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Synthesis Characterization and Viscosity Studies of Homo polymer of Methyl Methacrylate and its Copolymer with Styrene and 1 – Decene

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ABSTRACT

Homopolymer of methyl methacrylate (MMA) and its copolymer using different compositions of styrene and 1-decene were synthesized and characterized. The viscosity measurements of the synthesized homo polymer as well as the co polymer in the toluene solution at 313 K were performed. Different equations were used to calculate intrinsic viscosity, viscometric constants values and molecular weight of the synthesized polymers. The values of intrinsic viscosity and viscosity average molecular weight obtained by the two methods (single point determination and graphical extrapolation) were compared in order to verify the validity of the single point determination for the polymers. Viscometric properties derived included the determination of specific viscosity (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.

Keyords Homopolymer; Copolymer; Intrinsic viscosity; Specific viscosity:

INTRODUCTION

Polymers of alkyl methacrylate used as additives in lubricant composition for improving the viscometric and rheological properties of the lubricant. [1,4] They also looked upon to provide additional performance characteristic such as improved low temperature fluidity and disparsancy. Although poly alkyl methacrylates (PAMAs) are preferred type of additives in certain application, they often contribute to enhance formation of deposits in the engine due to thermal instability of these additives under high temperature conditions. Approach to overcome this shortcoming is always associated with a risk of affecting certain beneficial properties associated with normal polyalkylmethcrylates, such as pour point depressant (PPD) and good shear stability. Therefore, the recent research on methacrylate additives has been concerned on co polymer of methacrylates with various stabilizing monomer.

It is well known that inclusion of styrene in the composition of an additive increases the resistance of the co polymer compounded oil to the action of heat. Since homopolymers of styrene and 1-decene are insoluble in lube oil they are introduced in the composition of oil soluble polymer by copolymerization which may be useful PPD / VM (Viscosity modifier) for petroleum and synthetic oil.

In this paper the results of our investigation towards the synthesis, characterization and viscometric measurement of MMA + styrene copolymer and MMA+ 1- decene in compare to homo polymer of MMA will be discussed. Four copolymers of MMA were prepared by varying the mass fractions of styrene and 1-decene in the monomer mixture from 5 % to 10 % and employing free radical polymerization technique using benzoyl peroxide (BZP) as initiator in toluene solvent. Polymerization was carried out following the procedure as reported earlier.[3] Homo polymer of MMA was also prepared under identical condition.

Physical characterization of the co polymers was carried out employing gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), FT-IR and FT-NMR techniques. However, since performance of such kind of additives in field condition is very much dependent on the structure and morphology of the polymer in desired solvent [5], 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 [6,7] and almost nil for polymers used as lube oil additives – present research also include viscometric study of the co polymers as well as the homopolymer.
Viscometry is the simplest technique used to study the macromolecules in solution and determine their molecular weight. According to Mark Houwink – Sukurda relation (eq 1), the value of intrinsic viscosity changes with the molecular weight of the polymer in a solvent as:

$$[\eta] = K\,M^{a} \qquad (1)$$

Where the parameter ‘K’ and ‘a’ depends on the type of polymer, solvent, and temperature.

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

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

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

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

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

Where, C is concentration in $g.cm^{-3}$,
$\eta_r = t/t_0$, relative viscosity or viscosity ratio (where, t is time flow of pure solvent and t_0 is time flow of solution).
η_{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.

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

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

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

The use of these equations has been derived under the supposition of the validity of the relationship $k_h + k_k = 0.5$. [9]

The behavior 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 [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 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 viscometric parameters (intrinsic viscosity and the value of constants) of toluene solution for sample of poly methyl methacrylate and its co polymer were obtained by graphic extrapolation and single point determination. The viscosity average molecular weight determined by using different equations, were compared. The validity of single point determination method for these types of polymers, in the investigated condition, was also discussed.

EXPERIMENTAL SECTION

Polymerization

The polymerization was carried out in a four necked round bottom flask equipped with a stirrer, condenser, thermometer, an inlet for the introduction of nitrogen and a dropping funnel through which to add styrene drop wise. In the flask was placed desired mass of MMA and initiator (BZP) followed by the desired mass of styrene was added drop wise for 2 h in the presence of toluene as solvent. The reaction temperature was maintained at 353 K for 6 h. At the end of the reaction time, the reaction mixture was poured into methanol with stirring to terminate the polymerization and precipitate the polymer. The polymer was further purified by repeated precipitation of its hexane solution by methanol followed by drying under vacuum at 313 K. A homo polymer of MMA and copolymer with 1-decene were similarly prepared and purified under the same conditions for use in reference experiments.

Measurements

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

Viscometric measurements

Viscometric properties were determined at 313 K in toluene solution, using an Ubbelohde OB viscometer (having viscometer constant values are $K^{/}= 0.00268 cm^2/sec^2$, $L= -19.83 cm^2$ and volume of the bulb is 3 cm^3 and length of the capillary 11.3 cm). Experimental determination was carried out by counting time flow at least nine different concentration of the sample solutions. The time flow of the solution was manually determined by using a chronometer. In a single measurement the lowest value of solution concentration was chosen for the calculation. The viscometer was calibrated frequently with distilled water. The viscosity results were checked against viscosity of known solutions and accuracy was found to be nearly 0.2 %. Precautions regarding prevention of evaporation of solvent were taken in all the cases. For the viscosity – average molecular weight determination, the constants K = 0.00387 dl/ g (deciliter/g) and a = 0.725 [13, 14] were employed.

Thermo gravimetric analysis (TGA)

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

RESULTS AND DISCUSSION

IR spectra of the homo polymer showed a peak at 1732 cm^{-1} due to the presence of ester carbonyl group stretching vibration. The broad peak ranging from 1260 to 1000 cm^{-1}appeared owing to the ester C-O stretching vibration along with broad band from 950 to 650 cm^{-1} (C-H bending) and from 3100 to 2900 cm^{-1} due to presence of stretching vibrations. The existence of copolymer was confirmed by IR and NMR (Figure 1) analysis. Carbonyl stretching vibration at 1732 cm^{-1} of the homo polymer shifted to 1720 cm^{-1} in the copolymer. Peaks at 760 cm^{-1} and 697 cm^{-1} were attributed to the C-H bond of the phenyl group of styrene. In its ^1H NMR spectra the copolymer indicated the presence of phenyl group at 7.2 ppm and the –OCH_2 group from the acrylate at 3.9 ppm.

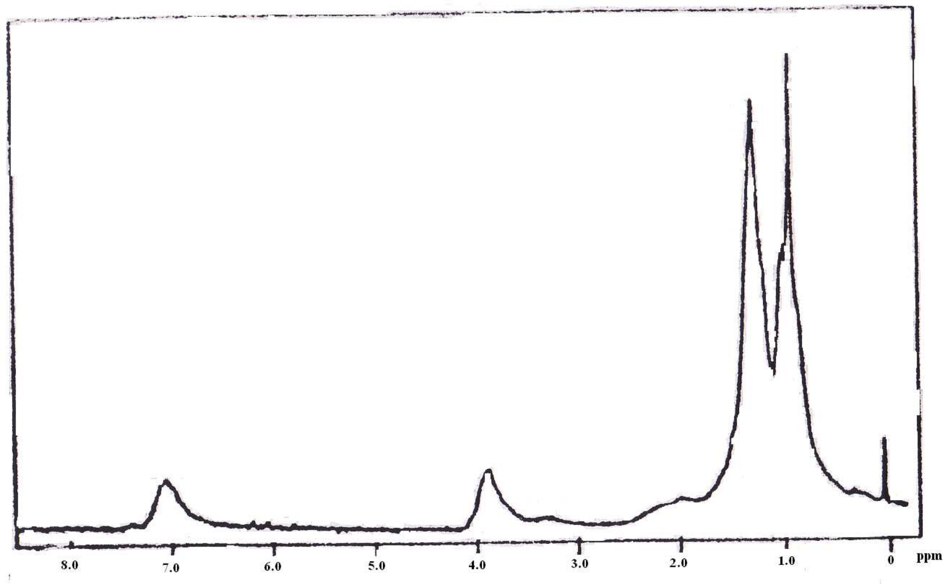

Figure 1. NMR spectrum of copolymer of Methyl methacrylate + styrene

The extent of incorporation of styrene in the polymer chain (Table 1) was determined through a comparison of area of –OCH_2 group at 3.9 ppm in the area of signal due to phenyl protons at 7.2 ppm based on earlier reports [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 as also discussed in our earlier paper.[3]

The formation of copolymer of MMA with 1-decene was also confirmed by IR and NMR (Figure 2) analysis. Carbonyl stretching vibration at 1732 cm^{-1} of the homo polymer (MMA) shifted to 1729 cm^{-1} in the copolymer. ^1H NMR spectra the copolymer indicated the absence of any vinylic protons and showed the presence of ester methyl's at 3.60 ppm. The extent of incorporation of 1-decene in polymer chain was similarly determined from analysis of the proton NMR through a comparison of the area of the signal due to -OCH_2 group appearing at 4.35 ppm with the area of signals due to other protons which was further confirmed through the analysis of FT-IR data.

Table 1. Composition of the monomers in the co polymers in terms of mass fraction determined by PMR and FT-IR spectro photometric method. Poly-1 is homopolymer of methyl methacrylate (mma); Poly-2 and Poly-3 are the copolymer of mma + different mass fractions of styrene and Poly-4 and Poly-5 are the copolymer of mma + different mass fractions of 1-decene,

Polymer sample	Mass fraction in the feed		Mass fraction of styrene in co polymer by PMR method	Mass fraction of styrene in co polymer by FT-IR
	MMA	Styrene (poly-2 and poly-3) / 1-decene (poly-4 and poly-5)		
Poly-1	1	-	-	-
Poly-2	0.95	0.05	0.02	0.023
Poly-3	0.90	0.10	0.04	0.045
Poly-4	0.95	0.05	0.028	0.03
Poly-5	0.90	0.10	0.049	0.051

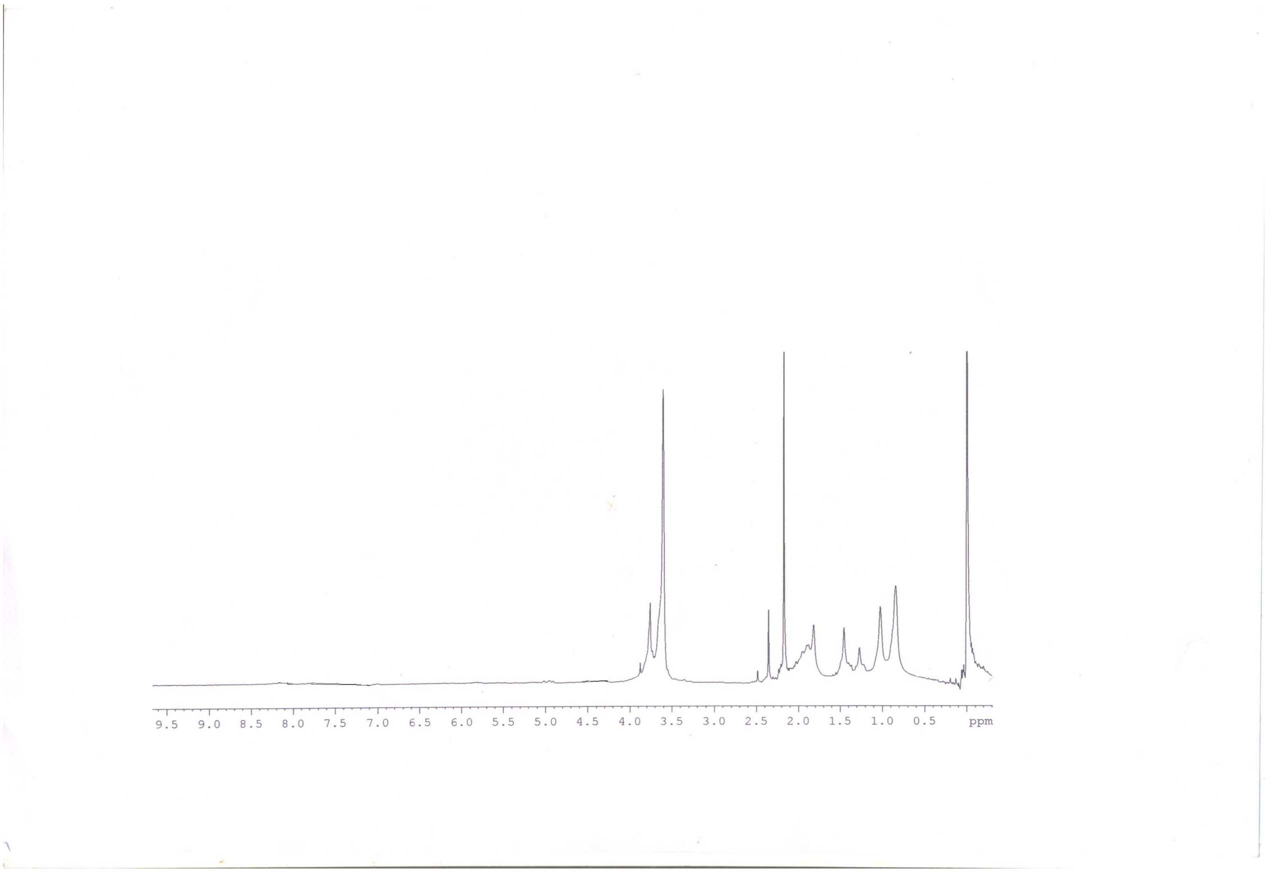

Figure 2. ^{1}H NMR spectrum of copolymer of Methyl methacrylate + 1- decene

Comparison showed that the extent of incorporation of 1-decene in the copolymer is always greater than styrene incorporation.

Table 2 presents a comparison between the values of molecular mass obtained by GPC. The molecular weight increases with the increase in the concentration of the co monomer (styrene and 1-decene). Molecular mass is always lower in case of 1-decene copolymer.
Thermal stability (Table 2) as determined by thermogravimetric analysis (TGA) showed that the copolymers are better in thermal stability than the homo polymer, except poly-5, where the increased 1-decene concentration assist the degradation of the polymer as a whole. Incorporation of styrene raises the thermal stability much more than 1-decene.

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

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

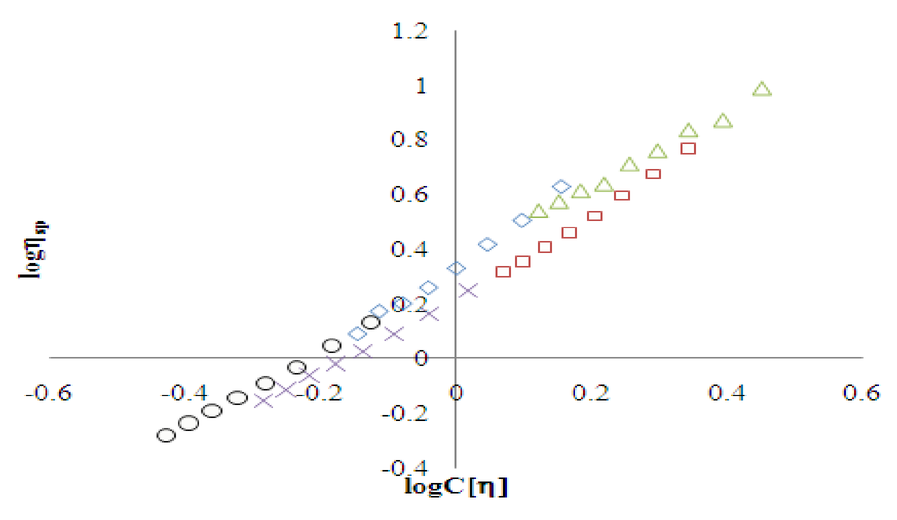

Figure 3. Plot of logC[η] vs logη$_{sp}$: ◊, Poly-1; ▫,Poly-2; Δ, Poly-3; x,Poly-4, o,Poly-5

Viscometric data were obtained using the six equation mentioned. A linear relation for the plot of logη_{sp} vs logC[η] obtained for all samples (Figure 3) indicated that measurements were performed in Newtonian flow. [16,17]

Using the graphic extrapolation method respective intrinsic viscosities and constants were evaluated. In single point determinations, SB, SC and DC equations were employed to determine the intrinsic viscosity. Although dependent on a constant, the SB equation is commonly applied in single point determination because the constant k_{sb} is found to be very close to 0.28 in most of the polymer solvent system.[6–10] The same is used here also.

Table 3 presents intrinsic viscosity values ($[\eta]_{int}$) related to all equation for the sample analysed. Taking into account the data for homo and all co polymer samples, it can be noticed that, except one or two cases values are consistent. Comparison among the co polymers indicated that there is a gradual increase of [η] values with the increase of styrene content in the monomer composition. This indicated more extended conformation of the polymer chain compared to PMMA itself. However, beyond a concentration of 2.5 % of styrene, hydrodynamic volume of it exceeds that of PMMA which may reach a limiting value when the concentration of styrene is raised to 5 % in the feed. Therefore a sharp increment of [η] is observed at 5 % styrene content. [18, 19] But incase of 1-decene incorporation, intrinsic viscosity values gradually decreases with increase in mass fraction of 1-decene. This opposite behaviour can be explained on the basis of the extent of hydrodynamic volume of the two kinds of copolymers in the same solvent

Values of intrinsic viscosities (Table 3) obtained by graphic extrapolation method of Huggins, Kraemer, Martin and SB equation (eq 2 to 6) did not show much variation for the homopolymers as well as for the copolymers studied. $[\eta]_{int}$ values obtained by Huggins and Kraemer's equation were found identical for both homo and copolymers.

Table 3. 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

Sample	$[\eta]^a_h$	$[\eta]^a_k$	$[\eta]_m{}^a$	$[\eta]^a_{SB}$	$[\eta]^b_{SB}$	$[\eta]^c_{SC}$	$[\eta]^c_{DC}$
Poly-1	7.69	9.38	7.75	9.71	9.83	9.95	10.72
Poly-2	13.5	14	14.78	15.61	15.39	15.81	17.68
Poly-3	15.12	15.02	16.88	18.2	16.694	18.17	21.41
Poly-4	5.59	5.89	6.27	6.28	6.25	6.25	6.549
Poly-5	4.02	4.48	4.39	4.63	4.86	4.86	5.040

Both homo polymer and co polymers in toluene medium indicating poor solvation (Table 4) as is evident from the respective viscometric constant values, and thus points towards the formation of micelle or spherical structures as discussed earlier.[5]This conclusion is further supported by positive values of Kraemer coefficient of the all the systems analyzed. However, it is interesting to notice that for all the polymers in toluene, k_{sb} values were close to 0.28. Thus it can be concluded that the relation $k_h + k_k \neq 0.5$ did not put any restriction for the application of SB equation.

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

Samples	k_h	k_k	k_m	k_{sb}	$k_h + k_k$
Poly-1	1.006	0.093	0.740	0.294	1.099
Poly-2	0.639	0.0006	0.337	0.247	0.640
Poly -3	0.678	0.038	0.356	0.227	0.716
Poly -4	0.657	0.046	0.343	0.289	0.703
Poly -5	1.058	-0.026	0.611	0.42	1.032

The relation $k_k + k_h = 0.5$ was not observed for the samples analyzed (Table 4), but found similar as reported elsewhere.[17] Maximum deviation for the homo polymer of MMA may be attributed to the comparatively poor solubility of the polymer in toluene

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

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

Table 5. Percentual differences ($\Delta = ([\eta]/[\eta]_h) -1$) obtained for intrinsic viscosity values, Huggins equation taken as a reference. a- data from extrapolation; b – data from single point determination

Sample	K^a	M^a	SB^a	SB^b	SC^b	DC^b
			100 Δ			
Poly 1	21.97	0.78	26.31	27.88	29.39	39.36
Poly-2	3.70	9.48	15.55	14.01	17.11	30.96
Poly-3	-0.66	11.64	20.37	10.41	20.15	41.60
Poly-4	5.30	12.08	12.24	12.34	11.71	17.05
Poly-5	11.64	9.20	15.31	21.98	21.01	25.30

A close observation of the intrinsic viscosity values (Table 3) indicated that, for the co polymer system analyzed, the SB equation which is widely applied in industry quality control laboratories should be the most suitable for the application in one point determination. This table also indicated that for PMMA the graphical extrapolation method seemed to be more suitable in toluene rather than the single point determination and Martin equation produced the lowest deviation value among the four when compared to those obtained from the Huggins equation. Table 6 presents the value of viscometric molecular weights obtained for homo polymer and co polymers analyzed. The trend is similar as was observed in case of GPC molecular weight and is in line with their respective intrinsic viscosity values. However, as expected, a difference was observed in the values of molecular weight obtained by GPC and viscometric method. This is probably due to the differences in analysis conditions, like solvents, temperature techniques and standard employed.[20]

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

Sample	M_h^a x 10^{-4}	M_k^a x 10^{-4}	M_m^a x 10^{-4}	M_{sb}^a x 10^{-4}	M_{sb}^b x 10^{-4}	M_{sc}^b x 10^{-4}	M_{dc}^b x 10^{-4}
Poly-1	3.54	4.65	3.58	4.88	4.97	5.05	5.59
Poly-2	7,67	8.09	8.71	9.99	9.22	9.56	11.16
Poly-3	8.99	8.91	10.47	11.62	10.31	11.58	14.54
Poly-4	2.28	2.44	2.66	2.67	2.67	2.65	2.83
Poly-5	1.44	1.68	1.63	1.75	2.77	1.87	1.97

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

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

Table 7. Percentual differences obtained for viscometric molecular weight values $\Delta = (M/M_h) - 1$, Huggins equation taken as a reference. a- data from extrapolation; b- data from single point determination.

Sample	M_k^a	M_m^a	M_{sb}^a	M_{sb}^b	M_{sc}^b	M_{dc}^b
			100 Δ			
Poly-1	31.52	1.07	38.02	40.38	42.67	58.06
Poly-2	50.14	13.30	29.80	19.80	24.34	45.12
Poly-3	-0.91	16.40	29.10	14.60	28.80	61.00
Poly-4	7.30	16.90	17.20	17.40	16.40	24.10
Poly-5	16.40	12.90	21.60	91.80	30.00	36.40

CONCLUSIONS

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

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

In general, copolymers showed greater thermal stability than the homopolymer.
Incorporation of styrene raises the thermal stability of MMA more than 1- decene does.
In general, increased styrene concentration in the feed is directly proportional to intrinsic viscosity of the copolymer solution but reverse is observed in case of MMA- 1- decene copolymer.

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

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

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

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

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