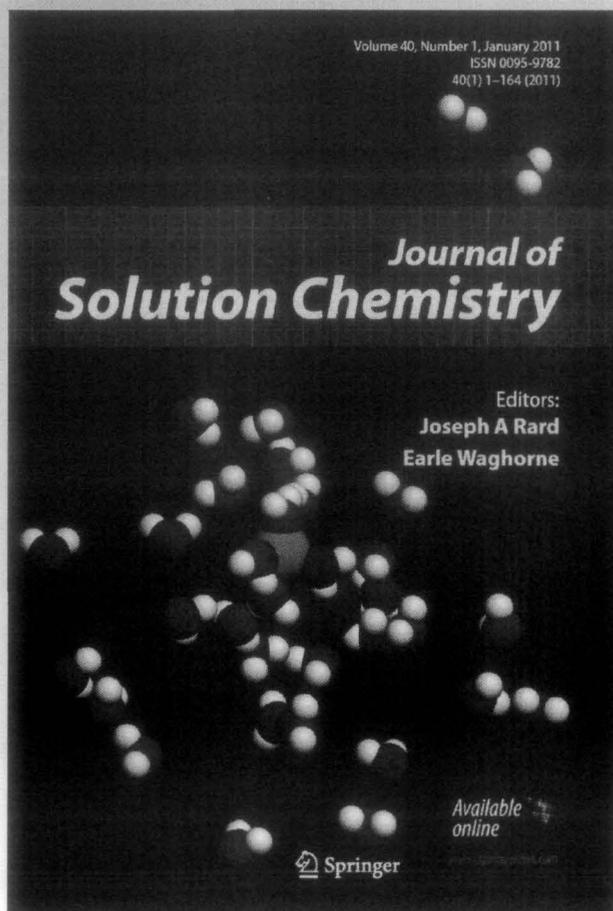


*Synthesis Characterization and Viscosity  
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## Synthesis Characterization and Viscosity Studies of Homopolymer of Methyl Methacrylate and Copolymer of Methyl Methacrylate and Styrene

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

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

### 1 Introduction

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

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

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

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

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

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

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

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

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

Huggins

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

Kremer

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

Martin

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

and Schulz-Blaschke

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

## 2 Experimental

### 2.1 Polymerization

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

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

## 2.2 Measurements

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells, and the spectra were recorded at room temperature over the wave number range (400 to 4000)  $\text{cm}^{-1}$ . NMR spectra were recorded in a Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe.  $\text{CDCl}_3$  was used as solvent and TMS as the reference material. Average molecular weights ( $M_w$  and  $M_n$ ) were obtained by SEC (GPC) using THF as mobile phase in a Water GPC system at  $(303 \pm 1)$  K. The retention times were calibrated against known monodisperse polystyrene standards [5].

## 2.3 Viscometric Measurements

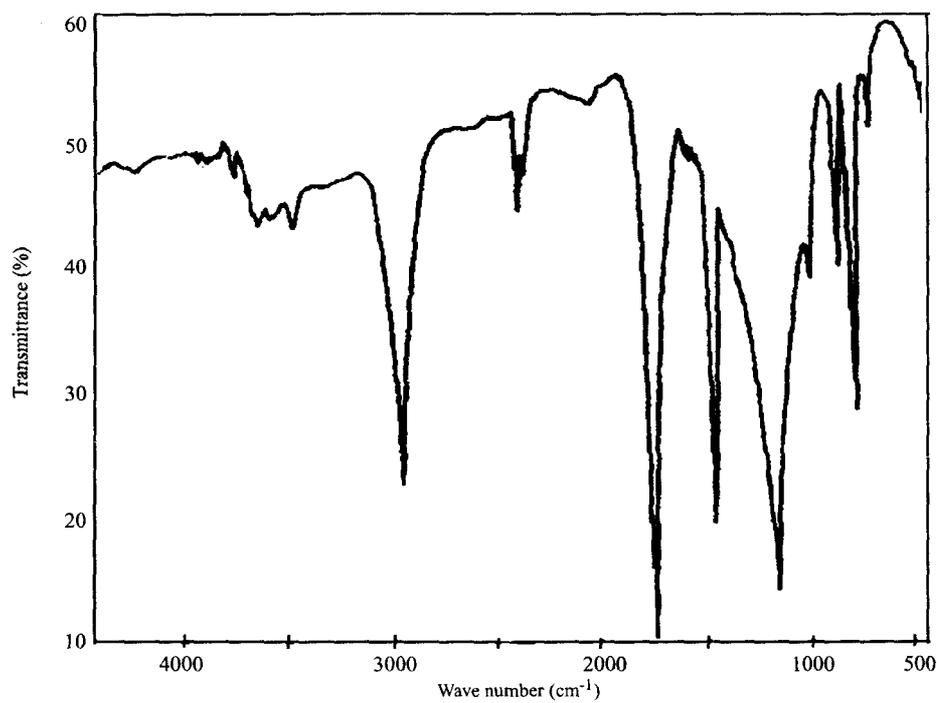
Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values  $K' = 0.00268 \text{ cm}^2 \cdot \text{s}^{-2}$ ,  $L = -19.83 \text{ cm}^2$ , the volume of the bulb is  $3 \text{ cm}^3$  and length of the capillary 11.3 cm). Experimental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

## 2.4 Thermogravimetric Analysis (TGA)

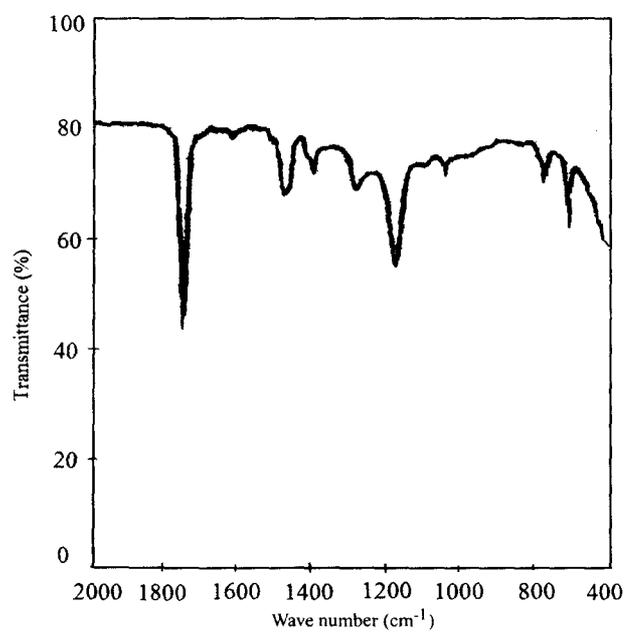
The thermograms were obtained in air on a Mettler TA-3000 system, at a heating rate of  $10 \text{ K} \cdot \text{min}^{-1}$ .

## 3 Results and Discussion

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



(a)



(b)

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

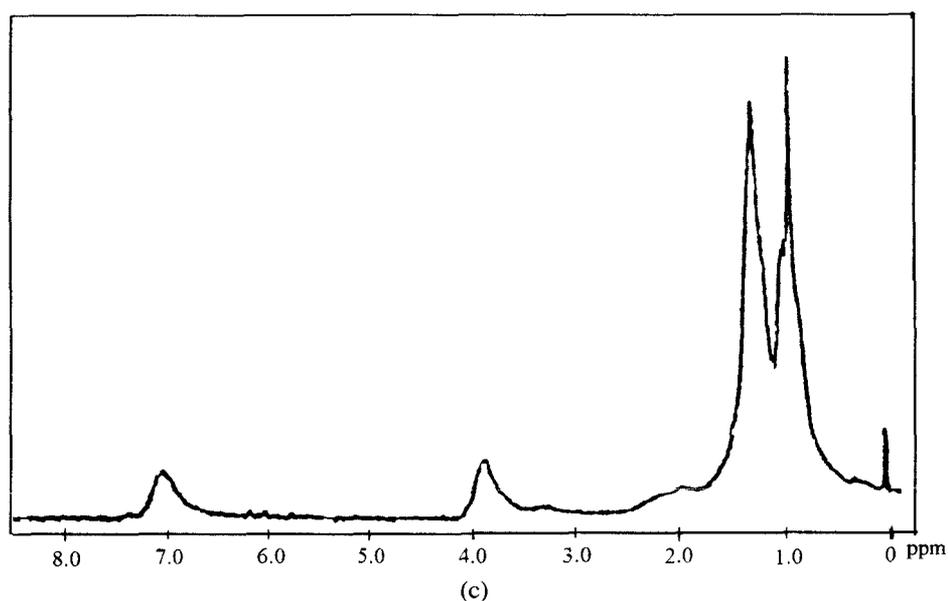


Fig. 1 (Continued.)

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

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

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

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

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

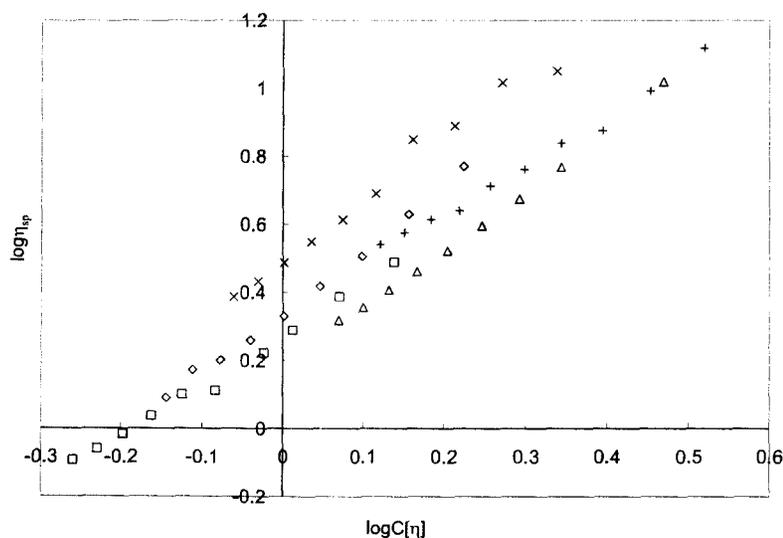
Using the graphic extrapolation method the respective intrinsic viscosities and constants were evaluated. In single point determinations, the SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is

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

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

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

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



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

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

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

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

<sup>a</sup>From extrapolation of graph

<sup>b</sup>Single point determination ( $k_{sb} = 0.28$ )

<sup>c</sup>Single point determination: h, k, m, sb, sc and dc refers Huggin, Kraemer, Martin, Schulz-Blaschke, Solomon-Ciute and Deb-Chanterjee equations, respectively

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

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

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

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

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

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

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

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

Sample	100 $\Delta$					
	K <sup>a</sup>	M <sup>a</sup>	SB <sup>a</sup>	SB <sup>b</sup>	SC <sup>b</sup>	DC <sup>b</sup>
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

<sup>a</sup>Data from extrapolation

<sup>b</sup>Data from single point determination

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

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

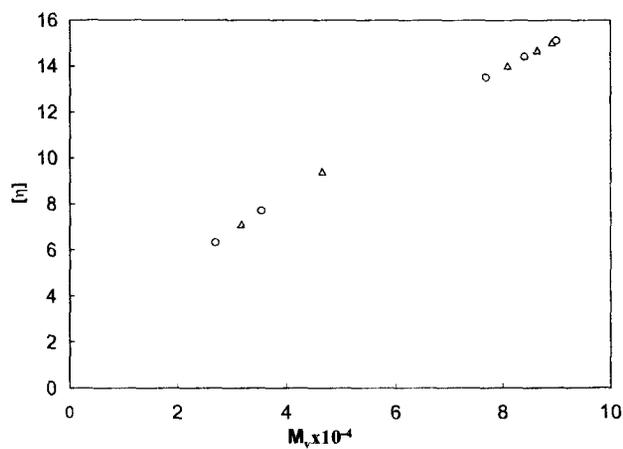
<sup>a</sup>Data from extrapolation

<sup>b</sup>Data from single point determination

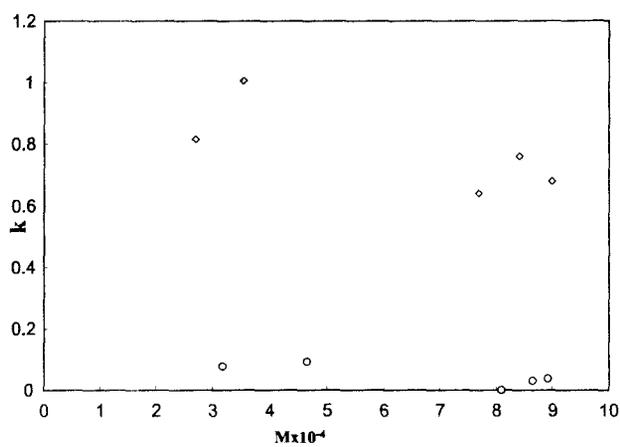
(-15.43 to 26.31%, Table 6) is narrow when compared to values obtained through the single point method using the SB, SC and DC equations (10.43 to 41.40%). Again, the percentage differences ( $\Delta = ([\eta]/[\eta]_h) - 1$ ) for the homopolymer are always higher (except one in each case) than for the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

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

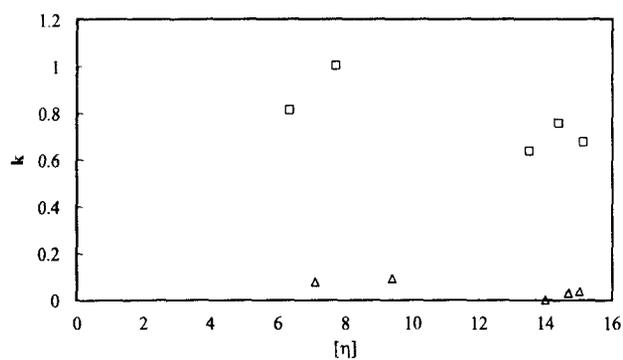
**Fig. 3** (a) Plot of the intrinsic viscosity ( $[\eta]$ ) versus the viscometric molecular weight ( $M_v \times 10^{-4}$ ):  $\circ$ , Huggins' value;  $\Delta$ , Kraemer's value. (b) Plot of the viscometric constant ( $k$ ) versus the molecular weight ( $M \times 10^{-4}$ ):  $\diamond$ , Huggins'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



(a)



(b)



(c)

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

Sample	100 $\Delta$					
	$M_k^a$	$M_m^a$	$M_{sb}^a$	$M_{sb}^b$	$M_{sc}^b$	$M_{dc}^b$
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

<sup>a</sup>Data from extrapolation

<sup>b</sup>Data from single point determination

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

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

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

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

#### 4 Conclusions

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

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

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## Abstract

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

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

## Introduction

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

Again, since the performance of such kind of additives in the field condition is very much dependent on the structure and morphology of the polymers in dissolved solvent<sup>3</sup>, viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation of the polymer in dilute solutions are concerned. Therefore, the study may be very useful for evaluating the performance of polymer blended oil as an additive for lube oil, where the structure and morphology plays a significant role. Despite this, such information regarding lube oil additives is not yet emphasized.

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

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

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

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

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

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

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

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

The method of single point determination (equation 5-6) has the advantage of being considerably faster and can be adequate when a large number of samples are to be analyzed in short periods of time, particularly in industry laboratories. The use of these equations has been derived under the supposition of the validity of the relationship<sup>7</sup>  $k_b + k_k = 0.5$ .

Polymer samples may present the same molecular mass but may also be linear or branched showing different sizes and shapes. The conformation of the chain in solution and, consequently, the volume it occupies in the solvent medium, is completely dependent on the type of solvent and the temperature of the measurement. The better is the solvent, the higher extended conformation the chain will assume<sup>1</sup>. Thus the viscometric study, which is a function of molecular size and not the molecular mass, of the polymer solutions in different solvents may yield very useful parameters required for the choice of end application of the polymers.

Huggins and Kraemer coefficients are adequate to evaluate the quality of the solvent. Huggins coefficient ( $k_h$ ) is accepted as a parameter related to polymer-solvent interactions. Experimental results indicate that the higher is the affinity between polymer and solvent, the lower is the  $k_h$  value. A range varying from 0.25 to 0.5 is attributed to good solvation whereas values above 0.5-1.0 are found for poor solvents and theta solvents<sup>3-7</sup>. At the same time, negative values for the Kraemer coefficient ( $k_k$ ) indicate good solvents and positive values indicate poor ones<sup>3-5</sup>.

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

## Material and Methods

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

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

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

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

## Results and Discussion

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

<sup>1</sup>H NMR spectra indicated the presence of a phenyl group at 7.2 ppm and a -OCH<sub>2</sub> group from the acrylate at 3.9 ppm. The absence of signals between 5 and 6 ppm indicated the absence of vinylic protons of styrene.

Table I presents a comparison between the values of molecular mass obtained by GPC for homo polymer and copolymers along with the polydispersity. As reported earlier<sup>9</sup>, the molecular weight increases with the increase in the concentration of styrene in the monomer composition. Higher values of polydispersity were observed for the copolymers.

Viscometric data were acquired using the six equations mentioned. Linear relationship for the plot of  $\log h_{sp}$  vs.  $\log c$  [h] (Fig 1a-1c) indicated that the measurements were performed in Newtonian flow<sup>10-12</sup>. Huggins (H), Kraemer (K), Martin (M) and Schulz-Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz-Blaschke (SB), Solomon-Ciuta (SC) and Deb-Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz-Blaschke (SB) equation

is commonly applied in single point determinations because it was found that  $k_{sb} = 0.28$  for many polymer-solvent systems<sup>4-8</sup>. In this work, this value has been used.

Tables IIA-IIC present intrinsic viscosity values related to all equations for the samples analyzed. Considering the different solvent employed ( $\text{CHCl}_3$ , Toluene,  $\text{CCl}_4$ ) and comparing  $[\eta]$  for homo and copolymers, it is noticed that the higher values were obtained in chloroform followed by carbon tetrachloride and toluene. Thus considering all the polymers (homo polymer and co polymers), chloroform appeared to be more compatible to the polymer, leading to more extended conformations of the polymers. Carbon tetrachloride leads to the lowest values for the homo and copolymers, which varied in a small range in comparison to the other solvents, indicating similar contracted structures with a star like conformation<sup>9</sup>. Variation of  $[\eta]$  obtained by graphic extrapolation method (equation 1-4) was found to be less compared to those obtained by single point determination method (equation 5-6) without any restriction of solvent.

As expected, the copolymer and also the homo polymers did not show a correlation or a constant variation as far as  $[\eta]$  values, molecular weights and compositions are concerned<sup>3</sup>. It is also observed that  $[\eta]$  values increase with the increase in styrene concentration except in one or two cases.  $[\eta]$  values obtained by using DC equation are always higher irrespective of the nature of the solvent. PMMA was insoluble in  $\text{CCl}_4$ .

Tables IIIA – IIIC present the viscometric constant calculated for homo and co polymers in  $\text{CHCl}_3$ ,  $k_b$  and  $k_k$  fitted in the range of good solvents, whereas  $\text{CCl}_4$  medium produced results indicating poor solvation suggesting the formation of micellar spherical structure.<sup>3</sup>

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

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

As expected different  $[\eta]$  values were obtained by graphic extrapolation of H, K, M and SB equations<sup>3-7</sup> in all

the three solvents analyzed. In  $\text{CHCl}_3$ , the percentage differences of  $[\eta]$  values obtained for both the homo and copolymers when K, M and SB equations (graphic extrapolation) were compared to H equation, varied in the range from -23.07 to 14.38 and are less compared to the values (-12.53 to 92.89) obtained by using SB, SC and DC equations (single point determination method). In toluene, the variation ranges are from -20.00 to 66.96 and 23.45 to 66.96 respectively. In  $\text{CCl}_4$ , the percentage variation is much higher in both the cases. This suggests that the contracted structure of the homo and copolymers in  $\text{CCl}_4$  solvent produces higher differences, both in graphic extrapolation and in one point determinations.

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

Table V presents the thermal stability of the polymers. As expected, the TGA data showed that the copolymers are better in thermal stability than the homopolymers. Table VI presents the molecular weight obtained by viscometric methods (Mv) for homo polymer and co polymers analyzed. The general trend is a gradual increase in molecular weight with the increase of styrene concentration. However, as expected, a difference was observed in the values of molecular weight (Mv) obtained by SEC and viscometry. This is probably due to the differences in analysis conditions like solvents, temperature, techniques and standard employed<sup>15</sup>.

By comparing viscosity molecular weight (Mv) obtained in different solvents with number average molecular weight obtained by SEC, it can be seen that Mv obtained in  $\text{CHCl}_3$  was found to be more close to the SEC values than the same obtained in other two solvents which may be attributed to the comparatively poor solubility of the polymer in these solvents as observed above in this study. It is also observed that in all the cases and irrespective of the solvents, the single point determination values are more close to that of the SEC values rather than the graphical extrapolation values.

## Conclusion

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

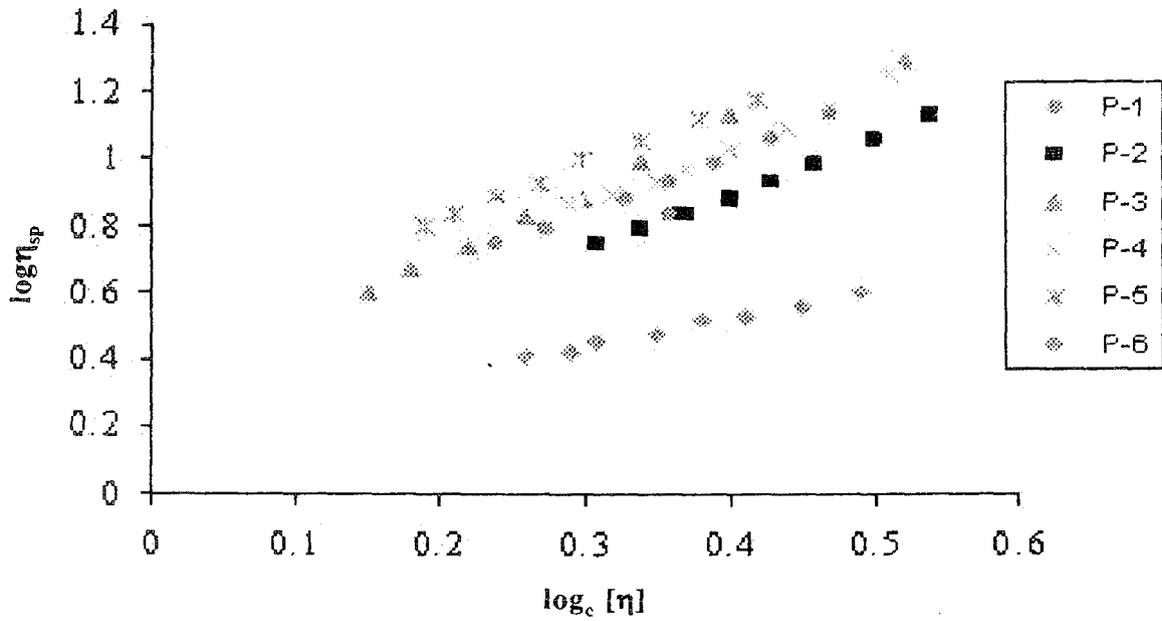


Fig. 1a: Plot of  $\log \eta_{sp}$  Vs  $\log_e [\eta]$  for chloroform solvent

Table I  
Molecular weight of the polymers

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

Table II A  
Intrinsic Viscosity Data in chloroform solvent

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

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

**Table II B**  
**Intrinsic Viscosity Data in toluene solvent**

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

**Table II C**  
**Intrinsic Viscosity Data in carbon tetrachloride solvent**

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

**Table III A**  
**Viscometric constant values in chloroform**

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

**Table III B**  
**Viscometric constant values in toluene**

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

**Table III C**  
Viscometric constant values in carbon tetrachloride

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

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

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

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

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

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

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

**Table V**  
TGA data for homo and co polymers

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

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

### Acknowledgement

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

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

Using chloroform solvent

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

Using toluene

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

Using carbon tetrachloride

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

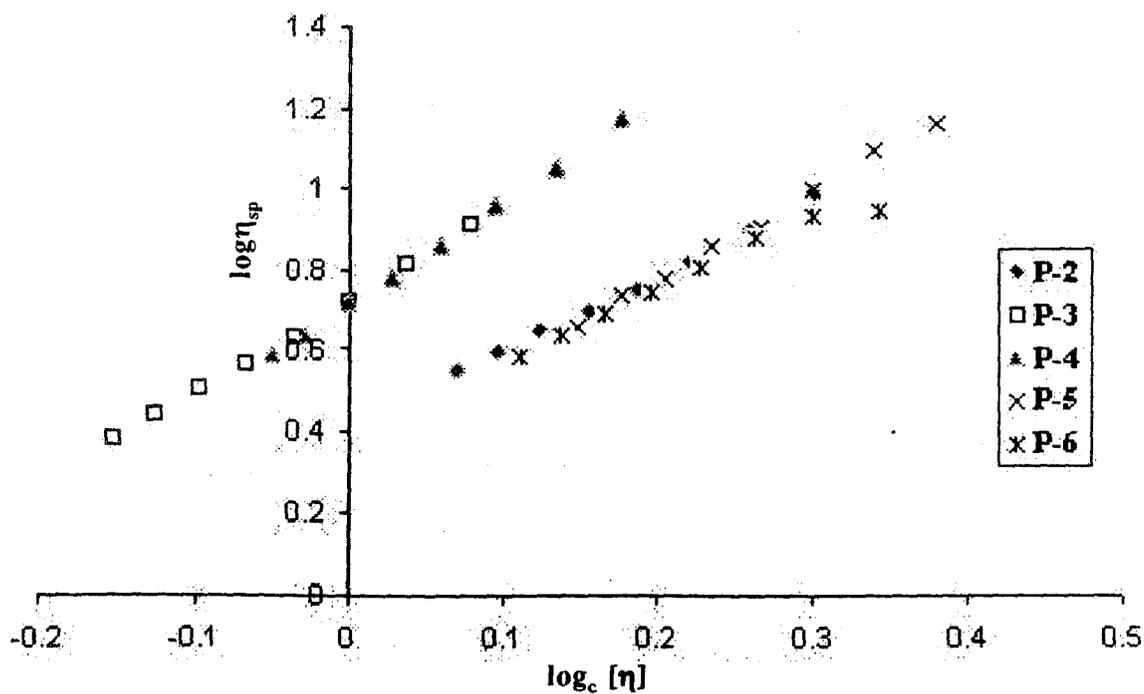
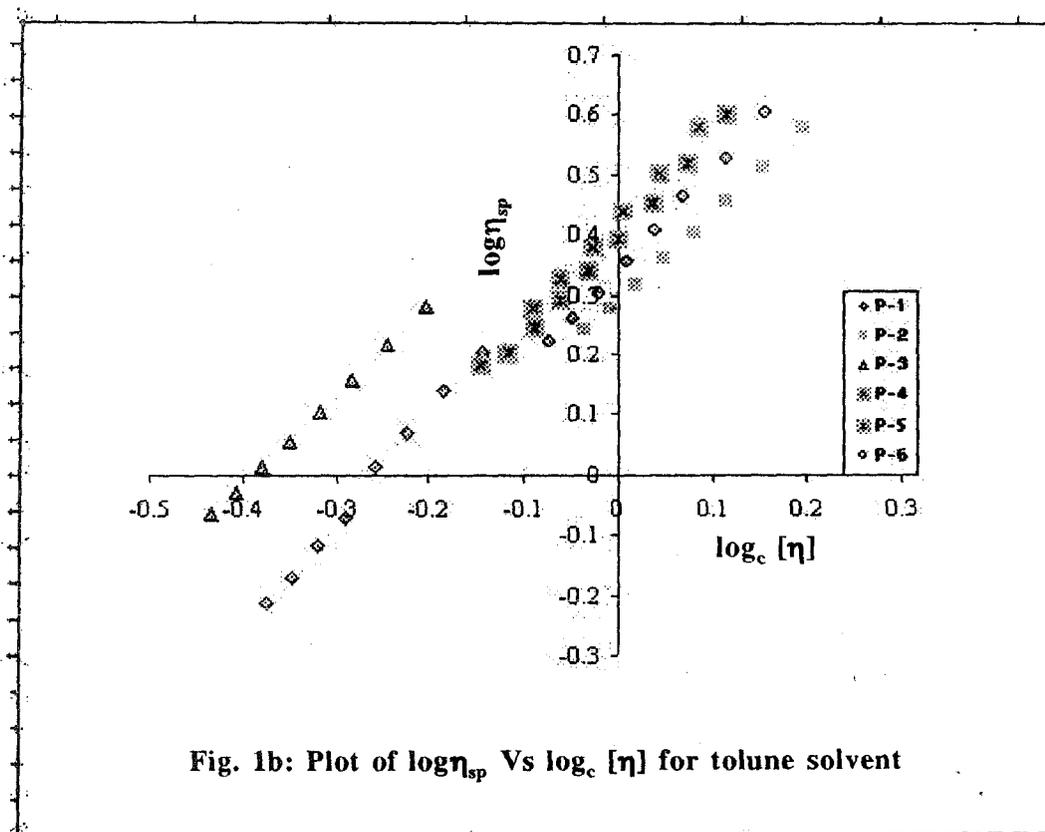


Fig. 1c: Plot of  $\log \eta_{sp}$  Vs  $\log_c [\eta]$  for carbon tetrachloride solvent

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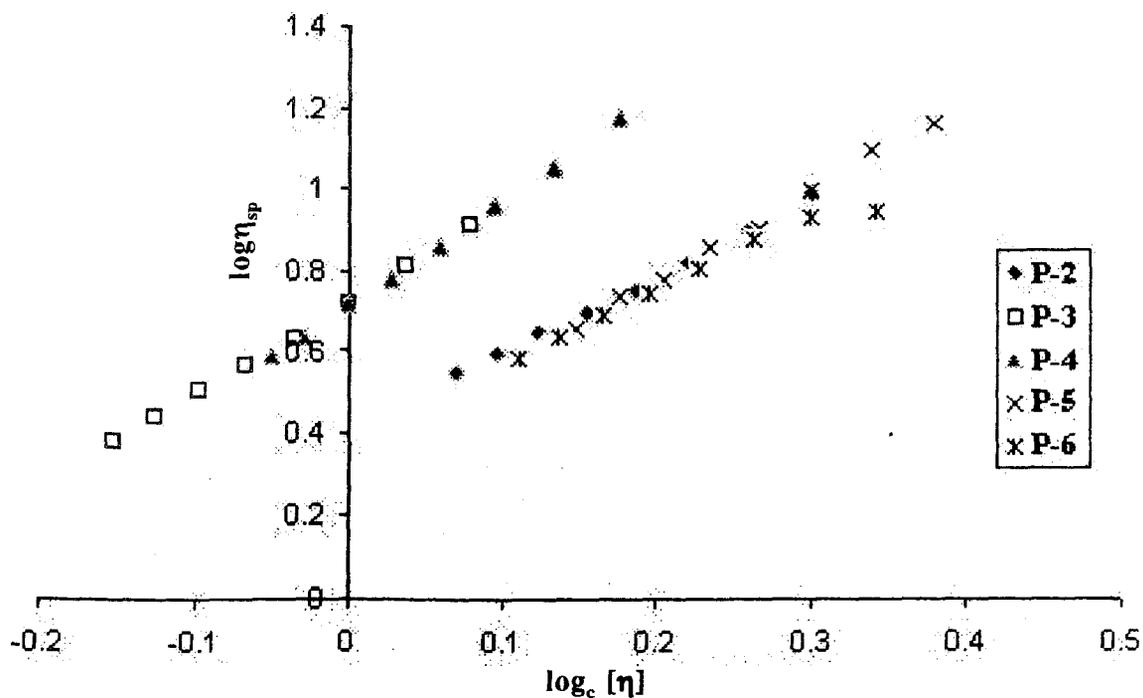
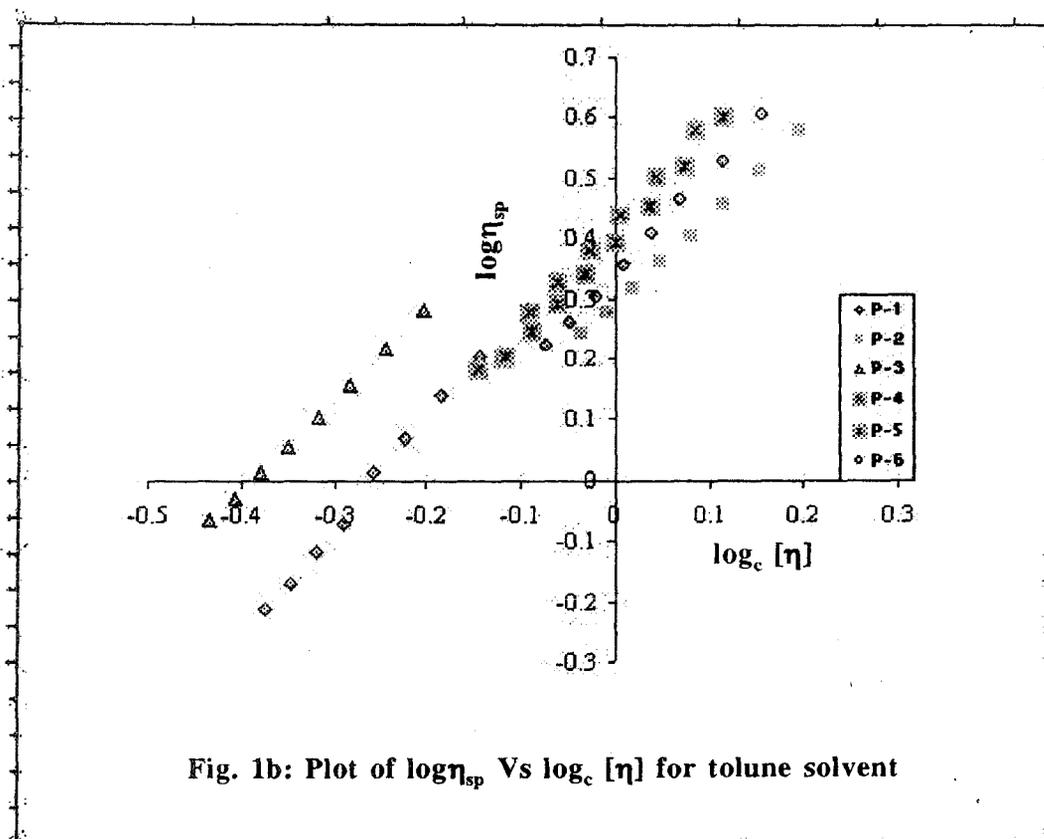


Fig. 1c: Plot of  $\log \eta_{sp}$  Vs  $\log_c [\eta]$  for carbon tetrachloride solvent

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

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### **ABSTRACT**

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

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

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

## 1.0 INTRODUCTION

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

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

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

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

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

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

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

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

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

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

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

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

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

Where,

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

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

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

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

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

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

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

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

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

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

## 2.0 EXPERIMENTAL

### 2.1 Materials used

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

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

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

Decyl acrylate was prepared by reacting acrylic acid with decyl alcohol (1.1:1 molar ratio). The reaction was carried out in a resin kettle in the presence of catalytic amount of concentrated sulphuric acid, 0.25% hydroquinone (with respect to the monomer) as polymerization inhibitor for acrylic acid, and toluene as a solvent under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 130<sup>0</sup>C using a well-controlled thermostat. The progress of reaction was followed by monitoring the amount of liberated water from the reaction mixture to give the ester, decyl acrylate.

## **2.3 Purification of prepared ester**

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

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

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

maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K. A homo polymer of DA was similarly prepared and purified under the same conditions for use in reference experiments.

## **2.5 Preparation of Polymer – base oil blend**

Base oils of three different viscosity grades, B1 and B2 and B3 (Table 5) were collected from two different refineries, A and B. In all the cases blending of the additives with the oils were carried out by taking required amount of polymer in the calculated amount of oil (w/w) and then heating the mixture at 60<sup>0</sup>C for 30 min with constant stirring.

## **3.0 MEASUREMENTS**

### **3.1 Spectroscopic measurements**

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells and the spectra were recorded at room temperature within the wave number range (400 to 4000) cm<sup>-1</sup>. NMR spectra were recorded in Bruker Avance 300MHz FT-NMR spectrometer using 5 mm BBO probe. CDCl<sub>3</sub> was used as solvent and TMS as reference material..

### **3.2 Viscometric measurements**

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

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

### **3.3 Thermo gravimetric analysis (TGA)**

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

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

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

## **4.0 RESULTS AND DISCUSSION**

### **4.1 Spectroscopic analysis**

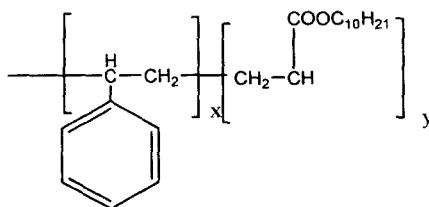
FT-IR spectrum of the homo polymer (Figure 1) exhibited absorption at  $1732 \text{ cm}^{-1}$  due to ester carbonyl stretching vibration. Peak at  $1260$  and at  $1175 \text{ cm}^{-1}$  can be explained owing to the C-O (ester bond) stretching vibration and the absorption bands at  $975$ ,  $750$ 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

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

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

at 4.06 ppm was due to the proton of the  $-OCH_2$  group. The absence of singlets between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer. Thus, as was expected, there is incorporation of styrene in the acrylate chain during copolymerization.

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



Structure-1

The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of  $-OCH_2$  group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports as well as on the basis of our earlier paper [8].

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

#### 4.2 Thermal stability of the prepared compounds

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

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

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

### 4.3 Viscometric analysis

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

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

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

### 4.4 Performance of the homo and copolymers as PPD

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

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

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

## 5.0 CONCLUSIONS

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

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

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

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

**Table 2:** Thermal Gravimetric Analysis Data of all prepared samples

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

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

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

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

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

**Table 5:** Base oil properties

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

**Table 6:** Pour Point of additive doped Base oils

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

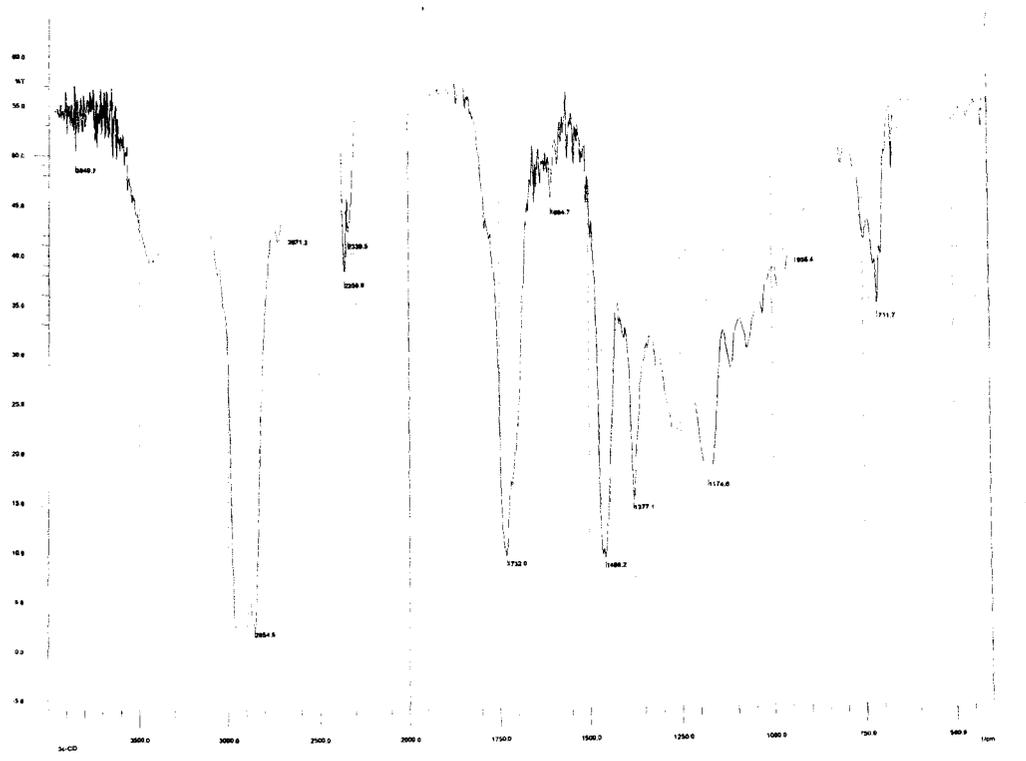


Figure 1 : FT- IR spectrum of homodecyl acrylate

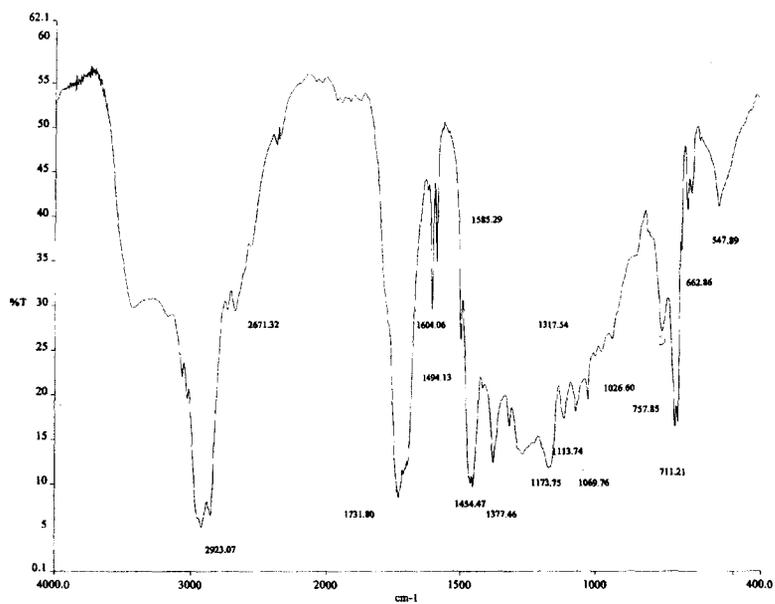


Figure 2: FT- IR spectrum of copolymer of Decylacrylate with styrene

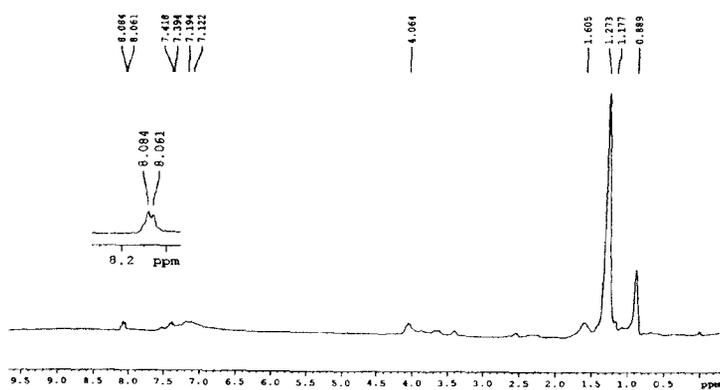
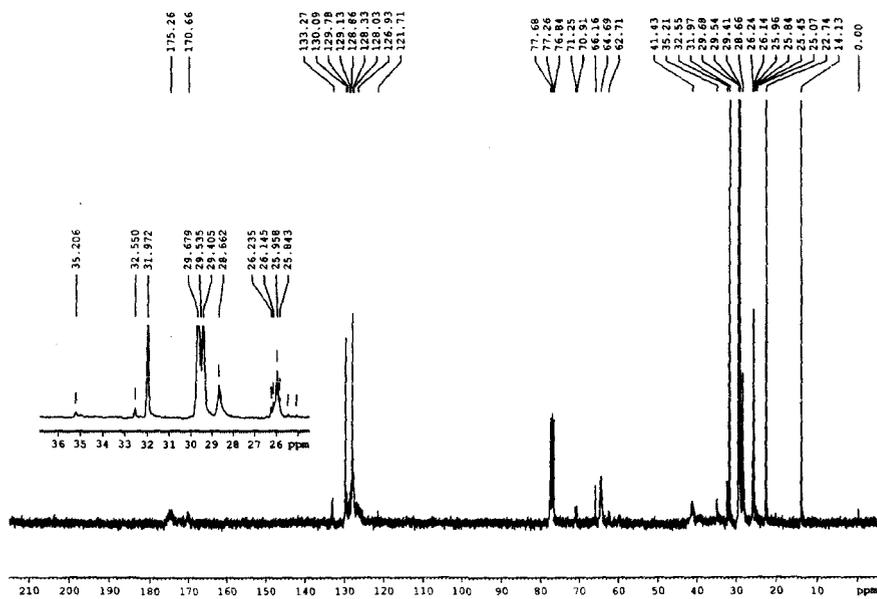


FIGURE 3: <sup>1</sup>H NMR spectrum of copolymer of Decylacrylate with styrene



**FIGURE 4:**  $^{13}\text{C}$  NMR spectrum of copolymer of Decylacrylate with styrene

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

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## Abstract

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

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

## Introduction

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

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

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

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

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

Many types of additives are used to improve the viscosity index and pour point depressants for lubricating oil. Additives are mainly polymers with molecular weights ranging from 25,000 to over one million, the most widely known among them are polyisobutene and polyalkylmethacrylates. It is anticipated that suitably tailored copolymers of these types can exhibit a better performance as lube oil additives. Styrene is one of the least expensive and most readily available monomers. It is used extensively in the synthesis of various polymeric products for lube oils<sup>1-3</sup>.

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

radical polymerization technique using benzoyl peroxide (BZP) as initiator in toluene solvent. Polymerization was carried out following the procedure as reported earlier<sup>4</sup>. Homo polymer of IDA and DDA were also prepared under identical condition.

Physical characterization of the copolymers was carried out employing Viscometrical Analysis, Thermo Gravimetric Analysis (TGA), IR and NMR techniques. However, since performance of such kind of additives in field condition is very much dependent on the structure and morphology of the polymer in desired solvent<sup>5</sup>, viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution is concerned. Viscometry is the simplest technique used to study the macromolecules in solution and determine their molecular weight. According to Mark Houwink – Sukurda relation (Eq. 1), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

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

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

When a polymer has a higher molecular weight, it has a bigger hydrodynamic volume; that is, the volume that the coiled up polymer takes up in solution. Being bigger, the polymer molecule can block more motion of the solvent molecules. It might be said that it can block off more lanes of the highway. Also, the bigger a polymer is, the stronger its secondary forces are. So the higher is the molecular weight, the more strongly the solvent molecules will be bound to the polymer. This enhances the slowing-down of the solvent molecules. Because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from other techniques, generally in determination of molecular mass of samples. A number of mathematical relations are available in literature for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation<sup>5-9</sup>. The most commonly used equations are:

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

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

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

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

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

Some relations have been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination method. This method has the advantage of being considerably faster and can be adequate when a large number of samples must be analysed in short period of time, practically in industrial laboratories. Most useful of them<sup>5-9</sup> are Solomon- Ciuta (SC, Eq. 6) and Deb –Chatterjee (DC, Eq. 7) relations.

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

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

The use of these equations has been derived under the supposition of the validity of the relationship  $k_h + k_k = 0.5$ <sup>9</sup>. 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<sup>5</sup> in the base stock, the process of polymerization in the presence of a suitable solvent has been attracting great interest now-a-days<sup>10,11</sup>. Since the behaviour of polymers especially the co polymers in solution is a complex phenomenon, a comparison involving the values of their intrinsic viscosity obtained by graphic extrapolation and by a single point determination should be interesting. In this work, viscometrical parameters (intrinsic viscosity and the value of constants) in toluene solution of the sample of poly acrylate and co-polymer having different percentage (w/w) of styrene are obtained by graphic extrapolation and single point determination method. The viscosity average molecular weight determined by using different equations were compared.

## Material and Methods

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

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

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

**Preparation of copolymer and homo polymer:** The copolymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which styrene is added drop wise. In the flask, desired mass of IDA and initiator (BZP) were placed followed by addition of the desired mass of styrene drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 4 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K. Homopolymer of IDA, homopolymer of DDA and copolymer of DDA with styrene were similarly prepared and purified under the same conditions for use in reference experiments.

**Measurements:** Spectroscopic IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells and the spectra were recorded at room temperature within the wave number range 400 to 4000  $\text{cm}^{-1}$ . NMR spectra were recorded in Bruker Advance 300 MHz FT-NMR spectrometer using 5 mm BBO probe.  $\text{CDCl}_3$  was used as solvent and TMS as reference material.

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

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

## Results and Discussion

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

The existence of its copolymer with styrene was confirmed by FT-IR,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR analysis. In its FT-IR spectra, the copolymer showed a broad peak ranging from 1722-1732  $\text{cm}^{-1}$  along with other peaks at 753.56, 712.15, 700.75, 667.98  $\text{cm}^{-1}$  which were due to C-H bond of the phenyl group of styrene. In the  $^1\text{H}$  NMR spectra of the copolymer, a broad multiplet ranging from 7.23 to 7.58 ppm indicated the presence of phenyl group of styrene. Broad singlet at 4.06 ppm was due to the proton of  $-\text{OCH}_2$  group. Methyls of the isodecyl chain appeared between 0.81 to 0.86 ppm. The absence of singlets between 5 and 6 ppm indicated the absence of any vinylic proton in the copolymer. The existence of copolymer was further confirmed by the presence of aromatic carbon ranging between 124 to 141 ppm in the  $^{13}\text{C}$ -NMR spectrum of the polymer. The carbonyl carbon appears at 174.47 ppm along with other carbons. The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of signal of  $-\text{OCH}_2$  group at 4.6 ppm. Area of signal of phenyl group at 7.40 ppm is based on earlier reports<sup>4</sup>. It was further confirmed through FT-IR spectral data. The intensity of carbonyl absorption in FT-IR spectra of the copolymer was analysed for quantitative determination of the content of acrylate component in the copolymer (Table I).

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

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

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

flow<sup>12-14</sup>. 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 systems<sup>6-9</sup>. Table II presents intrinsic viscosity values related to all equations for the samples analysed. Taking into account of the data for homo and all copolymer samples, it can be noticed that in both cases (P-1 to P-4 and P-5 to P-6), values are consistent. Comparison among the copolymers indicated that there is a gradual increase of  $[\eta]$  values with the increase of styrene content in the monomer composition. This indicates more extended conformation of the polymer chain compared to poly isodecyl acrylate and poly dodecyl acrylate itself.

Although different intrinsic viscosity values may be found by graphic extrapolation of Huggins, Kraemer, Martin and SB equation (eq 2 to 6), but in this work the data obtained from these four equations showed a tendency to be close for homo and copolymers. For the homopolymer and co-polymer  $[\eta]$  values obtained by Huggins and Kramer's equation were similar. Both homopolymer and copolymers in toluene medium indicated poor salutations (Table III) as is evident from the respective viscometrical constant values and thus point towards the formation of micelle or spherical structures as discussed earlier<sup>5</sup>.

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

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

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

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

## Conclusion

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

## Acknowledgement

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Table I

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

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

Table II

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

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

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

Table III

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

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

Table IV

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

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

Table V

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

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

Table VI

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

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

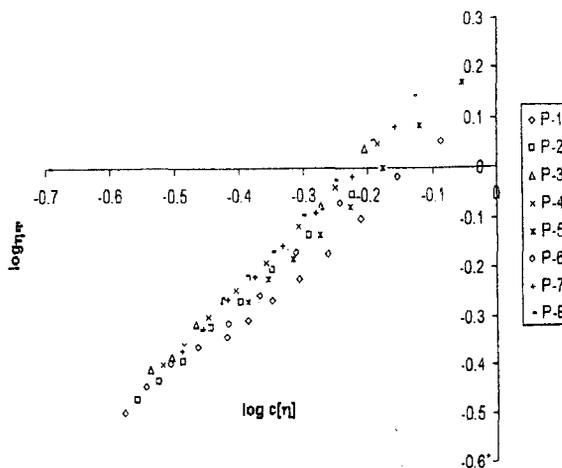
Table VII

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

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

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

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

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In continuation of our studies towards the development of polymeric additives for lubricating oil we report herein the synthesis, characterization and viscometric studies of homo polymer of decyl acrylate and its copolymer with styrene in different base stocks at 40<sup>0</sup>C. In order to get more information about the structure and morphology of the polymer when dissolved in base stocks (ie in field application), viscometric measurements of the synthesized homo polymer as well as that of the co polymer were performed in the base oils at 40<sup>0</sup>C. Different equations were used to calculate intrinsic viscosity and viscometric constants values and molecular weight of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight obtained by the two methods (single point determination and graphical extrapolation) were compared. Measurements of viscometric properties included the determination of specific viscosity (it determines the contribution of solute to the viscosity of the solution), the reduced viscosity (that provides the measurements of the polymer capacity of increasing the solution viscosity) and intrinsic viscosity.

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

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## Introduction

Base oil also known as lubricant base oil, is the basic building block of a lubricant. They are complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with molecular weights ranging from medium to high values, very low volatility and with high viscosity index. The proportions of different hydrocarbon components determine the characteristics of the base oils.

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

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

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

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

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

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

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

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

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

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

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

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

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

Where,

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

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

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

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

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

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

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

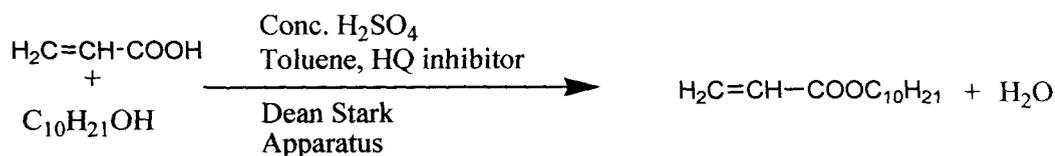
$$[\eta] = [2(\eta_{sp} - \ln\eta_r)]^{1/2}/C \quad (6)$$

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

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

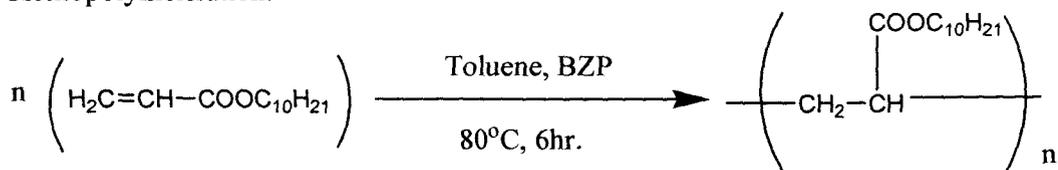
### Scheme I

Esterification:



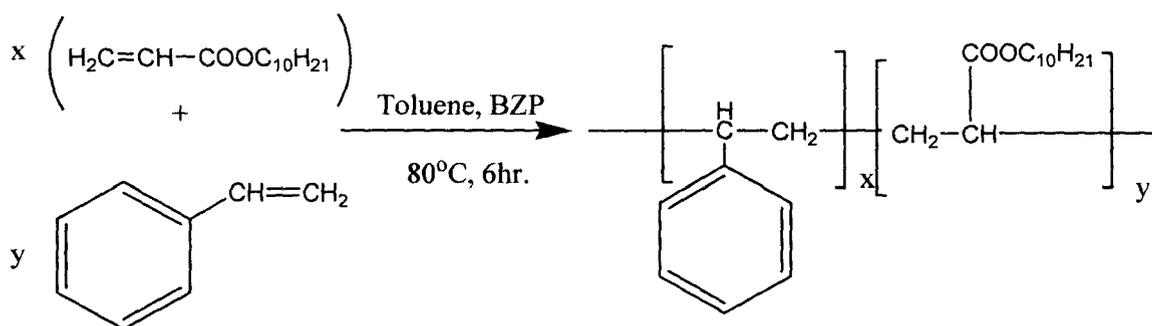
### Scheme-II

Homopolymerisation:



### Scheme-III

Copolymerisation:



## Experimental

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

Decyl acrylate was prepared by reacting acrylic acid with decyl alcohol (1.1:1 molar ratio). The reaction was carried out in a resin kettle in the presence of concentrated sulphuric acid as a catalyst, 0.25% hydroquinone as polymerization inhibitor for acrylic acid, and toluene as a solvent under a slow stream of deoxygenated nitrogen. The reactants, which were mixed with toluene, were heated gradually from room temperature to 130°C using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give the ester, decyl acrylate.

### ***Purification of prepared ester***

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

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

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

### ***Preparation of Polymer –base oil blend***

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

## Measurements

### *Spectroscopic measurements*

IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells and the spectra were recorded at room temperature within the wave number range (400 to 4000)  $\text{cm}^{-1}$ . NMR spectra were recorded in Bruker Avance 300MHz FT-NMR spectrometer using 5 mm BBO probe.  $\text{CDCl}_3$  was used as solvent and TMS as reference material.

### *Viscometric measurements*

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

### *Thermo gravimetric analysis (TGA)*

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

## Results and discussion

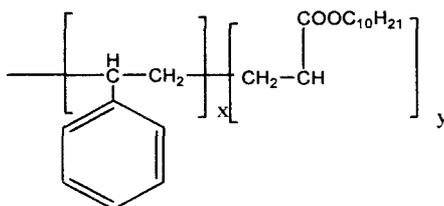
FT-IR spectrum of the homo polymer (Fig.1) exhibited absorption at  $1732 \text{ cm}^{-1}$  due to ester carbonyl stretching vibration. Peak at  $1260$  and at  $1175 \text{ cm}^{-1}$  can be explained

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

The existence of the copolymer was confirmed by FT-IR and NMR analysis. The copolymer in its IR spectrum (Fig. 2) showed broad peak ranging from 1732 to 1720  $\text{cm}^{-1}$ . This was attributed to the stretching vibration of the ester carbonyl group and to C-H bond of the phenyl group of styrene.

In the  $^1\text{H}$  NMR (Fig. 3) spectra of one of the respective copolymers, a broad multiplet centered at 8.07 ppm indicated the presence of a phenyl group. A broad singlet centered at 4.06 ppm was due to the proton of the  $-\text{OCH}_2$  group. The absence of singlets between 5 and 6 ppm indicated the absence of vinylic protons in the copolymer.

The proton decoupled  $^{13}\text{C}$  NMR spectrum (Fig. 4) of the above sample of copolymer was in complete agreement with the original structure-I



Structure-I

The extent of incorporation of styrene in the polymer chain was determined through a comparison of area of  $-\text{OCH}_2$  group at 4.06 ppm in the area of signal due to phenyl protons at 8.07 ppm based on earlier reports (Bataille et al., 1994) as well as on the basis of our earlier paper (Ghosh, et al., 1998).

It was further verified through an analysis of FT-IR spectral data (Abdel-Azim, et al., 1998). The intensity of C=O absorption in FT-IR spectra of present copolymers, as compared to the carbonyl absorption in a standard, were analyzed for quantitative determination of the content of acrylate component in the copolymer. The comparative results obtained on comparisons are presented in Table-2.

Viscometric data were obtained using the six equation mentioned. A linear relation for the plot of  $\log \eta_{sp}$  vs  $\log c[\eta]$  obtained for all samples [Fig. 5a & 5b] indicated that measurements were performed in Newtonian flow (Gundert, 1986; Morris, 1984)

Huggins (H), Kraemer (K), Martin (M) and Schulz–Blascke (SB) equations were applied in graphic extrapolation, providing the respective values of intrinsic viscosities and constants. In single point determinations, Schulz–Blaschke (SB), Solomon–Ciuta (SC) and Deb–Chanterjee (DC) equations were employed. SC and DC are independent of any constant value. In spite of being dependent on a constant, the Schulz–Blaschke (SB) equation is commonly applied in single point determinations because it was found that  $k_{sb} = 0.28$  for many polymer-solvent systems (Delpech,2002; Schoff, 1999; Abdel-Azim, 1998; Khan,1983; Oliveira 1991). In this work, this value was used.

Thermogravimetric analysis (TGA) in Table 3 showed that introduction of styrene raises the thermal stability of the copolymer in comparison to the homopolymer.

Table 4-5 presents intrinsic viscosity  $[\eta]$  values of polymer solution in base oils BO1 and BO2 related to all equations for the samples analysed. Considering the oils (BO1 and BO2) and comparing the values of  $[\eta]$  for homo and copolymers, it is noticed that the higher values were obtained in BO2 oil compared to BO1 oil. Thus considering all the polymers (homo and copolymers), oil BO2 appeared to be more compatible to the polymer and thus pointing towards providing more extended conformations of the polymers. This fact is further supported by the respective  $k_h+k_k$  values, which is well within 0.5 (Table 7). Lower values in BO1 oil in comparison to the BO2 oil, indicating contracted structures with star like conformation for the additive in this oil. Variation of  $[\eta]$  obtained by graphic extrapolation method (equation 2-5) was found to be less compared to those obtained by single point determination method (equation 6-7) without any restriction to lubricating oil .

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

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

values of the copolymer is more than what was observed in oil BO2 and the reduction in intrinsic viscosity values gradually increases with the increase in styrene concentration.

Table 6 & 7 presents values of viscometric constants calculated for homo and copolymers in BO1 and BO2 oil respectively,  $k_h$  and  $k_k$  fitted in the range of good solvents, whereas sample P-3<sup>o</sup> in BO1 oil indicating more incompatibility. Although  $k_{sb}$  values found different from 0.28 in case of BO1 oil, but it has a close tendency to acquire this value (except p-3<sup>o</sup>) in case of oil BO2. It is also important to observe that the relation  $k_h+k_k=0.5$  was not found for the great majority of samples analyzed. However, intrinsic viscosities obtained by using single point determination methods were similar to values obtained by using graphic extrapolation method with small percentage differences. So values different from 0.5 did not put any restriction for the application of SC and DC equation.

Table 8 - 9 presents the percentual differences of intrinsic viscosity values where Huggins value taken as references. In both the oils it is observed that that differences is smaller in graphic extrapolation method compared to single point determination method. It is also observed that the differences is smaller in oil BO2 compared to oil BO1

Table 10 – 11 presents viscometric molecular weight of all the polymers (homo and copolymer). Homopolymer showed higher molecular weight than the copolymer. As expected the molecular weights are greater in oil BO2 compared to oil BO1. Again in oil BO1, a gradual decrease in viscometric molecular weight of the copolymer was observed with increase in styrene concentration although such a variation was not observed in oil BO2.

### **Conclusions**

Viscometric analysis of the polymer may be carried out in lubricating oil to get more information about their morphological structure when added to the oil as a performance additive. Oil compatibility of the additive can be predicted easily through Viscometric analysis. Study also indicated that styrene incorporation enhances the thermal stability of this acrylate copolymer used as performance additive in lubricant formulation. This work is probably the first report of viscometric studies of polymeric additives in base oils.

### Acknowledgment

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Oliveira, C.M.F., Andrade, C.T., Delpech, M.C. (1991). Properties of poly(methyl methacrylate-g-propylene oxide) in solution. *Polym. Bull.* 26: 657.

**Table 1.** Base oil properties

Base oil	Density (g.cm <sup>-1</sup> )at 40 <sup>0</sup> C	Viscosity at 40 <sup>0</sup> C	Viscosity at 100 <sup>0</sup> C	Cloud point	Pour point
BO1	0.848	7.47	3.5	-8	-3
BO2	0.904	20.25	5.5	-10	-6

**Table 2.** Composition of the monomers in the co polymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. P-1 is homopolymer of decyl acrylate (DA); P-2 to P-3 is the copolymer of DA+ different mass fractions of styrene

Sample No	% of weight in the feed		% of weight in copolymer	
	DA	Styrene	By PMR method	By FT-IR
P-1	100	00		
P-2	95	5	1	1.5
P-3	90	10	2	2.1

**Table 3.** Thermal Gravimetric Analysis Data of all prepared samples

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

**Table 4.** Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method.

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

**Table 5.** Intrinsic viscosity values of all prepared samples in BO1 oil calculated by using different equation (eq 2 to eq 7). a- extrapolation of graph, b- single point determination method.

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

**Table 6.** Viscometric constant values in BO1 oil

Sample	$k_h$	$k_k$	$k_m$	$k_{sb}$	$k_h+k_k=0.5$
P-1	1.08	$3.64 \times 10^{-3}$	0.692	0.74	1.083

P-2	0.80	-0.186	3.374	1.72	0.614
P-3	0.70	-5.103	0.513	0.524	-4.40

**Table 7.** Viscometric constant values in BO2 oil

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

**Table 8.** Percentual differences ( $\Delta \% = 100 \times [\eta]/[\eta]_h - 100$ ) of intrinsic viscosity values (In BO1 oil), Where Huggins value taken as a reference.

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

**Table 9.** Percentual differences ( $\Delta \% = 100 \times [\eta]/[\eta]_h - 100$ ) of intrinsic viscosity values (In BO2 oil), Where Huggins value taken as a reference.

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

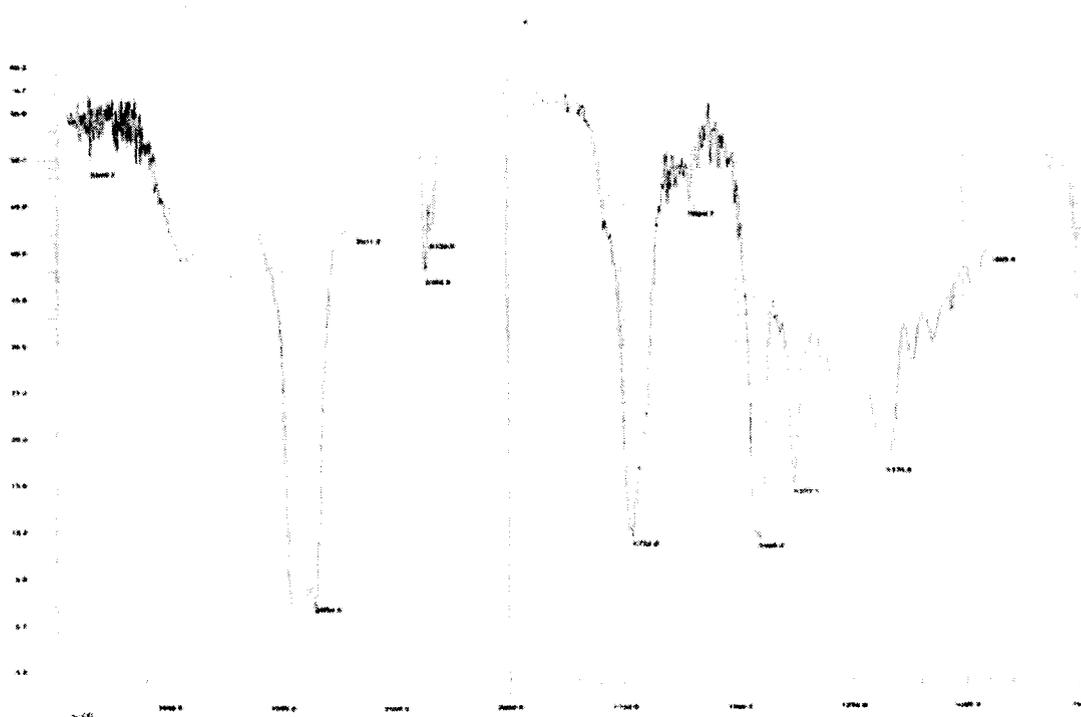
**Table 10.** Viscometric molecular weight of all prepared sample in BO1 oil by using Mark –Houwink equation  $[\eta] = KM^a$ , Where  $K = 0.00387$  and  $a = 0.725$ .

Sample	$M_h^a$	$M_k^a$	$M_m^a$	$M_{sb}^a$	$M_{sb}^b$	$M_{sc}^b$	$M_{DC}^b$
--------	---------	---------	---------	------------	------------	------------	------------

P-1	8315	9995	9545	9355	12019	12156	12656
P-2	5396	5659	5729	5287	6148	6219	6349
P-3	3029	2181	2475	3188	5423	5484	5541

**Table 11.** Viscometric molecular weight of all prepared sample in BO2 oil by using Mark –Houwink equation  $[\eta] = KM^a$ , Where  $K= 0.00387$  and  $a = 0.725$ .

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



**Figure 1.** FT-IR spectrum of poly decylacrylate

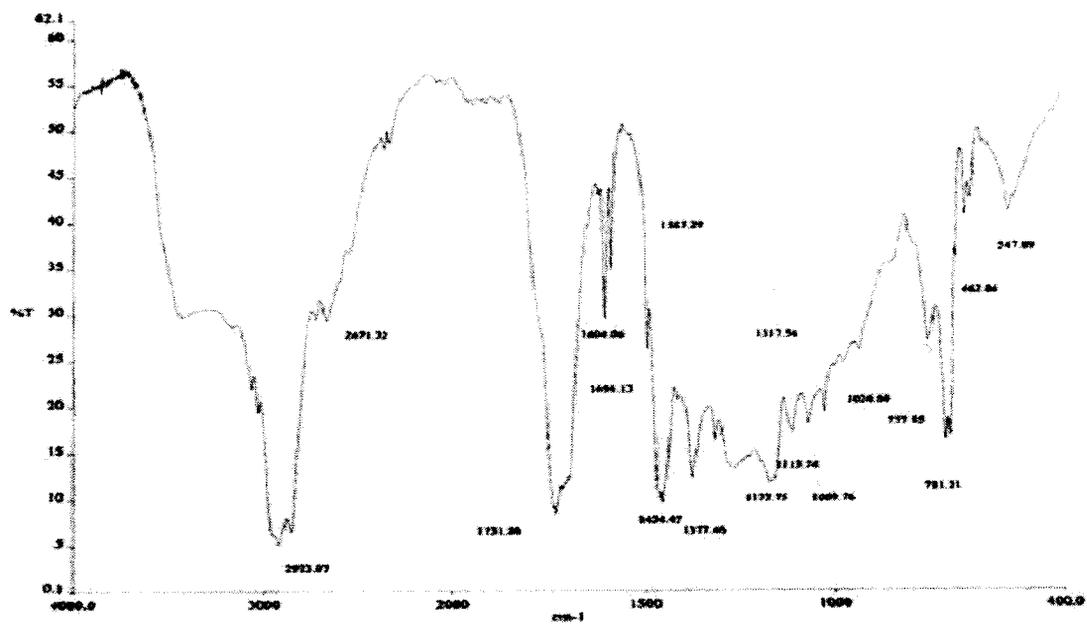
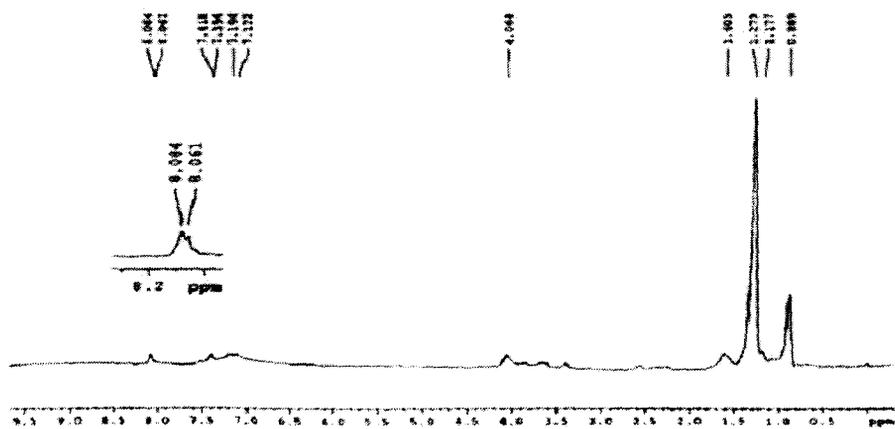
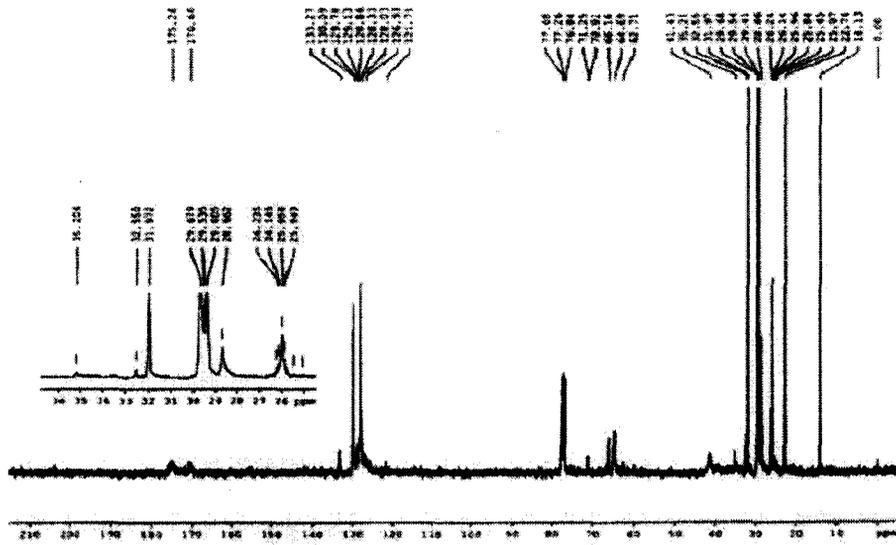


Figure 2. FT-IR spectrum of copolymer of decyl acrylate with styrene



**Figure 3.**  $^1\text{H}$  NMR spectrum of copolymer of decyl acrylate with styrene



**Figure 4.**  $^{13}\text{C}$  NMR spectrum of copolymer of decyl acrylate with styrene

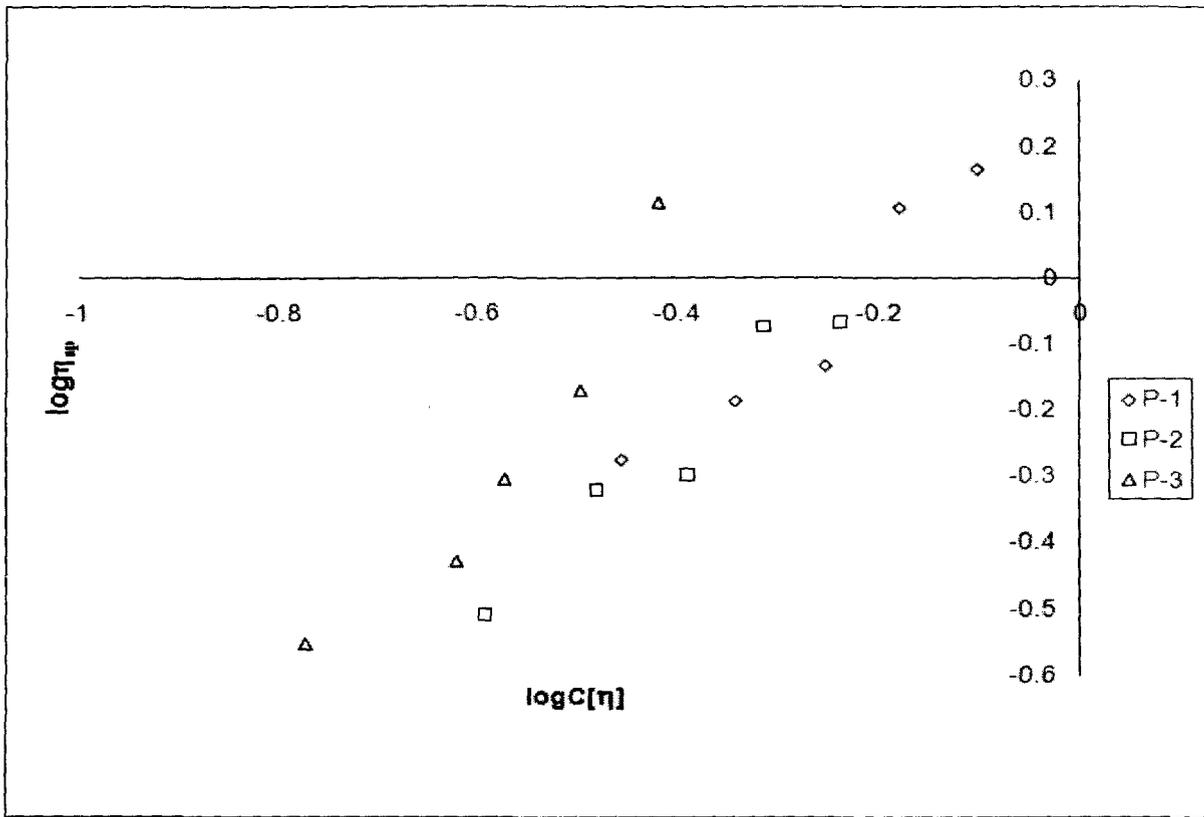
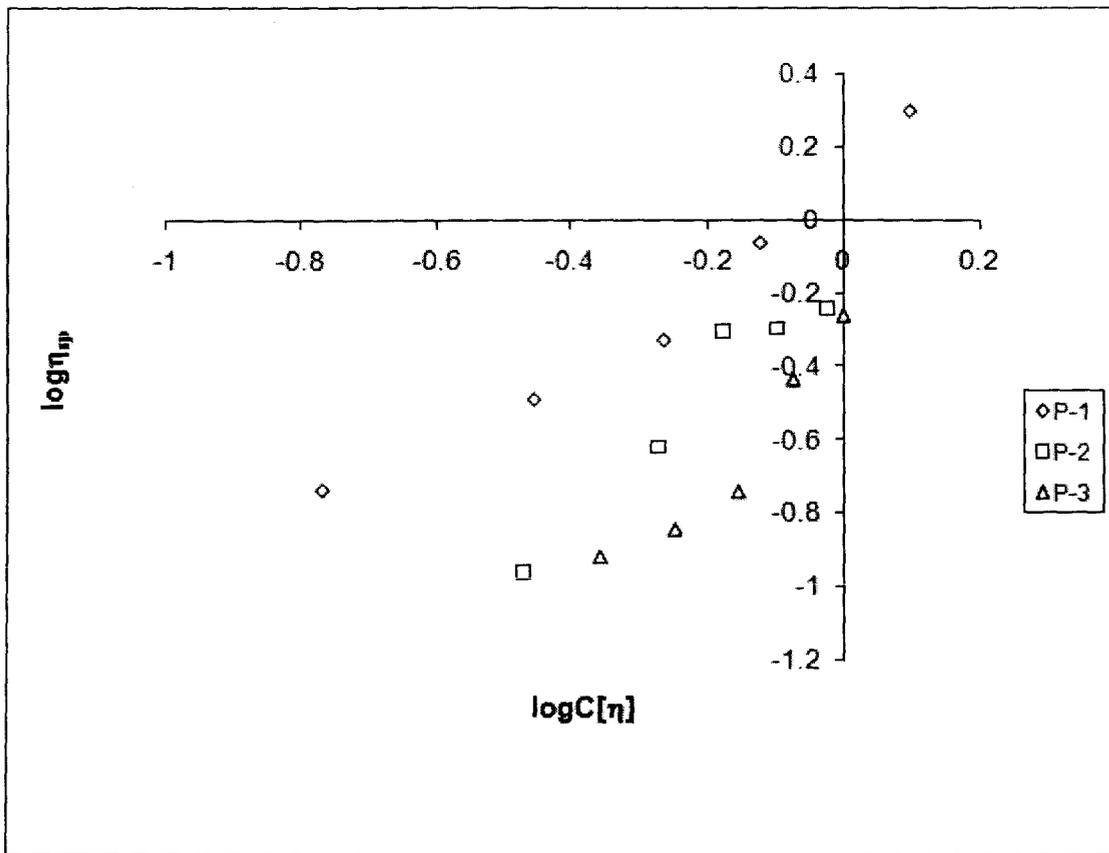


Figure 5a. Plot of  $\log \eta_{sp}$  vs  $\log C[\eta]$  for BO1.



**Figure 5b.** Plot of  $\log \eta_{sp}$  vs  $\log C[\eta]$  for BO2.

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### Synthesis and Characterization of Biodegradable Polymer - Used as a Pour Point Depressant for Lubricating Oil

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# Synthesis and Characterization of Biodegradable Polymer - Used as a Pour Point Depressant for Lubricating Oil

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

**Keywords** base oil, biodegradable additives, copolymer, pour point, viscometric studies

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## INTRODUCTION

The use of oil-soluble additives in lubricating oil to improve their performance is well-known. They improve performances by either enhancing the desirable properties already present or by introducing new properties into the oil without disturbing its original performance.

The decreasing of the natural resources of mineral oil and increasing environmental awareness have increased investigation into new environmental lubricant and additive chemistry. Keeping this view in mind, people have already started working in this direction to meet the above needs [1]. The use of biodegradable vegetable oils was known for a long time. Today, due to growing environmental concern, these oils are again finding application in lubricants for transportation as well as for industrial applications. They can offer significant environmental advantages with respect to fuel consumption, biodegradability and displaying satisfactory performance in field application. They are also reported to show excellent tribological properties when used as base stocks or as additives [2]. But the major limitations are their high cost and thermal and oxidative instability. Keeping this in mind and in continuation of our studies towards the development of chemical additives for lubricating and crude oils, in the present investigation an attempt has been made to synthesize a pour point additive based on sunflower oil.

Pour point is the temperature at which lubricating oil is just able to flow and below which there is complete absence of flow in it. Polymeric additives known as flow improvers or pour point depressants are generally used to lower the pour point, viscosity and yield stress of lubricating oil [3–7].

Since performance of such additives in field conditions is very much dependent on the structure and morphology of the polymer in the desired solvent [8], viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution are concerned. Since reports regarding such information are scanty [9,10] and almost nil for polymers used as lube oil additives the present research also include a viscometric study of the copolymers as well as the homopolymer.

According to the Mark Houwink–Sukurda relation (Eq. (1)), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

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

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

Because of the simplicity of the procedure, viscometry is usually employed to complement the results obtained from another technique, generally in

determination of the molecular mass of samples with the available literature value of the constants used in the particular equation. A number of mathematical relations are available in the literature for the study of viscometric properties of a dilute polymer solution at a particular temperature by graphic extrapolation [11–17]. The most commonly used equations are:

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

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

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

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

where  $\eta_r = t/t_0$ , relative viscosity or viscosity ratio;  $\eta_{sp}$  = specific viscosity

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

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

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

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

Some relations have been proposed for determining the intrinsic viscosity in dilute polymer solution from a single point determination. These methods have the advantage of being considerably faster and can be adequate when a large number of samples must be analyzed in a short period of time, practical in industrial laboratories. Most useful [13–17] are the Solomon-Ciute (SC, Eq. (6) and Deb-Chanterjee (DC, Eq. (7) relations.

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

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

The use of these equations has been derived under the supposition of the validity of the relationship  $k_h + k_k = 0.5$  [15].

## EXPERIMENTAL

### Measurements

Spectroscopic: IR spectra were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1 mm KBr cells and the spectra were recorded at room temperature within the wave number range 400 to 4000  $\text{cm}^{-1}$ . NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe.  $\text{CDCl}_3$  was used as a solvent and TMS as reference material.

## Viscometric Measurements

Viscometric properties were determined at 40°C in a toluene solution, using an Ubbelohde OB viscometer. Experimental determination was carried out by counting the time flow of at least eight different concentrations of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In the single point measurement the lowest value of solution concentration was chosen for the calculation. For the viscosity – average molecular weight determination, the constants  $K = 0.00387$  dl/g and  $a = 0.725$  were employed in Mark Houwink – Sukurda relation [15–17].

## Thermogravimetric Analysis (TGA)

The thermograms in air were obtained on a Mettler TA – 3000 system, at a heating rate of 10°C/min.

## Biodegradability Test

In this work we studied the biodegradability of the prepared polymer samples (both the copolymer and homopolymer) against five different fungal pathogens namely *Colletotrichum camelliae*, *Fusarium equisetiae*, *Alternaria alternata*, *Colletotrichum gloeosporioides* and *Curvularia eragrostidis*. All experiments were performed in petri dishes and were incubated at 37°C for 30 days after the addition of definite weight of polymer samples. The fungal growth was confirmed by a change of yellow to blackish color. Culture media for fungal strains were prepared by mixing suitable proportions of potato extract, dextrose and agar powder. All glass apparatus and culture media were autoclaved before use. The whole process was carried out in an inoculation chamber. After 30 days polymer samples were recovered from the fungal media and washed with chloroform, purified and dried in an open vessel. The dried samples were weighed [18].

## Evaluation of Prepared Polymer as Pour Point Depressant in Base Oils

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

## RESULTS AND DISCUSSION

$^1\text{H}$  NMR of sunflower oil indicated the presence of unsaturation ( $\delta$  5.31, 4.27 and 4.12 ppm) along with other peaks due to methyl and methylene protons ( $\delta$  0.87 to 1.27 ppm) and ( $\delta$  1.59 to 2.75) ppm), respectively. The existence of homopolymer was indicated by the disappearance of the peaks in the unsaturation region ( $\delta$  4.0 to 6.0 ppm) along with a shift in the methyl and methylene signals. Formation of copolymer of sunflower oil and styrene was indicated by the absence of unsaturation in the NMR spectrum (no peak between 4–6 ppm) and the appearance of broad multiplet centered at  $\delta$  8.2 ppm for the aromatic ring protons of styrene. Similar results were also obtained in the NMR spectrum of other copolymers, e.g., sunflower oil – MMA and sunflower oil – DA.

IR spectra of the homo and copolymer of sunflower oil showed characteristic peaks for ester carbonyl at  $1745.5\text{ cm}^{-1}$  and at  $3408\text{ cm}^{-1}$ .

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

Table 1 presents intrinsic viscosity values of all prepared samples in toluene solvent. In general it has been found that intrinsic viscosity values of homopolymer are greater than the copolymer except (P-3). Increase in monomer concentration (MMA, DA and styrene) intrinsic viscosity increases. It is interesting to note that by using several equations, values are identical for each polymer. For all polymeric samples intrinsic viscosity values obtained by using single point determination method are found to be greater than graphical extrapolation method.

**Table 1:** Intrinsic viscosity values of all polymeric samples. P-1 polymer of sunflower oil, P-2 copolymer of sunflower oil +5% MMA, P-3 copolymer of sunflower oil +10% MMA, P-4 copolymer of sunflower oil +5% DA, P-5 copolymer of sunflower oil +10% DA, P-6 copolymer of sunflower oil +5% styrene, P-7 copolymer of sunflower oil +10% styrene (a) graphic extrapolation method, and (b) single point determination method.

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

**Table 2:** Viscometric constant values of all samples.

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

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

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

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

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

**Table 3:** Percentual differences of intrinsic viscosity ( $\Delta\% = (100((\eta)/(\eta)_h) - 100)$ ) (a) graphic extrapolation method, and (b) single point determination method.

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

**Table 4:** Viscometric molecular weight determined by using the Mark—Houwink equation ( $\eta_r = KM^a$ ) where,  $K = 0.00387$  and  $a = 0.725$ .

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

**Table 5:** TGA data of all prepared samples.

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

**Table 6:** Results of biodegradability test.

Fungal pathogens	Polymer samples	Incubation period (Days)	Initial wt (gm)	Final wt (gm)	Wt loss (gm)
<i>Colletotrichum camelliae</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Fusarium equisetiae</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Alternaria alternata</i>	P-1	30	1.5	0.9	0.6
	P-2	30	1.5	1.1	0.4
	P-4	30	1.5	1.4	0.1
	P-6	30	1.5	1.48	0.02
<i>Colletotrichum gloeosporioides</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil
<i>Curvularia eragrostidis</i>	P-1	30	1.5	1.5	Nil
	P-2	30	1.5	1.5	Nil
	P-4	30	1.5	1.5	Nil
	P-6	30	1.5	1.5	Nil

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

Table 6 presents biodegradability test results obtained by using the disk diffusion method. Homopolymer and copolymer of sunflower oil with decyl acrylate showed that sunflower oil was found to have significant biodegradability against the fungal pathogen, *Alternaria alternata*. It was further confirmed by the shift of IR frequency of the ester carbonyl to 1712 after the biodegradability test. Copolymer of sunflower oil with MMA also shows biodegradability but in a smaller extent. Biodegradability was not found in the copolymer of sunflower oil with styrene. The presence of styrene (aromatic moieties) may be key to the observed less biodegradability.

Table 7 presents PPD properties of the polymers evaluated in two different base stocks, each of them collected from two different sources (S1 and S2), and indicates that P-2 and P-5 showed best performance in both the base oils. The

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

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

values are always better than the respective homopolymer and both of them are made from sunflower oil.

## CONCLUSIONS

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

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

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

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

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*Oral Presentation*

## PREPARATION, CHARACTERIZATION AND EVALUATION OF ACRYLATE POLYMERS AS POUR POINT DEPRESSANT FOR LUB OIL

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### ABSTRACT

The potential for the use of poly acrylates and their co polymer as pour point depressant in lubricating oil is well documented. In the present work free radical homo polymerization of methyl methacrylate (MMA) and co polymerization with styrene were performed at 70°C with BZP as initiator in toluene. The molecular weight of the polymer was determined by GPC and viscometric methods. Resulting polymers were characterized by intrinsic viscosity, FT-IR and <sup>1</sup>H NMR spectroscopy. All the resulting polymers will be tested for their PPD performance in lubricating oil as well as in crude oils

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## Ionic conductivity and phase transition Behaviour in $4\text{AgI}_{(1-x)}\text{PbI}_{2-2x}\text{CuI}$ system

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### Abstract

Samples of general formula  $4\text{AgI}_{(1-x)}\text{PbI}_{2-2x}\text{CuI}$ ,  $x = 0-0.4$ , have been prepared and studied by X-ray diffraction, DSC and electrical conductivity techniques. X-ray diffractograms showed the presence of binary system consisting of AgI and  $\text{PbI}_2$  in the sample  $x = 0$ . Cu-substituted samples showed very similar diffractograms to that of the pure compound which indicates that no effect for the substitution on the nature of the binary system. DSC Curves showed the presence of phase transition whose temperature increased with  $\text{Cu}^+$  ratio in the system. Ionic conductivity measurements confirmed the occurrence of the phase transition and showed that the high temperature phase is superionic conducting whose conductivity increases with the increasing  $\text{Cu}^+$  amount in the system.

**Keywords:** Ionic conductivity; Phase transition; XRD; DSC

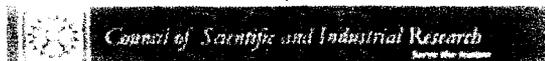
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# SYNTHESIS AND CHARACTERIZATION OF POLYMERIC P1 ADDITIVES FOR LUBRICATING OIL

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## ABSTRACT

Methacrylate based polymeric additives were prepared by free radical polymerization using toluene as a solvent. Resulting polymers were characterized by viscometric measurements and spectroscopic analysis. Thermal behaviors of the additives to be tested by TGA to find the suitability of the polymers in operating condition. Their performance as a viscosity index improver and pour point depressant will be tested following ASTM procedures. Effect of initiator concentration and temperature of polymerization on the performance of the additives will also be studied.

Similar study will be carried out of the homo and copolymer of acrylate esters.

## Copolymer Of Sun Flower Oil With Alkyl Acrylates - Synthesis, Characterization And Performance Evaluation In Lubricating Oil

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Different kinds of polymeric additives are used in lubricant composition for improving the viscometric and rheological properties of the lubricant [1-4]. They prolong the useful life of machines, achieve greater performance and provide fuel economy. However, the present specification laid down by the Original Equipment Manufacturer (OEM) led us to synthesize additives which are eco-friendly or less hazardous to the environment, without disturbing their performances. Due to this present demand of greener technology, many researchers are embarking on the viability of the vegetable-based lubricants [5] and recently, much effort has been focused on research and development of new types of biodegradable lubricating oil additives to adapt new requirements and demands. Keeping this view in mind and to overcome the shortcoming always associated with the existing additive chemistry, we undertook a study to synthesize vegetable based lubricating oil additives by the copolymerization of alkyl acrylates with sun flower oil - their characterization and evaluation in lubricating oil. This paper comprises the results of our recent investigation which will be presented in the symposium.

### Keywords:

Additives, Lubricating Oil, Viscometric and Rheological properties, Copolymerization, Original Equipment Manufacturer,

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## Synthesis, Characterization and Viscometric Studies of Homo and Copolymer of Decylacrylate

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### ABSTRACT

Homopolymer of decylacrylate (DA) and its copolymer using different concentrations of styrene were synthesized, characterized and evaluated for their performance as lubricating oil additives. of the co polymers was carried out employing GPC, TGA, IR and NMR. However, since performance of such kind of additives in field condition is very much dependent on the structure and morphology of the polymer in desired solvent [1,2], viscometric studies in dilute solutions may give valuable information as far as the quality of the solvent or base stock employed and chain conformation in dilute solution are concerned. Since report regarding such information is scanty [3, 4] and almost nil for polymers used as lube oil additives – present research also include viscometric study of the synthesized polymers. The viscometric measurements of the synthesized homopolymer as well as the co polymers in different base stocks at 400 C were performed [5]. Results are interesting and will be presented in the Symposium.

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