CHAPTER II

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

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

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

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

2.1.1 Introduction

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

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

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

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

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

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

$$[\eta] = K M^a \tag{1}$$

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

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

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

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

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

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

Where, C is mass concentration in gm/cc.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

## 2.1.2 Results and discussion

Spectroscopic analysis

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

The existence of copolymer was confirmed by IR (Figure 1b) and NMR (Figure 1c) analysis. Carbonyl stretching vibration at 1732 cm^{-1} of the homopolymer shifted to 1720 cm^{-1} in the copolymer. Peaks at 760 cm^{-1} and 697 cm^{-1} were attributed to the C-H bond of the phenyl group of styrene. In its ^{1}H NMR spectra the copolymer indicated the presence of phenyl group at 7.2 ppm and the –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 –OCH$_2$ group at 3.9 ppm in the area of signal due to phenyl protons at 7.2 ppm based on earlier reports [26] as well as on the basis of our earlier paper [16], which was further verified through an analysis of FT-IR spectral data following a method as also discussed in our earlier paper [16]. From above discussion structure of homopolymer and copolymer may be presented by structure I and structure II respectively.
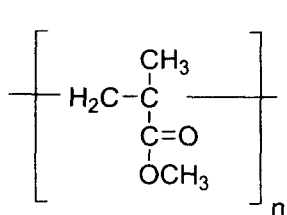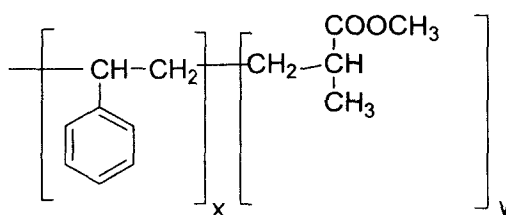
Structure I   Structure II

Thermogravimetric analysis (TGA)

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

Viscometric analysis

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

Using the graphic extrapolation method respective intrinsic viscosities and constants were evaluated. In single point determinations, SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent system [19-23].The same is used here also.
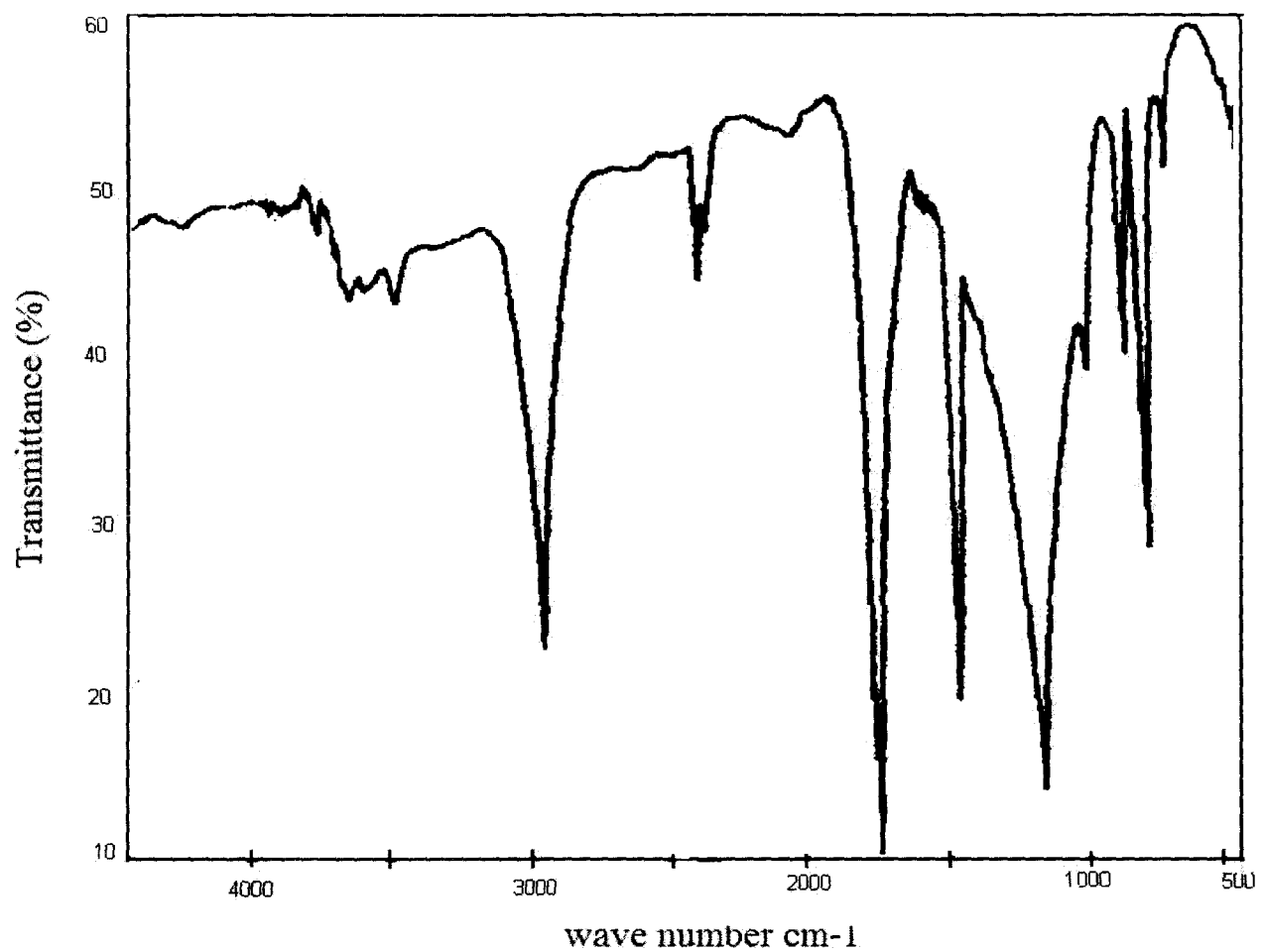
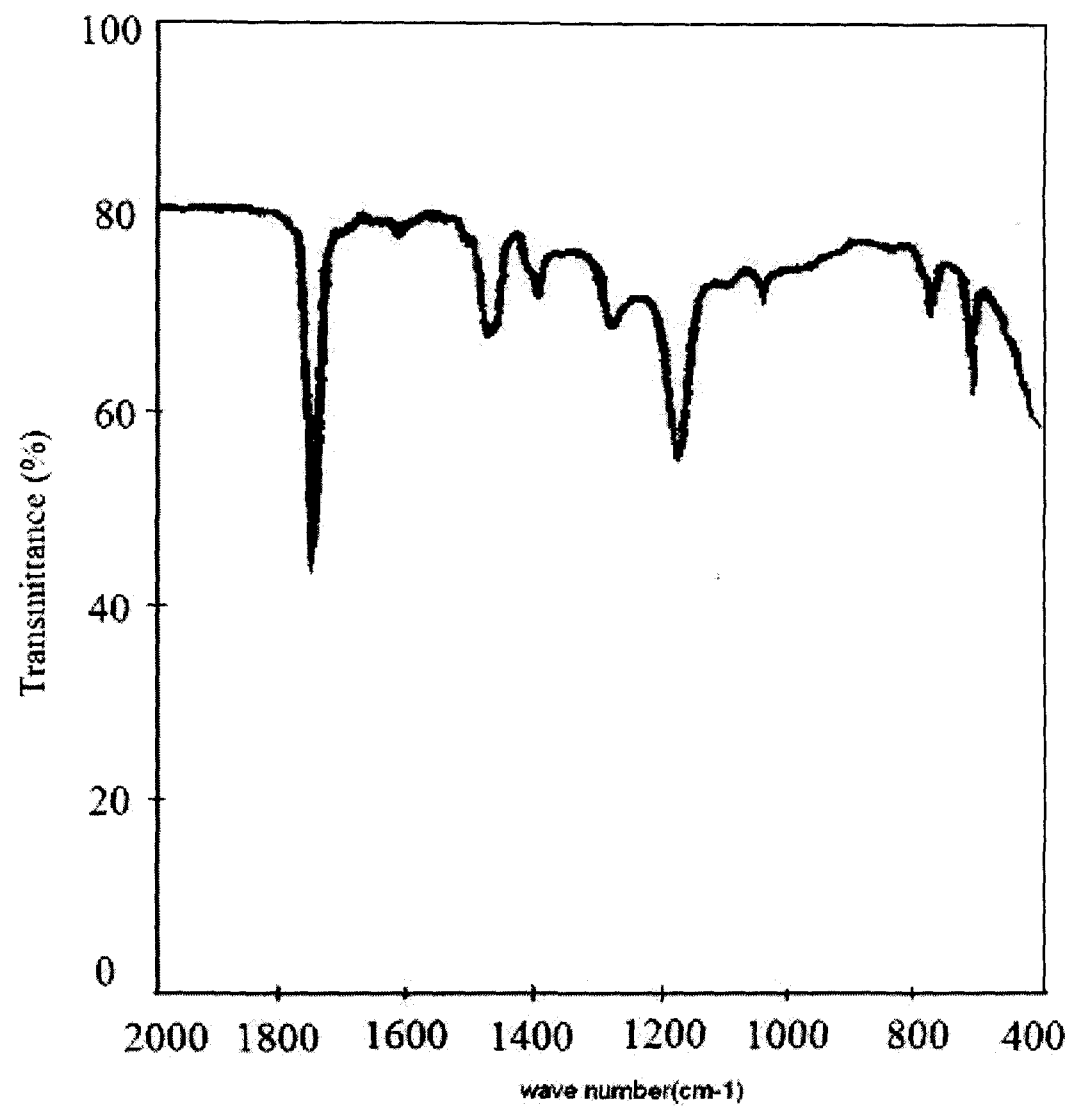**Fig. 1a** FT-IR spectrum of poly(methyl methacrylate)

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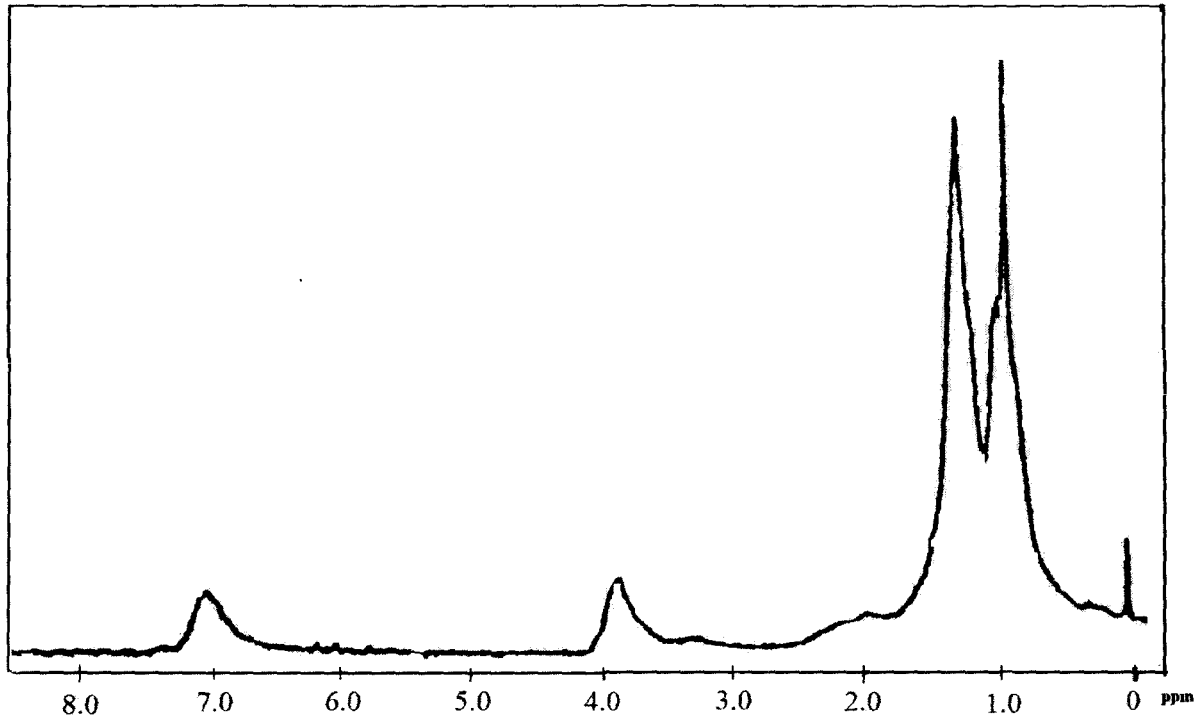
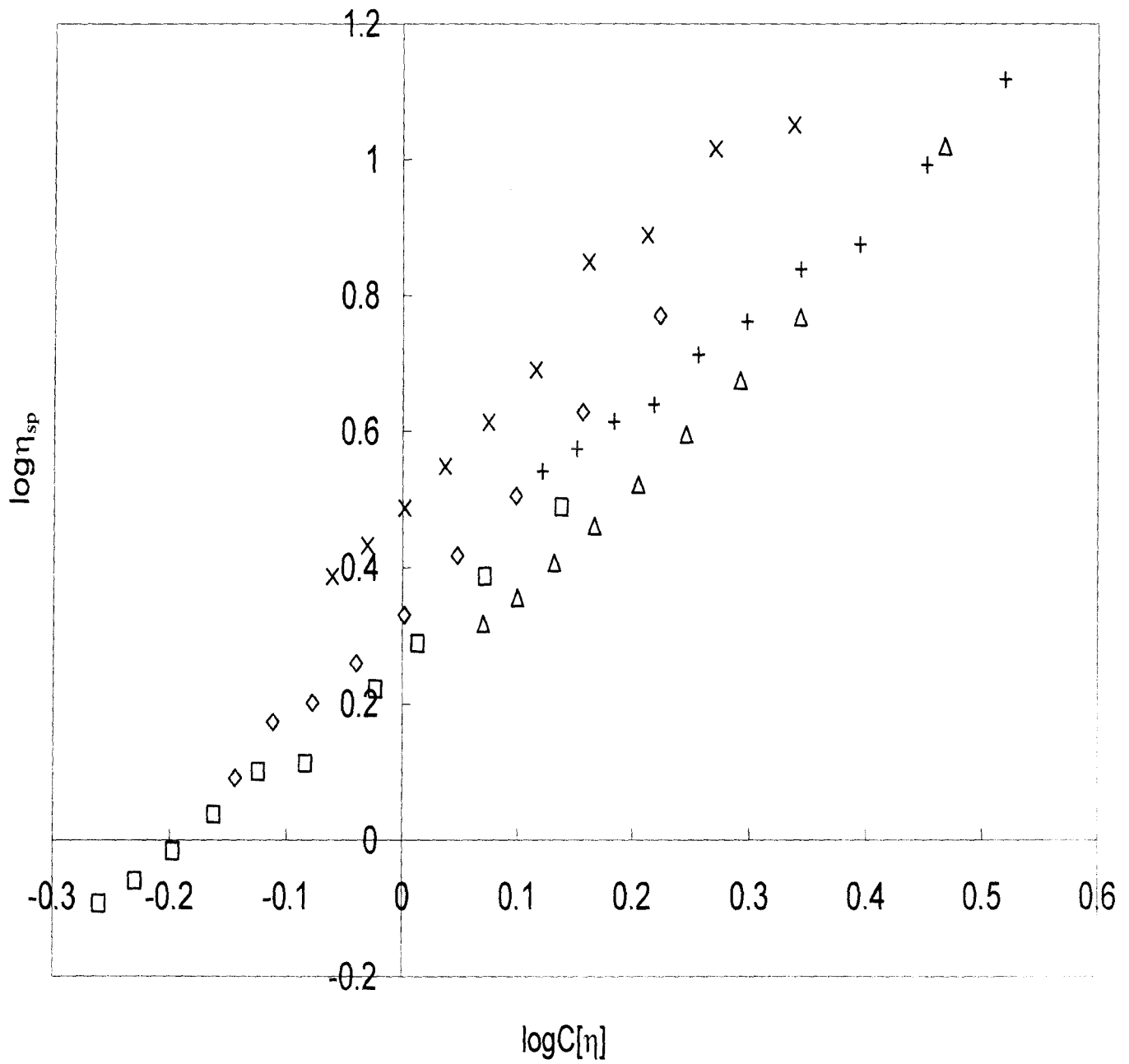**Fig. 1c** NMR spectrum of copolymer of Methyl methacrylate + styrene

Fig. 2 Plot of logC[η] vs logη$_{sp}$: ◊, Poly-1; □,Poly-2; Δ, Poly-3; x,Poly-4, +, Poly-5
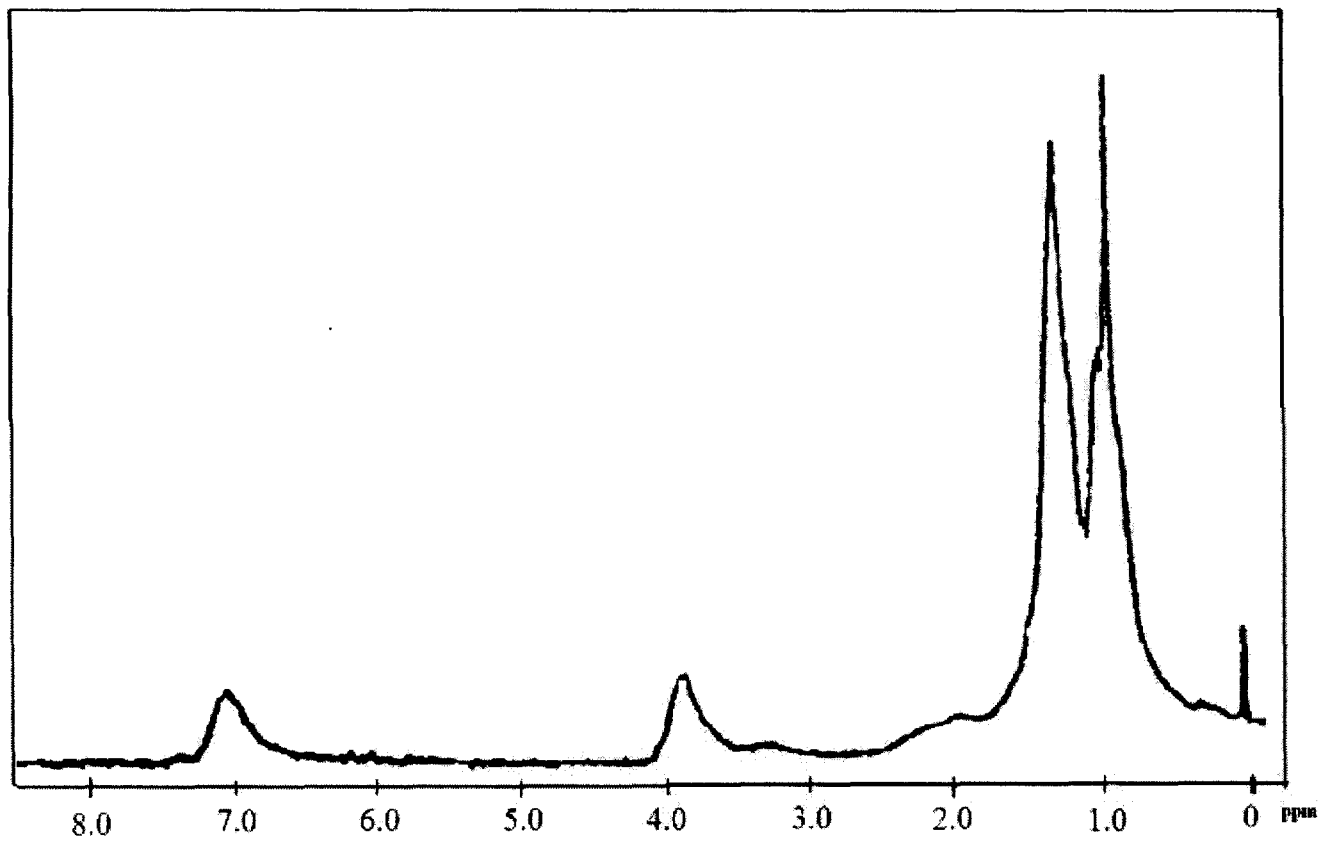
Fig. 1c NMR spectrum of copolymer of Methyl methacrylate + styrene

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

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

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

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

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

This may be because of the fact that, the homopolymer, PMMA, with lowest molecular mass (M_n 45000 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 6) indicated that, for the copolymer system analyzed, the SB equation which is widely applied in industry quality control laboratories should be the most suitable for the application in one point determination. This table also indicated that for PMMA the graphical extrapolation method seemed to be more suitable in toluene rather than the single point determination and Martin equation produced the lowest deviation value among the four when compared to those obtained from the Huggins equation.

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

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

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

Performance of the homo and copolymers as PPD

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

2.1.3 Conclusion

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

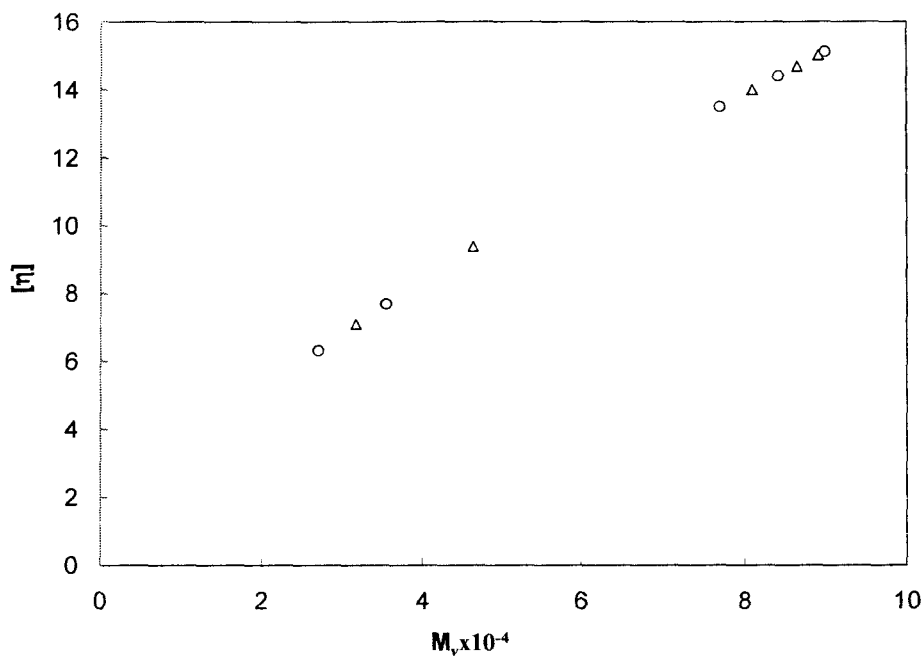**Fig. 3a** Plot of viscometric molecular weight (M_vx10^{-4}) vs intrinsic viscosity ([η]): ○,Huggins value ; △, Kraemers value.
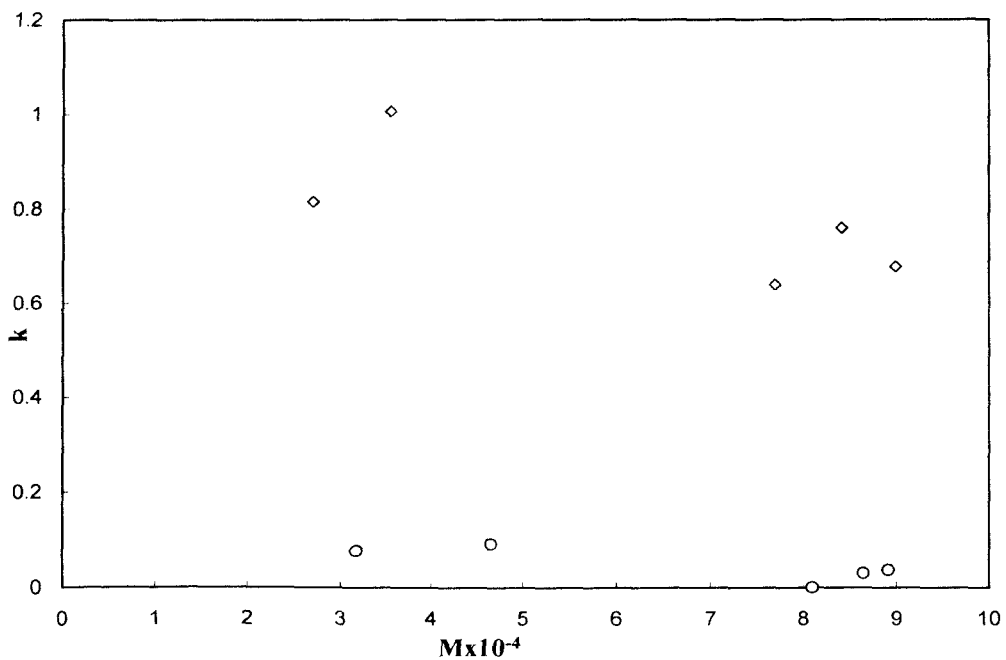
Fig. 3b Plot of viscometric molecular weight (Mx10^{-4}) vs viscometric costant (k): ◊, Huggins value; ○, Kraemers value

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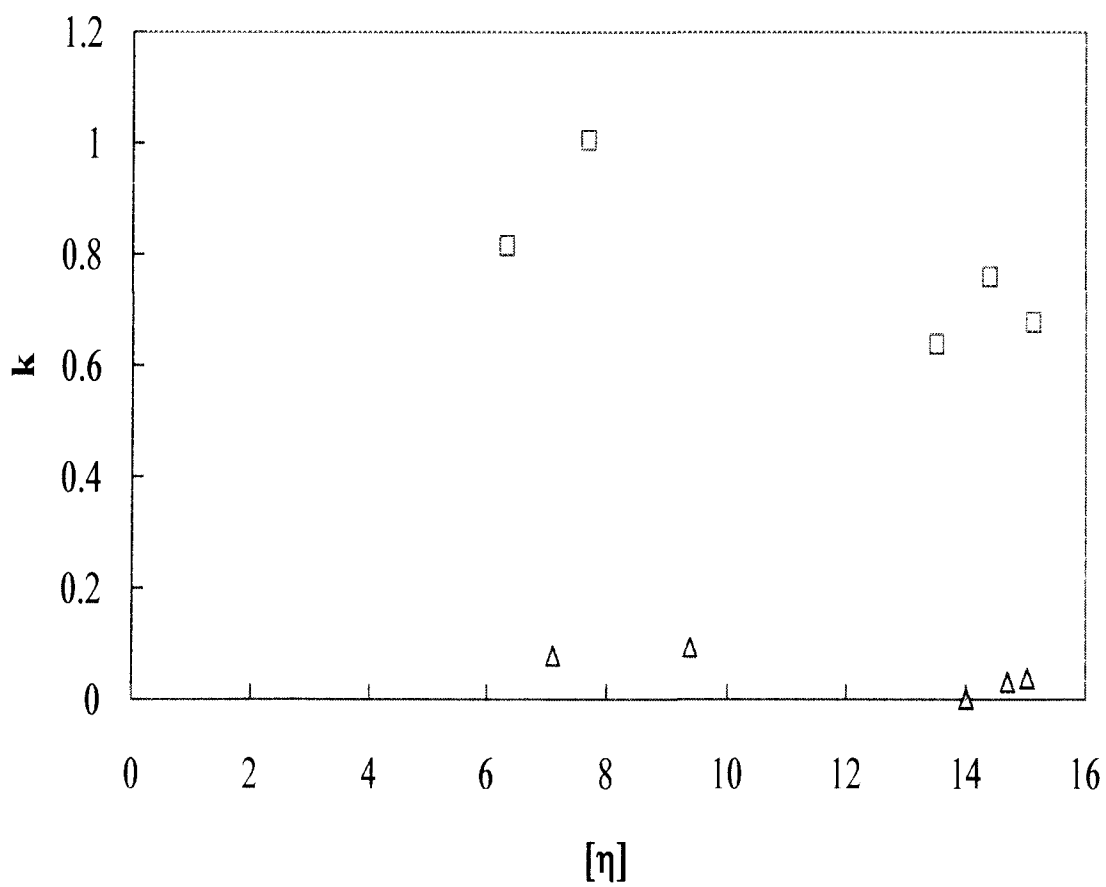
Fig. 3c Plot of intrinsic viscosity ([η]) vs viscometric constant (k) : □, Huggins value; Δ, Kraemers value

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

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

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

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

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

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

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

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

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

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

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

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

Table 7 Determination of molecular weight by Mark- Houwinks equation $[\eta] = KM^a$ where, $K = 0.00387$ 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	2.70	3.17	3.04	3.33	3.43	3.43	3.70
Poly-3	7.69	8.09	8.71	9.99	9.22	9.56	11.16
Poly-4	8.41	8.64	6.67	9.65	10.17	11.38	13.54
Poly-5	8.99	8.91	10.47	11.62	10.31	11.58	14.54

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

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

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

Table 9 Base oil properties

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

Table 10 Pour Point of additive doped Base oils

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

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

2.2.1 Introduction

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

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

2.2.2 Results and Discussion

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

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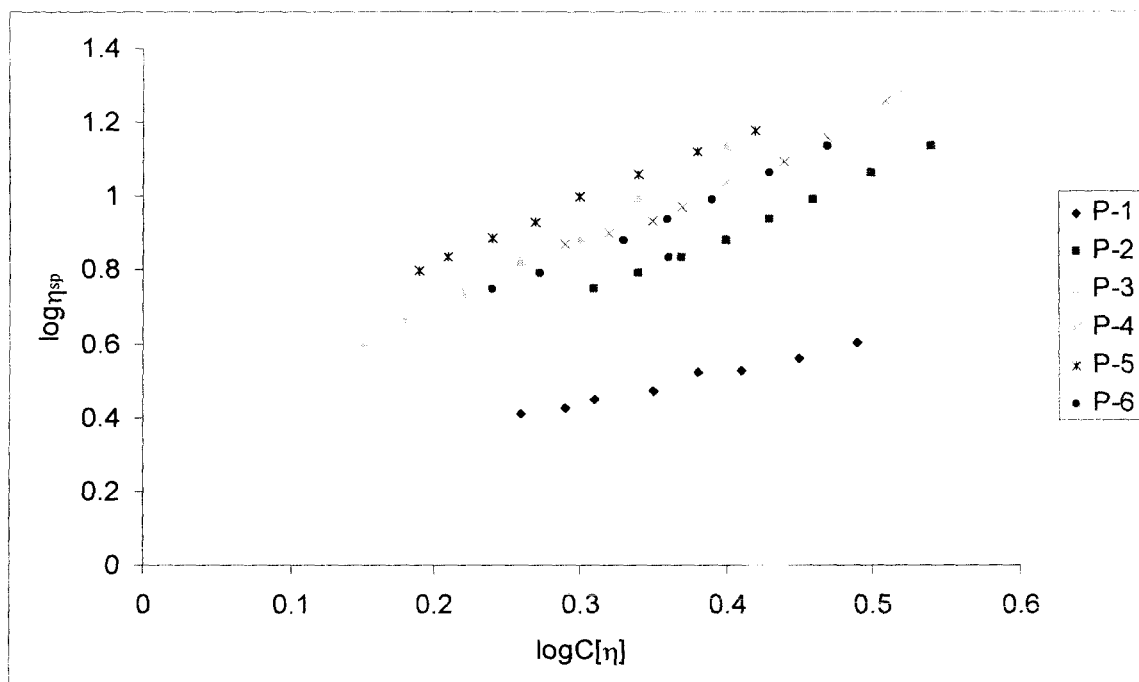
Fig 1a. Plot of logc[η] Vs logη$_{sp}$ for all polymeric samples in chloroform solvent. Where P-1 poly (methyl methacrylate), P-2 polystyrene, P-3 to P-6 are the copolymer of methyl methacrylate + different mass fractions of styrene.

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

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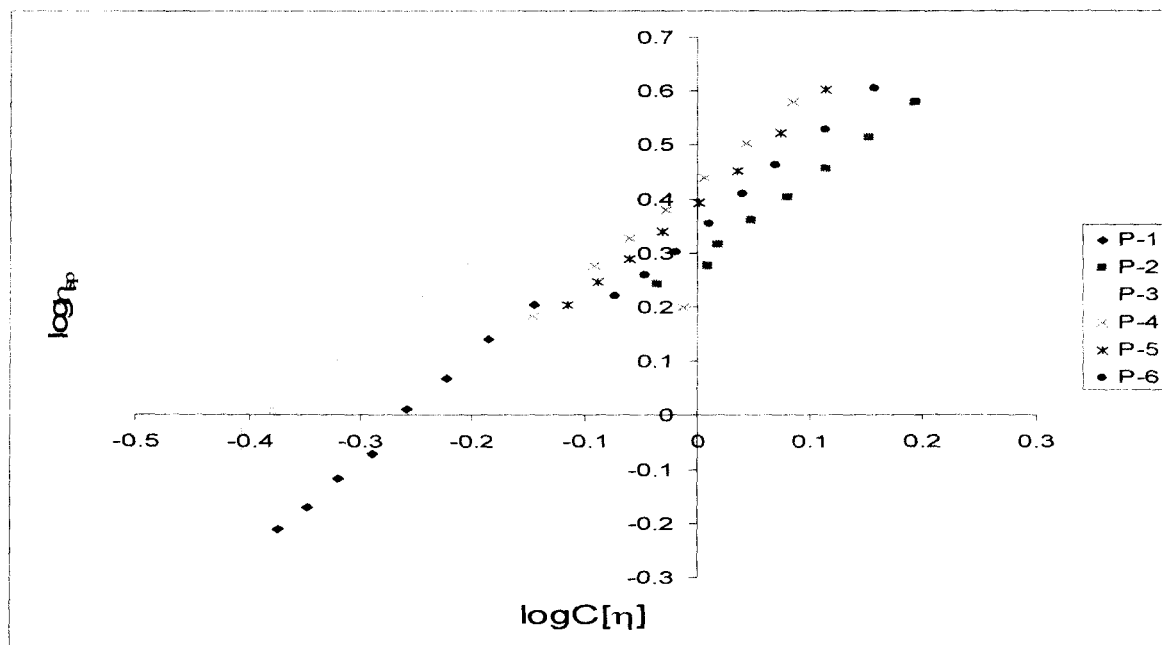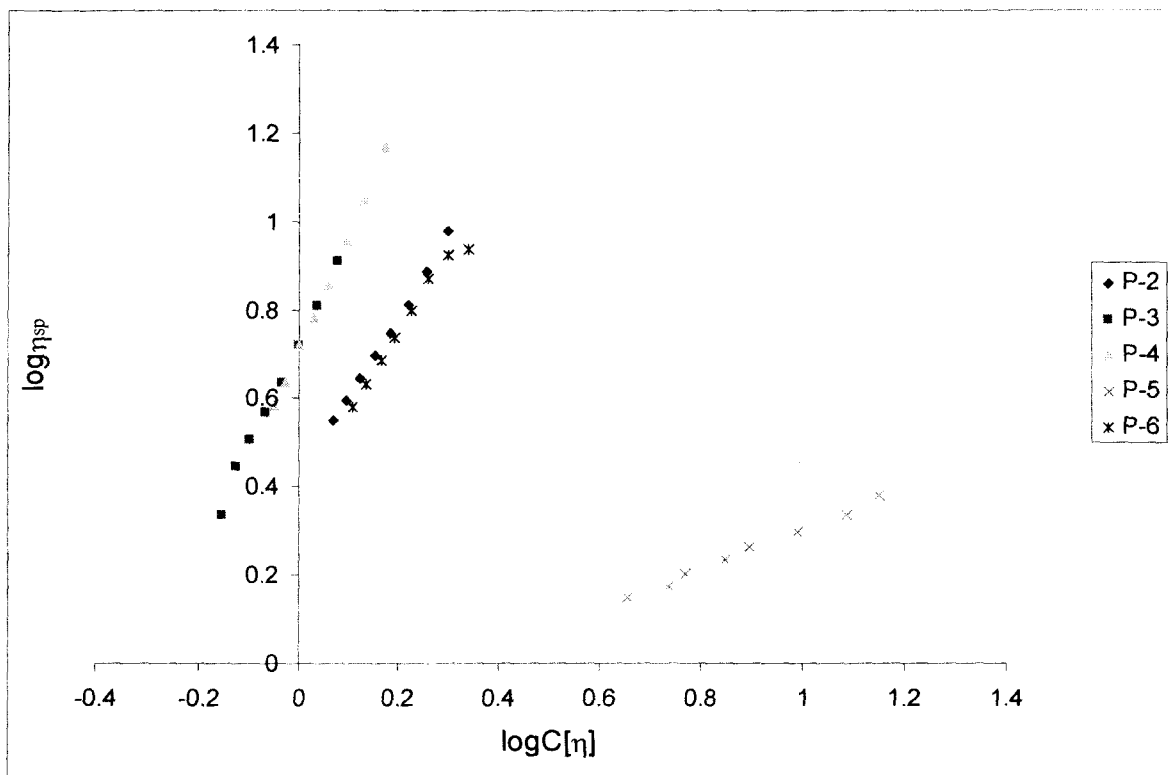**Fig 1c.** Plot of logC[η] Vs logη$_{sp}$ for all polymeric samples in carbon tetrachloride solvent. Where P-2 polystyrene, P-3 to P-6 are the copolymer of methyl methacrylate + different mass fractions of styrene.

Table 1A -1C presents intrinsic viscosity values related to all equations for the samples analyzed. Considering the different solvents employed (CHCl$_3$, Toluene, CCl$_4$) and comparing [η] for homo and copolymers, it is noticed that the higher values were obtained in chloroform followed by carbon tetrachloride and toluene. Thus considering all the polymers (homopolymer and copolymers) chloroform appeared to be more compatible to the polymer, leading to more extended conformations of the polymers in it. Carbon tetrachloride leads to the lowest values for the homo and copolymers, which varied in a small range in comparison to the other solvents, indicating similar contracted structures with a star like conformation [16]. Variation of [η] obtained by graphic extrapolation method (eq. 2-5) was found to be less compared to those obtained by single point determination method (eq. 6-7) without any restriction of solvent.

As expected, the copolymer and also the homopolymers did not show a correlation or a constant variation as far as [η] values, molecular weights and compositions are concerned [18]. It is also observed that [η] values increase with the increase in styrene concentration except in one or two cases. [η] values obtained by using DC equation are always higher irrespective of the nature of the solvent. PMMA was insoluble in CCl$_4$.

Table 2A – 2C presents the viscometric constant calculated for homo and co polymers, in CHCl$_3$. k_h and k_k fitted in the range of good solvents, whereas CCl$_4$ medium produced results indicating poor solvation and suggesting the formation of miceller spherical structure [18].

Although, k_{sb} values found for the samples were different from 0.28 the use of these values for the single point determination produced [η]$_{sb}$ values close to the ones obtained by extrapolation. It is also interesting to notice that for the best solvent, CHCl$_3$, k_{sb} values for the copolymer were close to 0.28. It is also important to observe that the relation $k_h + k_k = 0.5$ was not found for the great majority of the sample analyzed. However, both [η]$_{sc}$ and [η]$_{dc}$ were similar to [η]$_h$, [η]$_k$, [η]$_m$ and [η]$_{sb}$, which were obtained by graphic extrapolation, with small percentage differences . So values different from 0.5 did not put any restriction for the application of SC equation.

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

As expected different [η] values were obtained by graphic extrapolation of H, K, M, and SB equations in all the three solvents analyzed. In CHCl₃ the percentage differences of [η] values obtained for both the homo and copolymers when K, M and SB equations (graphic extrapolation) were compared to H equation, varied in the range from -23.07 to 14.38 and is less compared to the values (-12.53 to 92.89) obtained by using SB, SC and DC equations (single point determination method). In toluene the variations range from -20.00 to 66.96 and 23.45 to 66.96 respectively. In CCl₄ the percentage variation is much higher in both the cases. This suggests that the contracted structure of the homo and copolymers in CCl₄ solvent produces higher differences, both in graphic extrapolation and in one point determinations.

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

By comparing viscosity average molecular weight (M_v) Table 4A- 4C obtained in different solvents, with number average molecular weight obtained by SEC, it can be seen that M_v obtained in CHCl₃ found to be more close to the SEC values than the same obtained in other two solvents. This observation may be attributed to the comparatively poor solubility of the polymer in these solvents as is observed above in this study. It is also observed that in all the cases and irrespective of the solvents the single point determination values are more close to that of the SEC values rather than the graphical extrapolation values.

2.2.3 Conclusion

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

Table 1A. Intrinsic viscosity data in chloroform solvent

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

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

Table 1B. Intrinsic viscosity data in toluene solvent

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

Table 1C. Intrinsic viscosity data in carbon tetrachloride solvent

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

Table 2A. Viscometric constant values in chloroform

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

Table 2B. Viscometric constant values in toluene

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

Table 2C. Viscometric constant values in carbon tetrachloride

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

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

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

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

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

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

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

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

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

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

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

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

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