

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.

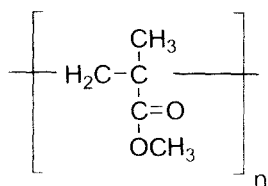
Since, viscometry provides very important data about the interaction of additive in base fluid and hence conformation of polymeric system [15] in the base stock, the process of polymerization in the presence of a suitable solvent has been attracting considerable interest [21-22].

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.

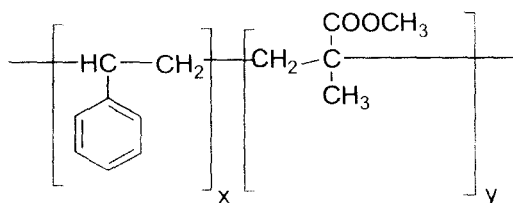
In this work viscometric parameters (intrinsic viscosity and the value of constants) of toluene solution for sample of poly methyl methacrylate and its copolymer were obtained by graphic extrapolation and single point determination. The viscosity average molecular weight determined by using different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



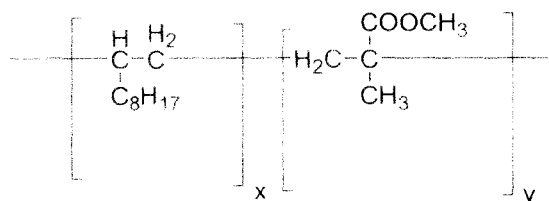
Structure 1



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.

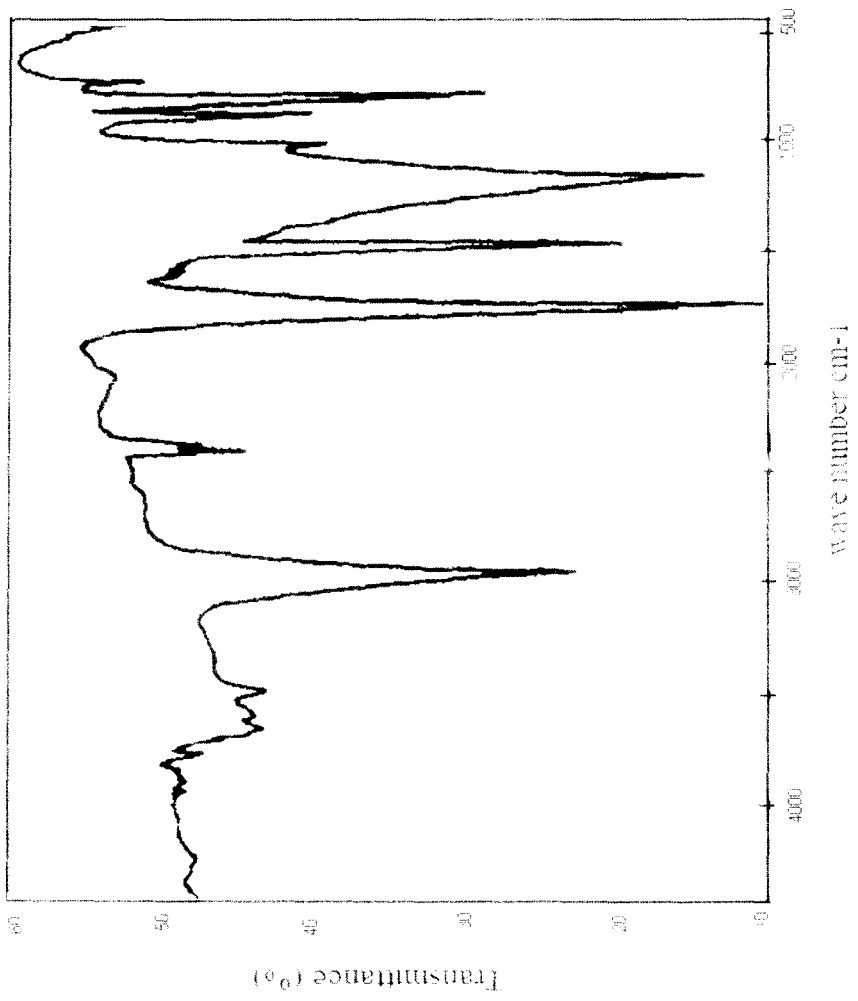


Figure 1: FT-IR spectrum of homopolymer of methyl methacrylate

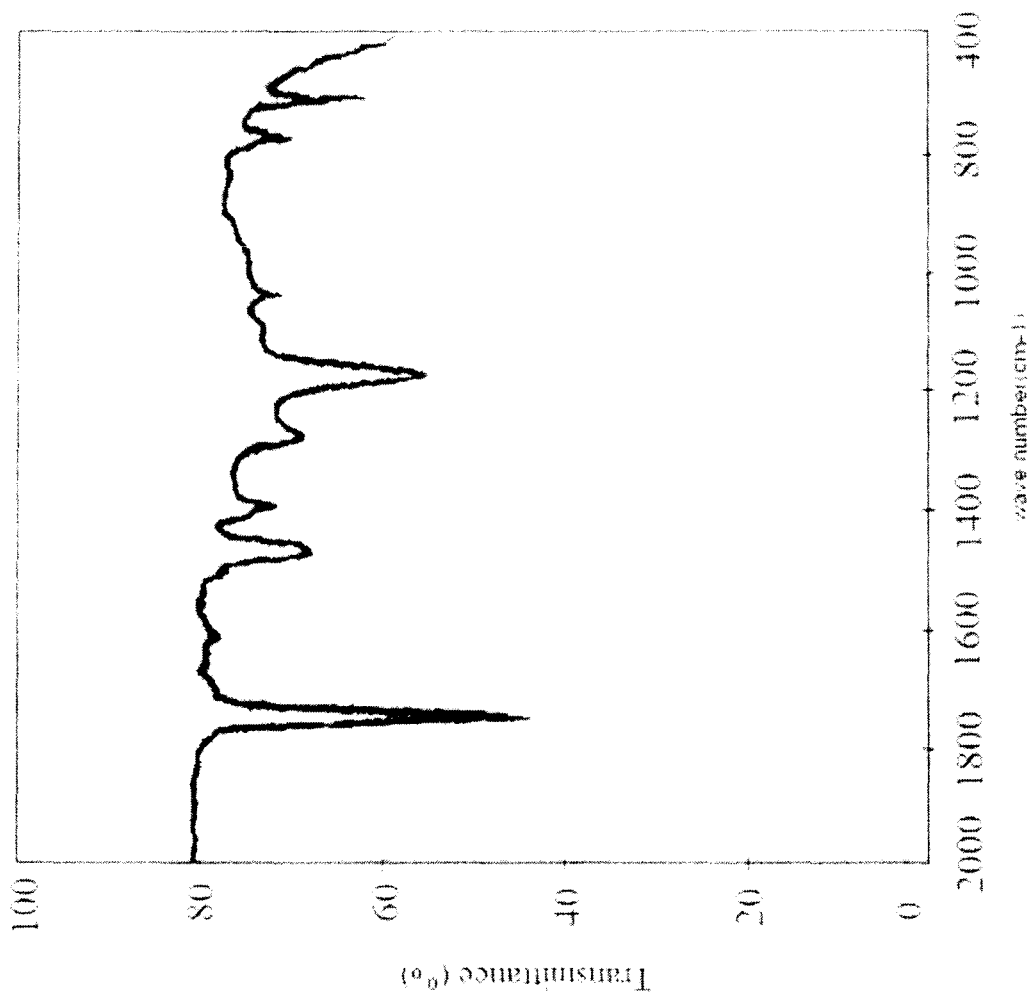


Figure 2: FT-IR spectrum of copolymer of methyl methacrylate with styrene

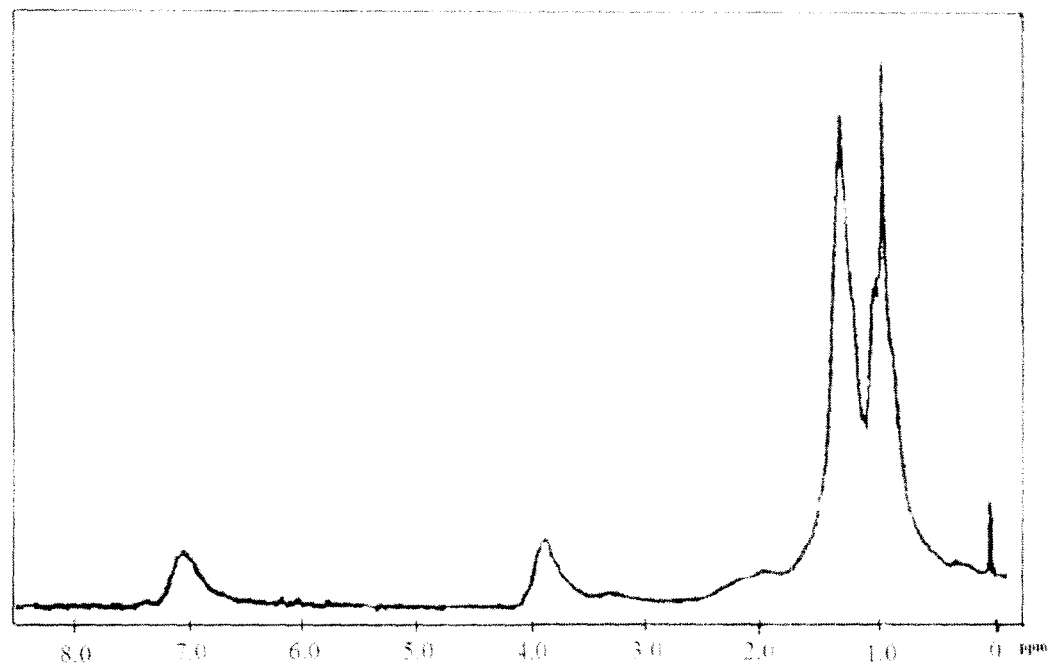


Figure 3: ^1H NMR spectrum of copolymer of methyl methacrylate with styrene

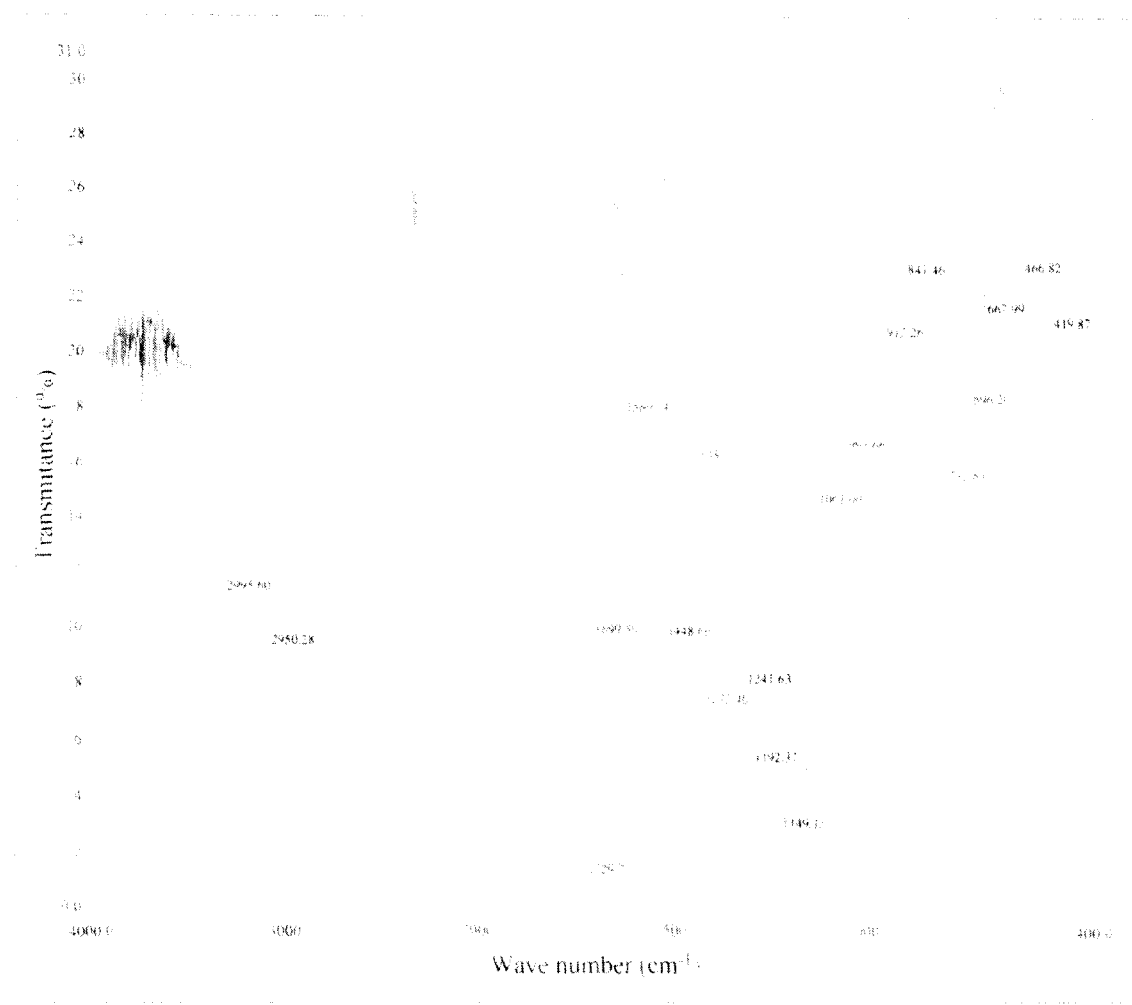


Figure 4: FT-IR spectrum of copolymer of methyl methacrylate with 1-decene

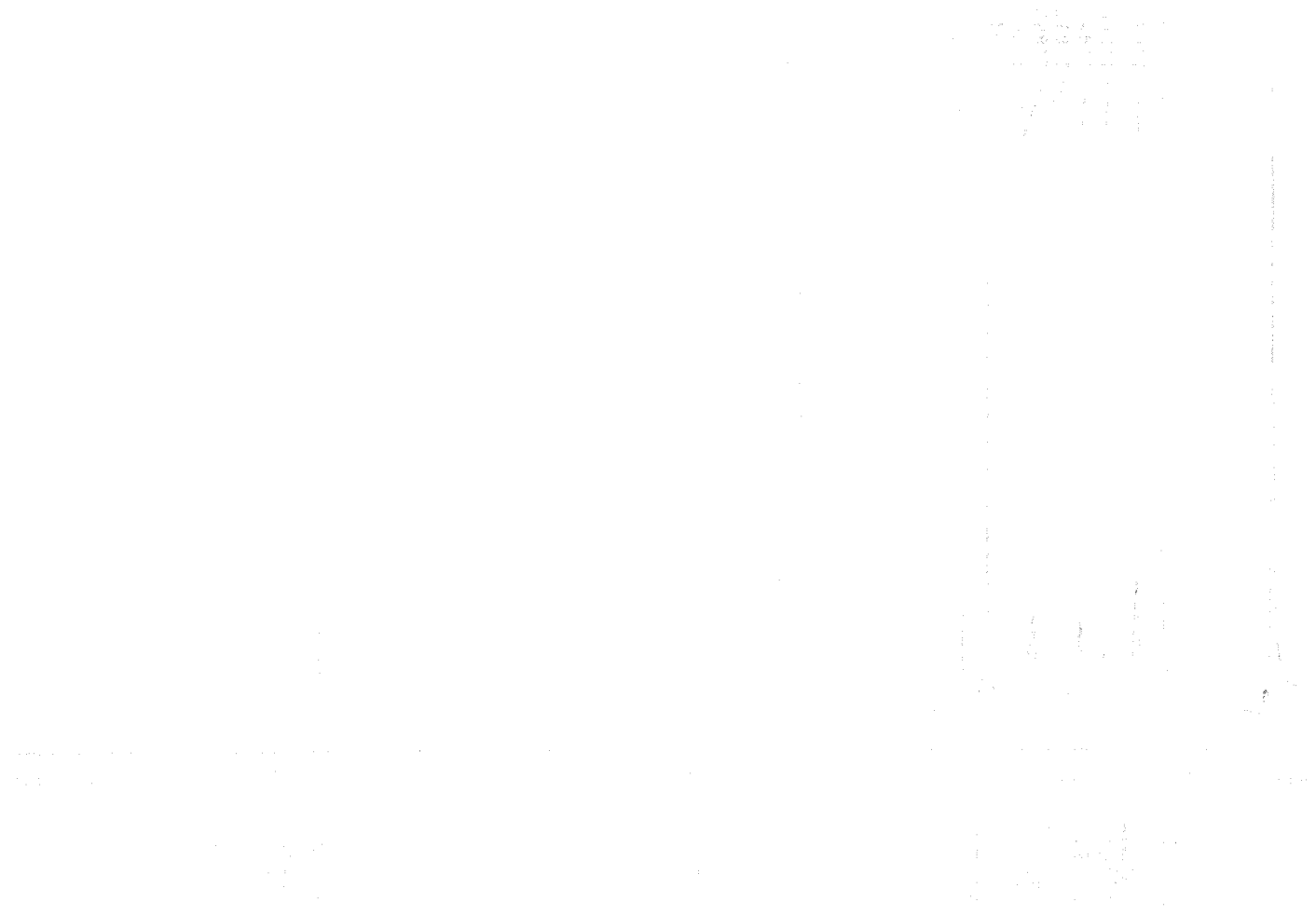


Figure 5: ¹H NMR spectrum of copolymer of Methyl methacrylate with 1-decene

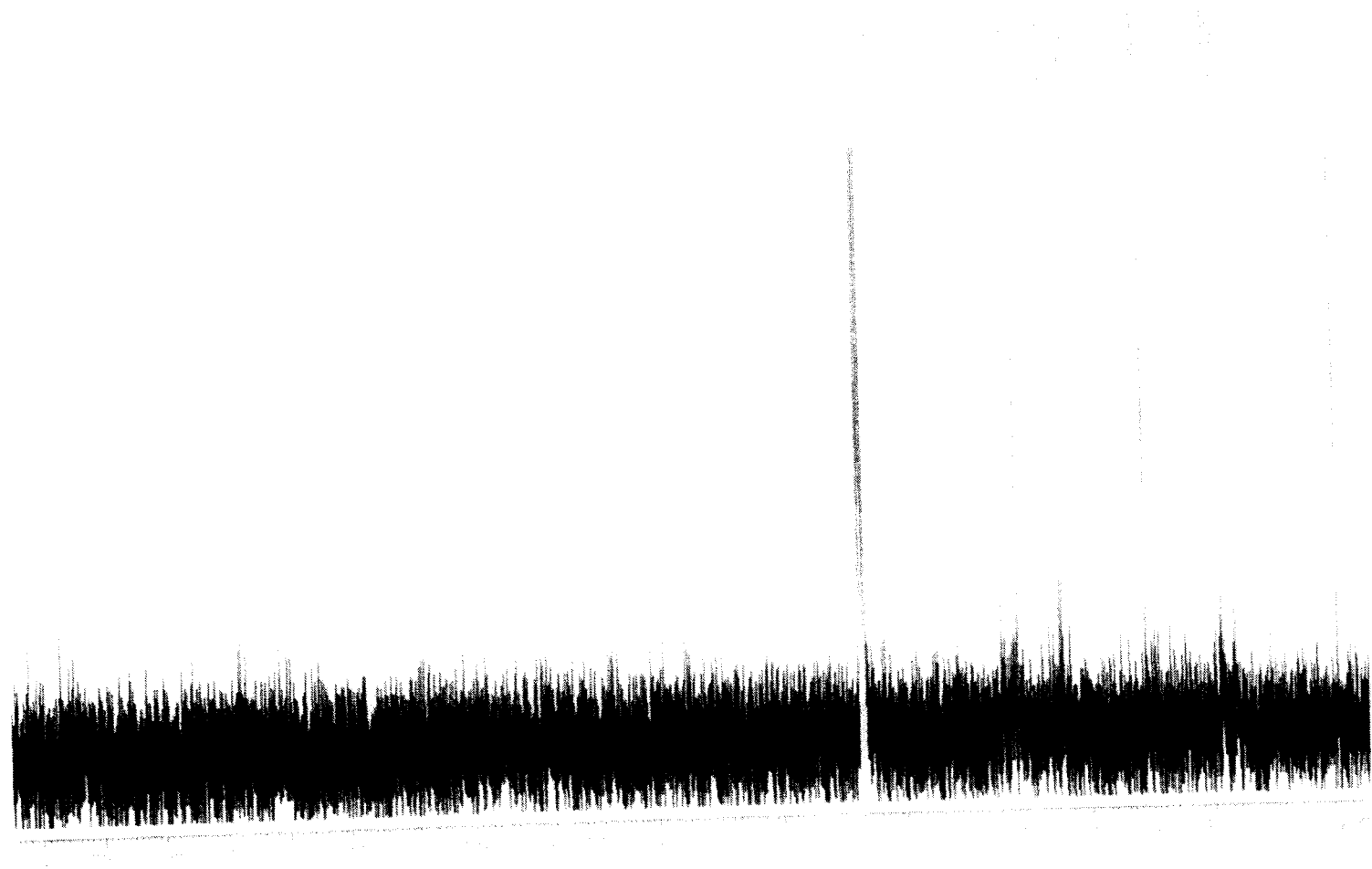


Figure 6: ^{13}C NMR spectrum of copolymer of Methyl methacrylate with 1-decene

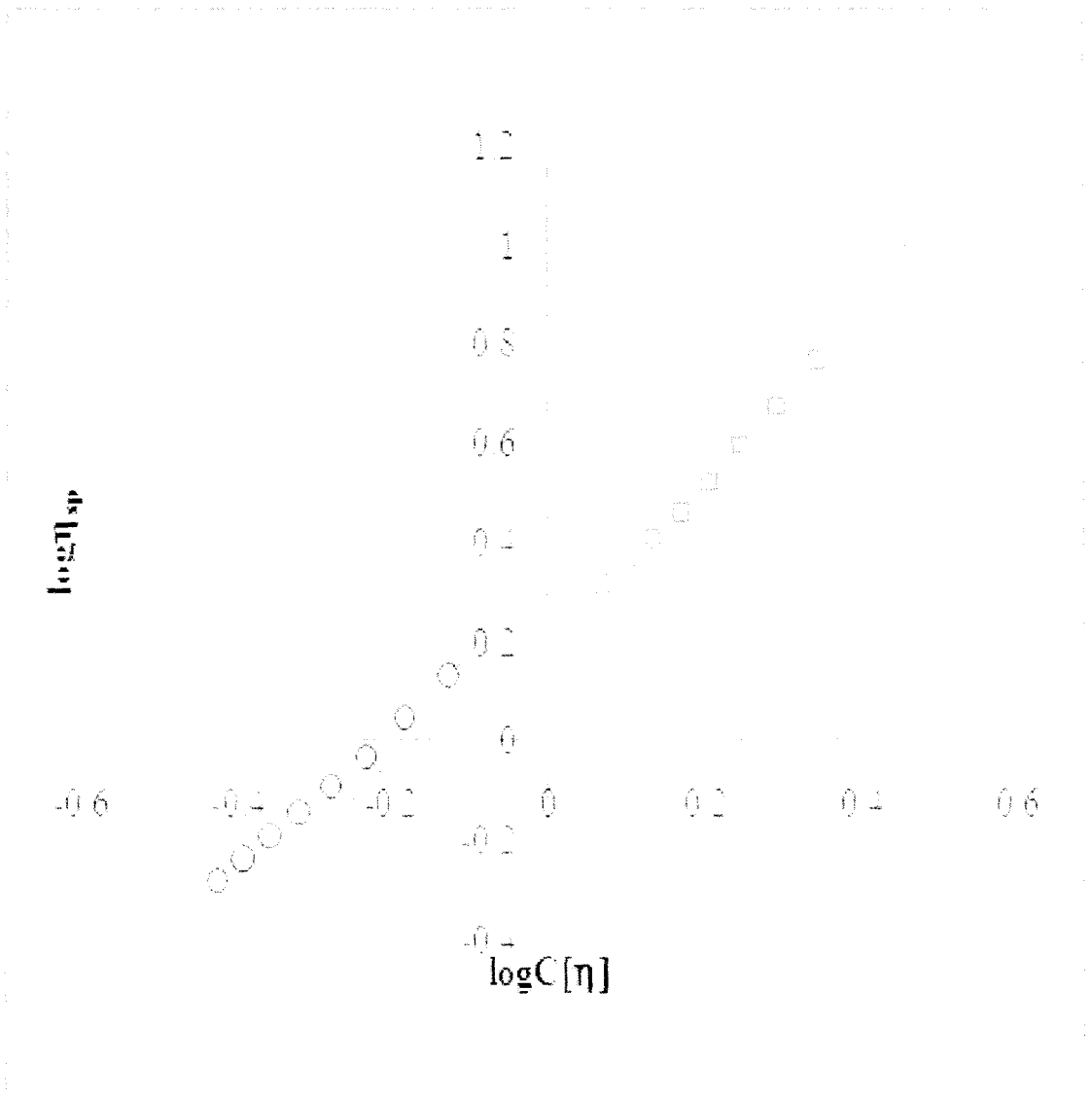


Figure 7: Plot of $\log C[\eta]$ vs $\log \eta_{sp}$: \diamond , Poly-1; \square , Poly-2; Δ , Poly-3; \times , Poly-4, \circ , Poly-5

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.

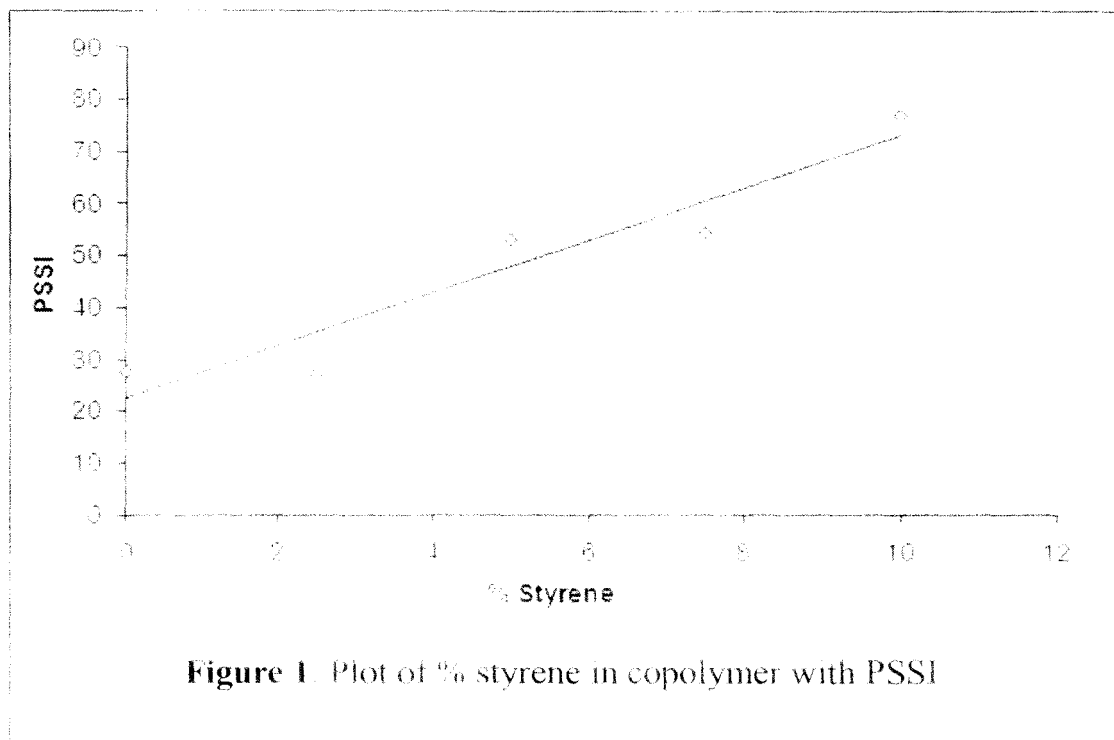


Table 1. Composition of the monomers in the copolymers in terms of mass fraction determined by PMR and FT-IR spectrophotometric method. P-1 is homopolymer of Methyl methacrylate (MMA); P-2 to P-5 are the copolymer of MMA with different mass fractions of styrene

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 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 grater 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