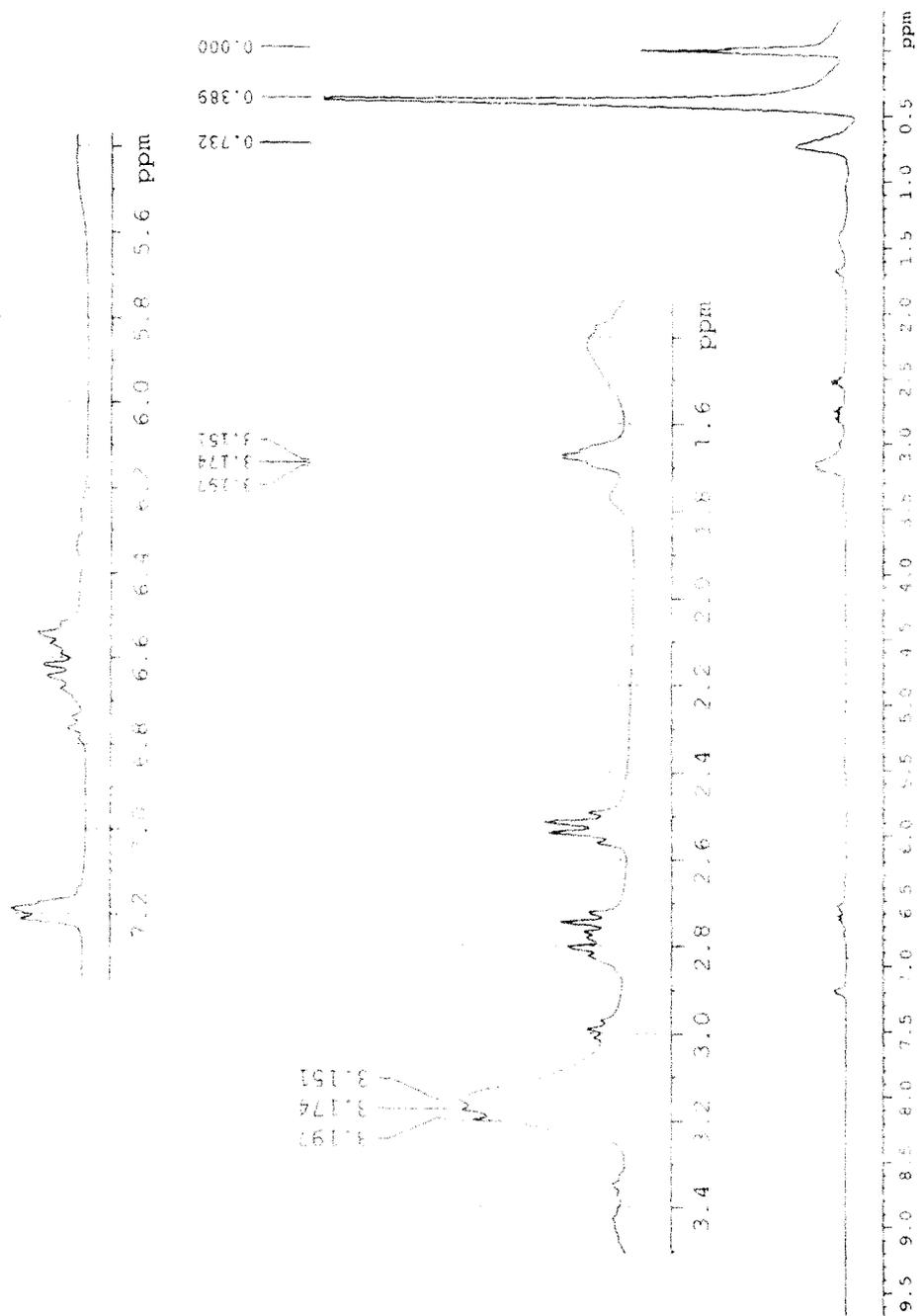


Figure 2: ¹H NMR spectrum of homopolymer of decyl acrylate

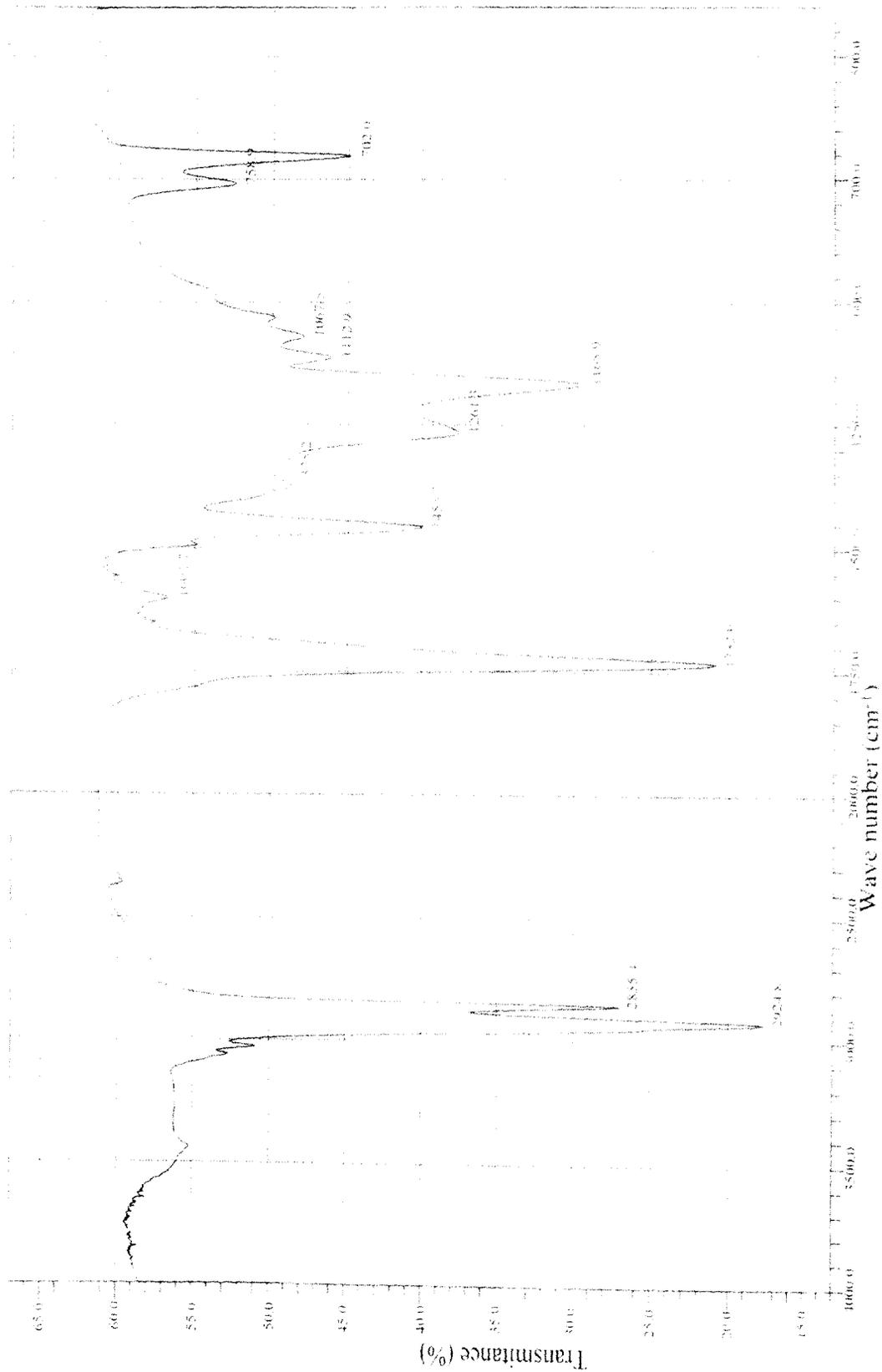


Figure 3: FT-IR spectrum of copolymer of decyl acrylate with styrene

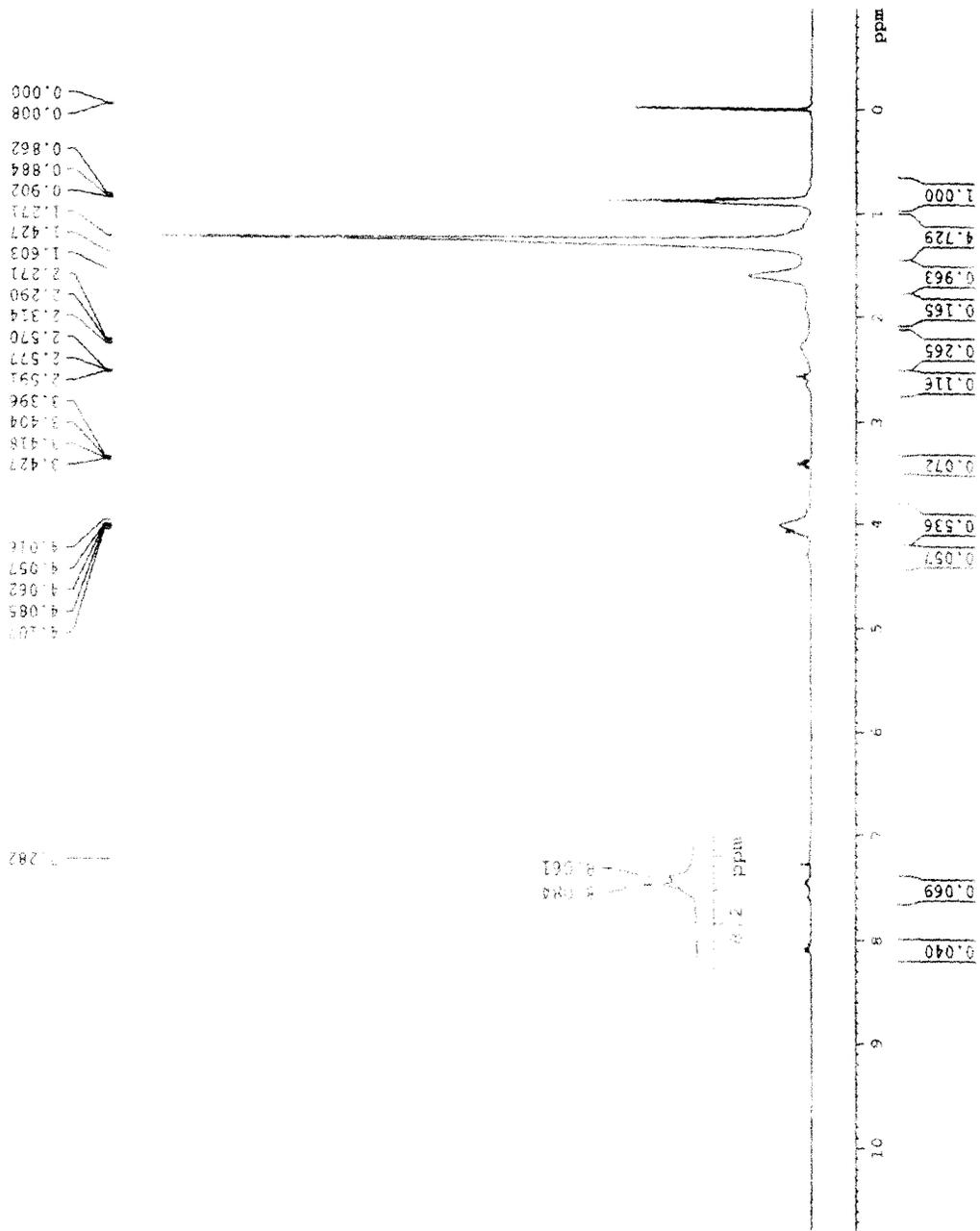
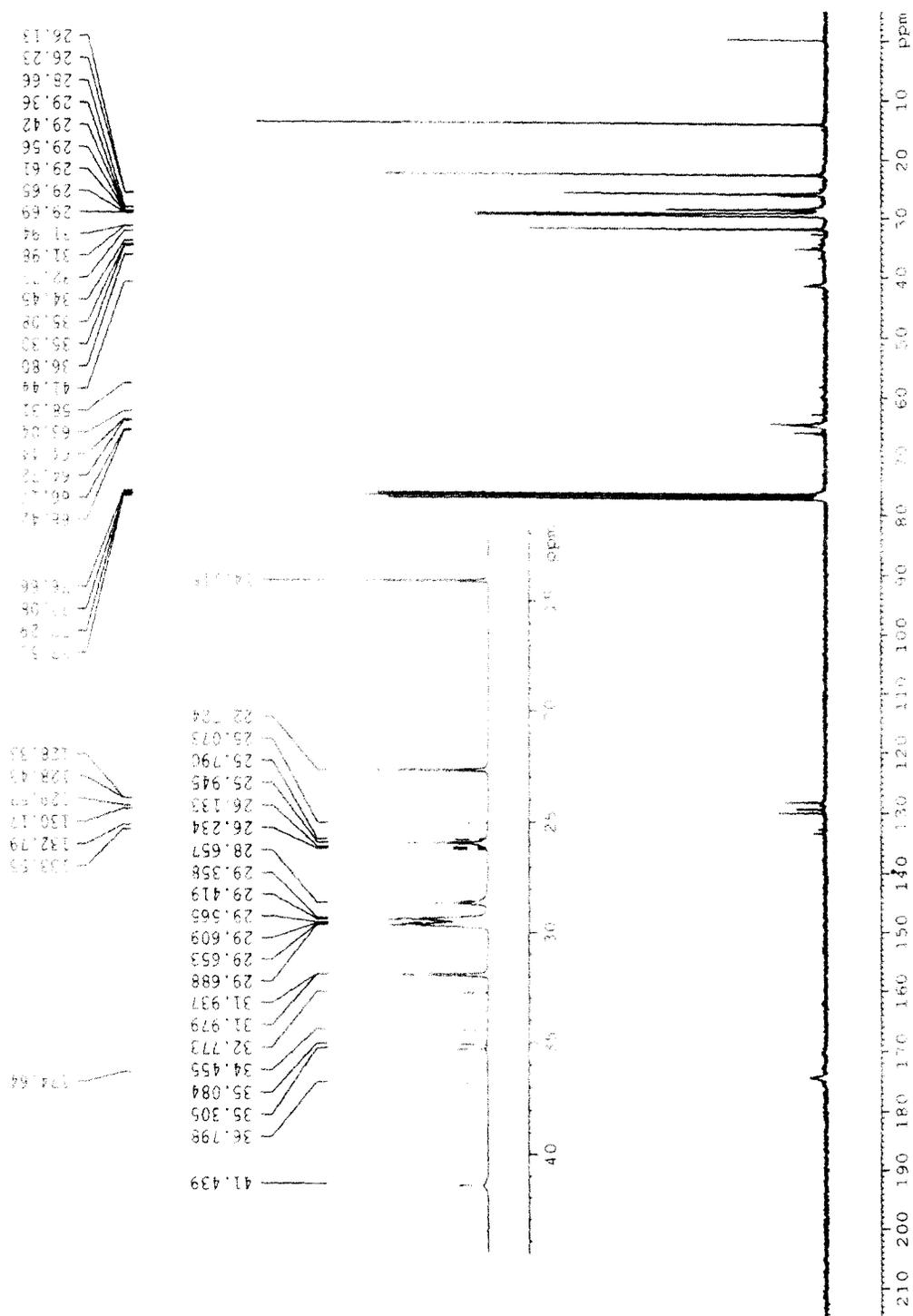


Figure 4: ¹H NMR spectrum of copolymer of decyl acrylate with styrene



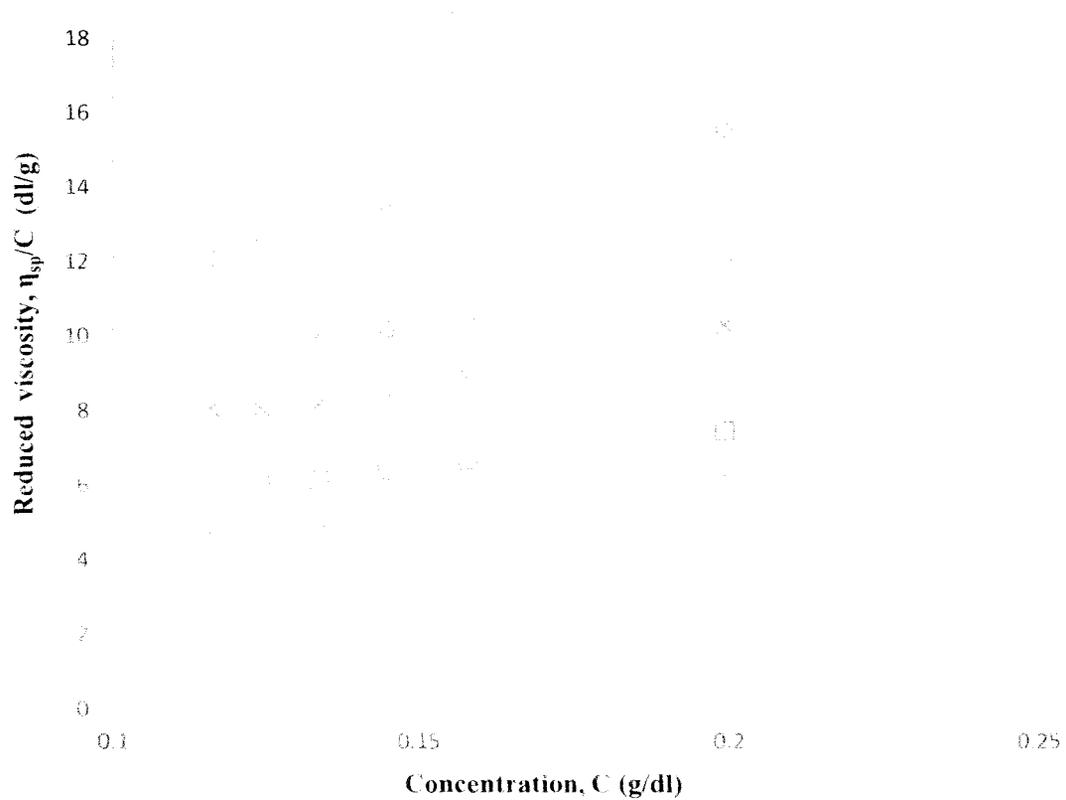


Figure 6: Plot of reduced viscosity, η_{sp}/C vs. concentration, C in Chloroform: \circ , P_1 ; \square , P_2 ; Δ , P_3 ; \times , P_4 ; $+$, P_5 .

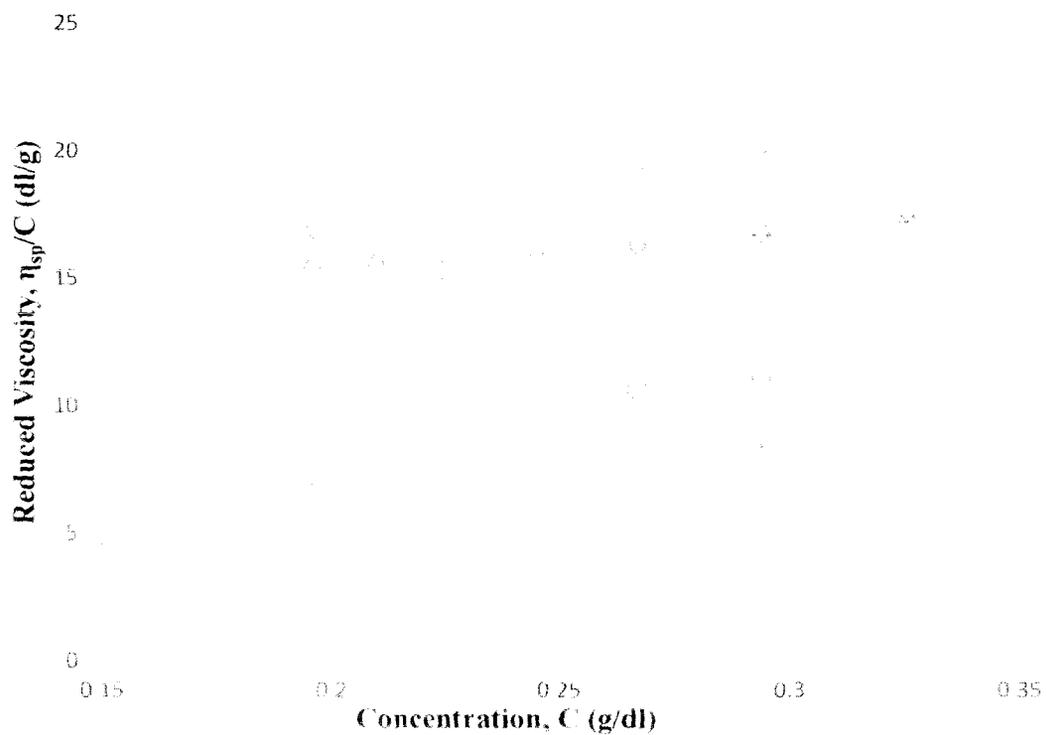


Figure 7: Plot of reduced viscosity, η_{sp}/C vs. concentration, C in Toluene:

\diamond , P_1 ; \circ , P_2 ; Δ , P_3 ; \times , P_4 ; $+$, P_5 .

Table 1. Composition of the monomers in the copolymer (prepared in toluene) in terms of mass fraction determined by PMR and FT-IR spectrometric method. P_1 is homopolymer of decyl acrylate (DA); P_2 is the copolymer of DA with 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 |
|----------------|---------------------------|---------|--|--|
| | DA | Styrene | | |
| P_1 | 1 | - | - | - |
| P_2 | 0.90 | 0.10 | 0.048 | 0.052 |

Table 2: Interaction parameters and intrinsic viscosity data for the individual polymers in different solvents at 313K.

| Polymer | In chloroform | | In toluene | |
|---------|---------------|------------|------------|------------|
| | b_{11} | $[\eta]_1$ | b_{11} | $[\eta]_1$ |
| P_1 | 33.659 | 10.334 | 41.334 | 7.346 |
| P_2 | 23.828 | 4.189 | 19.903 | 3.518 |

$$b_{11} = b_{12}, b_{21}$$

$$[\eta]_1 = [\eta]_2, [\eta]_3$$

P_1 = Polydecylacrylate

P_2 = Copolymer of decylacrylate with styrene

Table 3: Experimental and theoretical viscometric parameters for the ternary mixtures of DA and its copolymer with styrene at different percentage in chloroform at 313K.

| Polymer | Δb_m | b_m^{exp} | b_m^{theo} | $\Delta b_m^{\text{?}}$ | α | $[\eta]_m^{\text{exp}}$ | $[\eta]_m^{\text{theo}}$ | $\Delta[\eta]_m$ |
|----------------|--------------|--------------------|---------------------|-------------------------|----------|-------------------------|--------------------------|------------------|
| P ₃ | -VE | 14.579 | 20.424 | -5.845 | -0.212 | 12.73 | 8.797 | 3.933 |
| P ₄ | -VE | 25.608 | 14.379 | 11.229 | -0.343 | 8.902 | 7.261 | 1.643 |
| P ₅ | -VE | 18.098 | 15.524 | 2.574 | 1.139 | 3.056 | 5.724 | -2.667 |

P₃ = Polymer blend with DA + Copolymer of DA with styrene at ratio 3:1, P₄ = Polymer blend with DA + Copolymer of DA with styrene at ratio 1:1, P₅ = Polymer blend with DA + Copolymer of DA with styrene at ratio 1:3

Table 4: Experimental and theoretical viscometric parameters for the ternary mixtures of DA and its copolymer with styrene at different percentage in toluene at 313K.

| Polymer | Δb_m | b_m^{exp} | b_m^{theo} | $\Delta b_m^{\text{?}}$ | α | $[\eta]_m^{\text{exp}}$ | $[\eta]_m^{\text{theo}}$ | $\Delta[\eta]_m$ |
|----------------|--------------|--------------------|---------------------|-------------------------|----------|-------------------------|--------------------------|------------------|
| P ₃ | +VE | 35.113 | 24.495 | 10.618 | 0.295 | 5.293 | 6.384 | -1.09 |
| P ₄ | -VE | 28.316 | 15.31 | 13.006 | 0.317 | 4.540 | 5.43 | -0.89 |
| P ₅ | -VE | 20.148 | 13.795 | 6.353 | 2.799 | 2.290 | 4.47 | -2.18 |

Table 5: Base oil properties

| Base oil properties | Base oils | |
|--|-----------|--------|
| | B1 | B2 |
| Density (g.cm ⁻³) at 40 ⁰ C | 0.843 | 0.875 |
| Viscosity at 40 ⁰ C in cSt | 8.901 | 26.701 |
| Viscosity at 100 ⁰ C in cSt | 2.091 | 4.549 |
| Cloud point, ⁰ C | -8 | -10 |
| Pour point, ⁰ C | -3 | -6 |
| Viscosity Index | 86 | 97 |

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 | | | | |
|----------------|----------------|--|------|-----|-----|-----|
| | | 0.25 | 0.50 | 1 | 2 | 3 |
| B ₁ | P ₁ | -9 | -9 | -9 | -9 | -9 |
| | P ₂ | -15 | -15 | -15 | -15 | -15 |
| | P ₃ | -18 | -18 | -18 | -18 | -15 |
| | P ₄ | -21 | -21 | -24 | -21 | -21 |
| | P ₅ | -24 | -24 | -27 | -24 | -24 |
| B ₂ | P ₁ | -12 | -12 | -12 | -12 | -12 |
| | P ₂ | -18 | -18 | -18 | -18 | -18 |
| | P ₃ | -21 | -21 | -21 | -18 | -18 |
| | P ₄ | -24 | -24 | -27 | -27 | -24 |
| | P ₅ | -27 | -27 | -27 | -27 | -24 |

Table 7: Viscosity index of additive doped base oils

| Base oil | VII Sample | viscosity index of base oils containing different %(w/w) of VII | | | | |
|----------------|----------------|---|------|-----|-----|-----|
| | | 0.25 | 0.50 | 1 | 2 | 3 |
| B ₁ | P ₁ | 95 | 106 | 117 | 125 | 135 |
| | P ₂ | 92 | 103 | 107 | 119 | 127 |
| | P ₃ | 105 | 116 | 129 | 137 | 145 |
| | P ₄ | 107 | 117 | 132 | 145 | 157 |
| | P ₅ | 112 | 125 | 137 | 150 | 165 |
| B ₂ | P ₁ | 106 | 113 | 125 | 127 | 135 |
| | P ₂ | 102 | 111 | 121 | 126 | 133 |
| | P ₃ | 109 | 118 | 130 | 141 | 149 |
| | P ₄ | 111 | 120 | 133 | 143 | 152 |
| | P ₅ | 114 | 123 | 137 | 148 | 160 |

2.2 SECTION B: Viscometric Analysis of Homopolymer of Decyl Acrylate, its Copolymer with Styrene and their Polymer Mixture (Blends).

2.2.1 Introduction

A polymer blend is a physical mixture of two or more polymers [34]. In polymer blends structurally different polymers interact with each other with no covalent bonds. A wide range of physical and mechanical properties can be achieved in polymer/polymer blends by variation of such features as the molecular structure of the components, blend composition, morphology, and processing conditions [28, 34-37]. Blending of the polymers may result in a reduction in the basic cost and improved processing, and also may enable properties of importance to be maximized.

Different acrylate, methacrylate and olifinic polymer blends performed better as PPD and VII for lube oil than their homopolymers and copolymers [7, 3, 18]

As we discussed earlier in **chapter 1** of this part, polymer blends are mainly of three types- (1) miscible blends; (2) compatible blends or partially miscible blends and (3) immiscible blends or incompatible blends.

The mechanical, thermal, rheological and other properties of a polymer blend depend on its state of miscibility. However the highest degree of compatibility (that is miscibility) does not always mean the best engineering properties. The goal is to achieve a controlled level of phase separation. However, in most cases, due to the preponderance of immiscibility, the need is to increase compatibility. The mechanism and dynamics of phase separation in polyblends has long been a research subject in an attempt to obtain high performance materials by controlling morphology [9, 28].

Several homopolymer/copolymer blends were found to be miscible / compatible for a certain range of copolymer compositions even though no specific interactions between the component monomer units occurred [9, 28, 37-39].

The compatibility of polymer blends of homopolymer of decyl acrylate and its copolymer with styrene and evaluation of these blends as PPD and VII in different base oils were studied in **Section A** of this chapter.

Again, to the best of our knowledge, detailed viscometric analyses of these polymer blends are not reported so far.

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 [1], viscometric studies in different solutions may give valuable information about the chain conformation of the polymers and polymer blends. 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 [40].

So, detailed viscometric analysis of homopolymer of decyl acrylate, copolymer of decyl acrylate with styrene and their blends of different percentages in toluene and chloroform is discussed in this section.

2.2.2 Results and discussions

Viscometric data were obtained using the six equations mentioned in **Part I, Chapter I**. Huggins (H), Kraemer (K), Martin (M) and Schulz–Blaschke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants [41-45]. In single point determinations, Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chatterjee (DC) equations were employed [41-45]. 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.

Table 1 and **Table 2** present intrinsic viscosity $[\eta]$ values of all the prepared samples in toluene and chloroform, respectively. Of note, in both the solvents, a sudden drop of the $[\eta]$ values was observed as proceeded toward the copolymer from the homopolymer. In case of polymer blends there is a gradual decrease in the $[\eta]$ values with the increase in styrene concentration in the blends.

In chloroform, polymer blend with highest homopolymer percentage (P_3) showed highest $[\eta]$ values for H, M and both the SB equations. But in toluene homopolymer of decyl acrylate (P_1) gives highest $[\eta]$ values. The lowest values of $[\eta]$ were observed for the polymer blend with highest copolymer percentage (P_5) for all the equations applied in both the solvents.

For all the polymers and polymer blends, in both the solvents, the lowest $[\eta]$ values were observed by using Kreamer equation. In toluene, the values obtained by single point determination method were higher than that obtained by graphic

extrapolation method.

Table 3 and **Table 4** present viscometric constant values related to all equations in both toluene and chloroform solvents for the samples analyzed. The observed viscometric constant values of all the polymers and polymer blends were higher in chloroform than those in toluene. This is probably for the greater hydrodynamic volume of the polymers and polymer blends, which is, in turn, due to the better solvent effect of chloroform.

In both the solvents the copolymer showed higher values than the homopolymer (except K_k value). Interestingly, in cases of polymer blends the viscometric constant values increases with increasing copolymer concentrations in blends irrespective of the solvents and applied equations. This is may be due to the grater hydrodynamic volume of the blends which increases with increasing copolymer percentage. It can be noticed that for all the polymers in both solvent toluene, k_{sp} 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

Table 5 and **Table 6** 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 in toluene and chloroform. It can be noticed that the range was narrow by graphic extrapolation method when compared to the values obtained through a single point using SB, SC and DC equation in both solvents.

The values obtained in the case of homo polymer are always lower (except one in each case) than the co polymer, irrespective of the method of determination and solvent. Again it is interesting to note that with increasing copolymer percentage in polymer blends the percentual difference values increases irrespective of solvents.

In toluene the values obtained by single point determination are higher than the values obtained through graphic extrapolation method. But no such sequence observed in chloroform. Polymer blend with highest copolymer percentage showed highest values for all the equations applied in both solvents.

Viscometric molecular weight (M_v) obtained in toluene and chloroform by using Mark Houwink equation, are presented in **Table 7** and **Table 8**. As was reflected in the respective $[\eta]$ values, the homopolymer showed higher Viscometric Molecular weight (M_v) compared to the copolymers. In case of polymer blends, with increasing

copolymer percentage in the blends the molecular weight decreases.

2.2.3 Conclusion

In case of polymer blends increasing copolymer percentage in the feed inversely proportional to the intrinsic viscosity blend solutions. Due to incorporation of styrene intrinsic viscosity decreases from homopolymer to copolymer. Again, the intrinsic viscosity values are higher for all the polymers and polymer blends.

Amongst the single point determination method, SB equation found to be most suitable for all the polymers and polymer blends analyzed in both solvents.

The copolymer showed much higher viscosity constant values than the homopolymer in both solvents. Probably, due to incorporation of benzene ring of styrene the hydrodynamic volume of the copolymer increases, which in turn enlarge the conformation of the copolymer, though it has lower molecular weight than the homopolymer. Interestingly, it can be observed that, in both solvents the values of viscosity constant increases with increasing copolymer percentage in blends. With increasing copolymer percentage, the compatibility of the blends increases, which enlarges the size of the blend in solution.

Table 1. Intrinsic viscosity values for all prepared homopolymer, copolymer and polymer blends samples in toluene, calculated by using different equation. a- extrapolation of graph, b- single point determination ($k_{sb}= 0.28$), c- single point determination

| Sample | $[\eta]_h^a$ | $[\eta]_k^a$ | $[\eta]_m^a$ | $[\eta]_{SB}^a$ | $[\eta]_{SB}^b$ | $[\eta]_{SC}^c$ | $[\eta]_{DC}^c$ |
|----------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ₁ | 7.346 | 8.299 | 8.381 | 9.344 | 9.279 | 8.859 | 9.585 |
| P ₂ | 3.518 | 4.206 | 4.047 | 4.434 | 4.419 | 4.874 | 5.082 |
| P ₃ | 5.293 | 6.577 | 6.456 | 7.059 | 7.179 | 7.390 | 7.908 |
| P ₄ | 4.540 | 5.561 | 5.370 | 5.870 | 5.992 | 6.396 | 6.793 |
| P ₅ | 2.290 | 3.172 | 2.995 | 3.375 | 3.392 | 4.053 | 4.166 |

Where: P₁ = Polydecylacrylate, P₂ = Copolymer of decylacrylate with styrene, P₃ = Polymer blend with DA = Copolymer of DA with styrene at ratio 3:1, P₄ = Polymer blend with DA = Copolymer of DA with styrene at ratio 1:1, P₅ = Polymer blend with DA = Copolymer of DA with styrene at ratio 1:3

Table 2. Intrinsic viscosity values for all prepared homopolymer, copolymer and polymer blends samples in chloroform, calculated by using different equation. a- extrapolation of graph, b- single point determination ($k_{sb}= 0.28$), c- single point determination.

| Sample | $[\eta]_h^a$ | $[\eta]_k^a$ | $[\eta]_m^a$ | $[\eta]_{SB}^a$ | $[\eta]_{SB}^b$ | $[\eta]_{SC}^c$ | $[\eta]_{DC}^c$ |
|----------------|--------------|--------------|--------------|-----------------|-----------------|-----------------|-----------------|
| P ₁ | 10.334 | 9.10 | 12.001 | 13.021 | 12.945 | 9.816 | 11.306 |
| P ₂ | 4.189 | 5.546 | 5.669 | 6.453 | 6.40 | 6.171 | 6.773 |
| P ₃ | 12.730 | 9.069 | 13.105 | 13.462 | 13.486 | 9.326 | 10.679 |
| P ₄ | 8.902 | 8.059 | 10.084 | 10.843 | 10.820 | 8.591 | 9.744 |
| P ₅ | 3.056 | 4.339 | 4.204 | 4.788 | 4.843 | 5.022 | 5.421 |

Table 3. Viscometric constants obtained for all prepared homopolymer, copolymer and polymer blend samples in toluene. K_h , k_k , k_m and k_{sb} are the Huggins, Kraemer, Martin and Schulz- Blaschke coefficients, respectively

| Samples | k_h | k_k | k_m | k_{sb} | $k_h + k_k$ |
|----------------|-------|-------|-------|----------|-------------|
| P ₁ | 0.315 | 0.103 | 0.147 | 0.092 | 0.418 |
| P ₂ | 1.359 | 0.065 | 0.407 | 0.223 | 1.424 |
| P ₃ | 0.089 | 0.122 | 0.067 | 0.053 | 0.211 |
| P ₄ | 0.323 | 0.108 | 0.164 | 0.106 | 0.431 |
| P ₅ | 1.936 | 0.022 | 0.555 | 0.302 | 1.958 |

Table 4. Viscometric constants obtained for all prepared homopolymer, copolymer and polymer blend samples in chloroform. K_h , k_k , k_m and k_{sb} are the Huggins, Kraemer, Martin and Schulz- Blaschke coefficients, Respectively

| Samples | k_h | k_k | k_m | k_{sb} | $k_h + k_k$ |
|----------------|-------|--------|-------|----------|-------------|
| P ₁ | 0.766 | 0.089 | 0.380 | 0.218 | 0.855 |
| P ₂ | 1.608 | -0.122 | 0.778 | 0.473 | 1.486 |
| P ₃ | 1.253 | 0.041 | 0.504 | 0.308 | 1.294 |
| P ₄ | 1.374 | -0.006 | 0.608 | 0.373 | 1.368 |
| P ₅ | 3.842 | -0.470 | 1.260 | 0.705 | 3.372 |

Table 5. Percentual differences ($\Delta = ([\eta]/[\eta]_h) - 1$) obtained for intrinsic viscosity values in Toluene, 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 | 12.96 | 14.08 | 27.19 | 26.31 | 20.59 | 30.47 |
| P ₂ | 19.55 | 15.03 | 26.03 | 25.61 | 38.54 | 44.45 |
| P ₃ | 24.25 | 21.97 | 33.36 | 35.63 | 39.61 | 49.40 |
| P ₄ | 22.48 | 18.28 | 29.29 | 31.98 | 40.88 | 49.62 |
| P ₅ | 38.51 | 30.78 | 47.37 | 48.12 | 76.98 | 81.92 |

Table 6. Percentual differences ($\Delta = ([\eta]/[\eta]_h) - 1$) obtained for intrinsic viscosity values in Chloroform, 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 | -12 | 16.13 | 26 | 25.35 | -5.02 | 9.40 |
| P ₂ | 32.07 | 35 | 34.44 | 52.41 | 46.96 | 61.30 |
| P ₃ | -28.76 | 2.94 | 5.46 | 5.93 | -26.74 | -16.12 |
| P ₄ | -9.50 | 13.27 | 21.80 | 21.54 | -3.52 | 9.45 |
| P ₅ | 41.98 | 37.56 | 56.67 | 58.47 | 64.33 | 77.38 |

Table 7. Determination of molecular weight (M_v) by Mark Houwinks equation $[\eta] = KM^a$ in toluene 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 | 33189 | 38637 | 39810 | 46345 | 45920 | 42954 | 47973 |
| P ₂ | 12023 | 15382 | 14588 | 16588 | 16482 | 18880 | 19953 |
| P ₃ | 21135 | 28510 | 27797 | 31477 | 32137 | 33419 | 36728 |
| P ₄ | 17100 | 22594 | 21577 | 24322 | 25119 | 27479 | 29785 |
| P ₅ | 6653 | 10423 | 9638 | 11350 | 11455 | 14622 | 15205 |

Table 8. Determination of molecular weight (M_v) by Mark Houwinks equation $[\eta] = KM^a$ in chloroform where, $K = 0.00480 \text{ dl.g}^{-1}$ and $a = 0.80$

| Sample | M_h^a | M_k^a | M_m^a | M_{sb}^a | M_{sb}^b | M_{sc}^b | M_{dc}^b |
|----------------|---------|---------|---------|------------|------------|------------|------------|
| P ₁ | 14655 | 12517 | 17679 | 19577 | 19452 | 13752 | 16507 |
| P ₂ | 4758 | 6736 | 6924 | 8140 | 8057 | 7698 | 8648 |
| P ₃ | 19031 | 12457 | 19735 | 20341 | 20455 | 12899 | 15279 |
| P ₄ | 12174 | 10747 | 14223 | 15573 | 15532 | 11641 | 13626 |
| P ₅ | 3198 | 4949 | 4735 | 5606 | 5686 | 5950 | 6547 |

CHAPTER III

3.1 Experimental

3.1.1 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, and was purified by crystallization from methanol-chloroform mixture prior to use. Toluene (GC Purity 99.5 %) and chloroform (GC Purity 99 %), obtained from Merck, India, were used as a solvent.

3.1.2. Esterification of decyl acrylate (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 403K using a well-controlled thermostat. The progress of the reaction was followed by monitoring the amount of liberated water from the reaction mixture to give the ester, decyl acrylate.

3.1.3. Purification of the 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

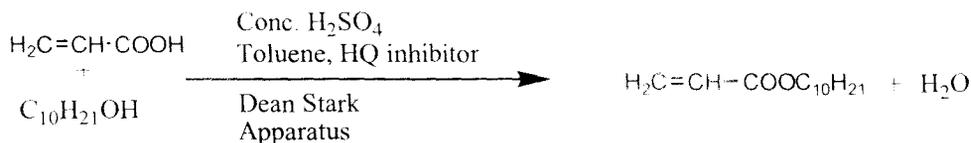
pressure and was used in the polymerization process.

3.1.4. Preparation of homopolymer 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 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 dropwise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353K for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and to 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 homopolymer of DA was similarly prepared and purified under the same conditions for use in reference experiments.

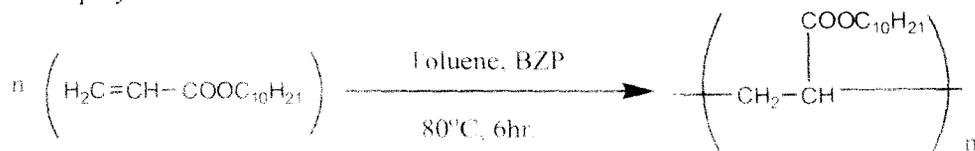
Scheme I

Esterification:



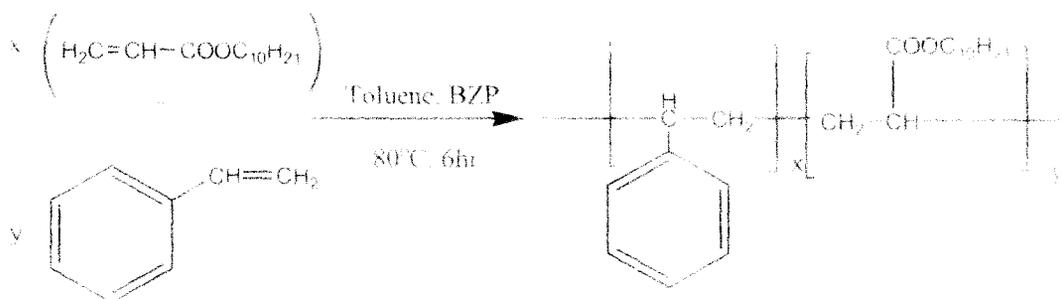
Scheme-II

Homopolymerisation:



Scheme-III

Copolymerisation:



3.1.5. 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 a Bruker Avance 300 MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl_3 was used as solvent and TMS as reference material.

3.1.6. Viscometric Measurements

Viscosities were determined at 313K in chloroform and toluene, using an Ubbelohde OB viscometer placed in a thermostatically controlled bath. The temperature was measured close to the capillary by a thermometer with an accuracy of

0.01K. 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 the solvent were taken in all the cases.

All the binary solutions were prepared by dissolving a measured weight of the polymer in chloroform and toluene and diluting to a measured volume. All the ternary solutions were prepared by dissolving a measured weight of the polymers with a DA : copolymer of DA with styrene weight ratio of 3:1, 1:1 and 1:3 in chloroform and toluene and then diluting to a measured volume.

For the viscosity – average molecular weight determination, the constants $K = 0.00387 \text{ dl/g}$ and $a = 0.725$ [41, 46] were employed in toluene and the constants $K = 0.00480 \text{ dl/g}$ and $a = 0.80$ [47] were employed in chloroform.

3.1.7. Evaluation of prepared additive as pour point depressants (PPDs) in base oils

The prepared additives were evaluated as pour point depressant using two different base oils collected from the same source, (**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 for individual polymers (binary) and polymer blends (ternary). All the ternary blend solutions were prepared by dissolving a measured weight of the polymers with DA: copolymer of DA with styrene at the weight ratio of 3:1, 1:1 and 1:3 in base oils. The effect of additive concentration was investigated by using different doping concentrations from 0.25% to 3% (w/w). The experimental data were noted by taking an average of three experimental results under identical conditions.

3.1.8. Evaluation of prepared additive as viscosity index improvers (VIIs) in base oils

Different binary and ternary blends were prepared by using two different types of base oil. Viscosities and the viscosity index (VI) of these oils were calculated according to ASTM D2270. Different weight percentages of concentration from 0.25 to 3.0 were used to study the effect of concentration on VI of the additive-doped lube oil. The experiment was done for both binary and ternary blends. In this respect, the kinematic viscosity of the oil containing different concentrations of the prepared polymers, copolymers and polymer blends were determined at 313K and 373K. The experimental data were noted by taking an average of three experimental results under identical conditions.

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