Diluted Solution Properties of Poly (3,5-Dimethylphenylacrylate) in Toluene at 25°C and 30°C

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Abstract

Poly(3,5-dimethylphenylacrylate) (35PDMPA) was synthetized by radical polymerization under nitrogen atmosphere. It was divided to eleven fractions of lower polydispersity samples by precipitation fractionation method in toluene and hexanes. The structure of polymer was confirmed by H-and ^{13}C-NMR spectroscopy. The molecular mass and polydispersity of samples were determined by Viscotek GPC-Max-triple arrowed detector system in tetrahydrofuran at 30°C. The viscosities of the samples in toluene were measured by capillary micro-viscometer in a Cannon thermostated water bath at 25° and 30° C. Value of intrinsic viscosity was estimated by the common intercept of Huggins and Kraemer's methods. Two parameter models of Kuhn-Mark-Houwink-Sakurada relationship and Stockmayer-Fixman semi-empirical equation were used to determine the unperturbed dimensions of the polymer in solution. The results showed that increasing 5°C temperature improved quality of solvent but did not have any effects on the unperturbed dimensions, characteristic ratio, and rigidity parameter of the polymer. The rigidity parameter of 35PDMPA find to be larger than poly(methylacrylate) but smaller than poly(3,5-dimethylphenylmethacrylate) under same conditions of temperature and solvent.

Introduction

The viscosity study of polymers has been of continuing interest, mainly due to its simplicity and its importance in the characterization of the intermolecular interaction between the two different polymers. Viscosity is said to be the measure of the resistance to flow of a material, mixture, or solution. The equation that is generally used to represent the relationship between the intrinsic viscosity, [η], and the weight-average molecular mass, M_w, is the Mark-Houwink-Kuhn-Sakurada (MH) equation:

$$[\eta]=K_\alpha\ M_w^{\alpha} \qquad (1)$$

The proportionality constant K_α is characteristic of the polymer and solvent and the exponential α is a function of the shape of the polymer coil in a solution. The ideal statistical coil has an α value of 0.5. The value of α increases as the coil expands in thermodynamically good solvents; α has a value between 1.8 and 2.0 for a rigid polymer chain extended to its full contour length. Therefore, information on polymer conformation is given by the value of α.

Viscosity properties of poly(3,5-dimethylphenylacrylate), (35PDMPA) in toluene at 25° and 30°C is not reported; therefore, this work studied the influence of temperature on dimensional properties of the polymer[1]. The influence of side chain group on the physical properties of polyethylene chains is well documented [2]. In the case of polyacrylates and polymethacrylates, interests have focused on the changes induced by altering the length of alkyl ester group [3] or identity of the ester linkage such as phenyl with alkyl substituent in various positions [4]. One way to evaluate and analyze the properties of such polymers is to correlate the dependence of their equilibrium configuration to their structure. Among the theoretical methods of evaluating configurational properties are the application of matrix methods in the form of rotational isomeric state (RIS) model to calculate conformational properties such as Flory's characteristic ratio (C_∞) [5] and or application of the wormlike model based one Ymakawa-Fujii theory [6] and its simplified form by Bohdaneky [7].

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In this work, viscometric data in conjunction with weight average molar mass (Mw) were treated based on semi-empirical theories such as two parameter theories known as Kuhn-Mark-Houwink-Sakurada (MH) and Stockmayer-Fixman (SF) relationships.[8] The rigidity of 35PDMPA compared with nearest chemical structural polymers: poly(methyl acrylate) [9] (PMA) and poly(3,5-dimethyl phenyl methacrylate) (35DMPMA)[10].

The intrinsic viscosity of 35PDMPA samples are estimated according to the Huggins'[11] and Kraemer's[12] relationship; the Huggins' constant (K_H) of each sample was determined; the variation of K_H and molar mass was studied and related to the nature of polymer samples. Then the intrinsic viscosity in conjunction with the molecular mass data of 35PDMPA solutions is treated according to the theories of intrinsic viscosity of flexible polymers to estimate the unperturbed dimension of 35PDMPA in toluene at 25° and 35°C.

Experimental

Materials

3,5-dimethylphenol (35DMP) was purchased from Sigma-Aldrich; acryloyl chloride, hexanes, triethylamine, and tetrahydrofuran (THF) were purchased from Fisher Scientific. Other solvents and reagents were purchased from the above mentioned companies. They were used without further treatments.

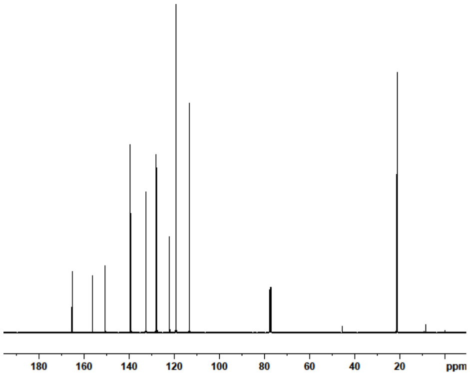
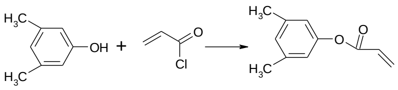


Figure 1. C-NMR 35DMPA in $CDCl_3$

Monomer. 3,5-Dimethyphenylacrylate (35DMPA) was obtained by the reaction of corresponding phenol and acryloyl chloride at low temperature (in an ice bath) using triethylamine as base to trap HCl produced and hexanes as solvent as shown in Scheme 1. Acryloly chloride and 3,5-dimethylphenol are slightly soluble in hexanes but 35DMPA is miscible in hexanes. It was purified by re-distillations under reduced pressure (~7 torr). The monomer was characterized by density, NMR, and IR. Figure 1 shows the ^{13}C-NMR of 35DMPA in CDCl3 at room temperature.



Scheme 1. reaction of preparing the monomer

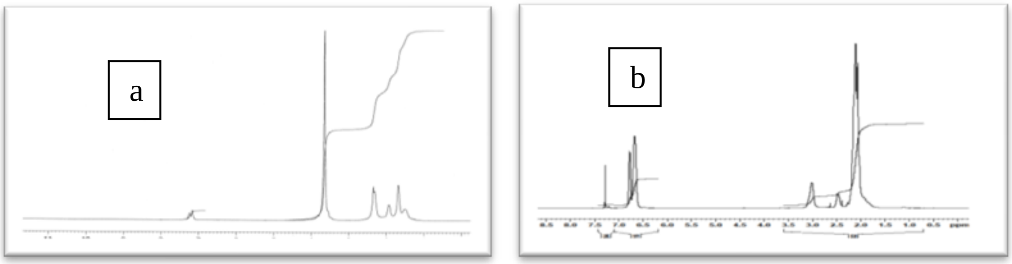


Fig 2. (a) H-NMR of poly(methylacrylate) in toluene and (b) H-NMR of 35PDMPA in $CDCl_3$

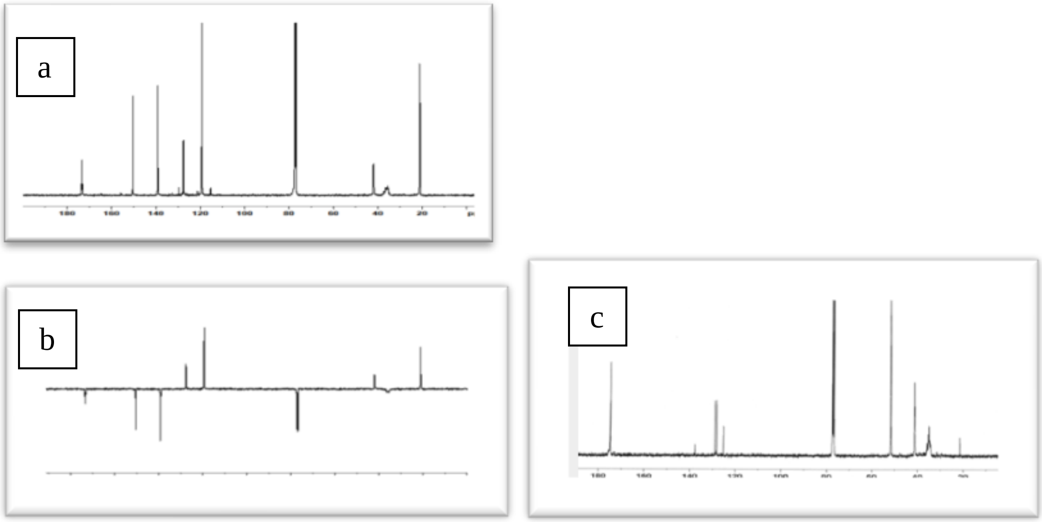


Fig. 3 (a & b) ^{13}C-NMR of 35PDMPA in $CDCl_3$ (c) ^{13}C-NMR of poly(methylacrylate) in mixture of toluene and $CDCl_3$

Polymer. Poly(3,5-Dimethyphenylacrylate) (35DMPA) obtained by the reaction of corresponding monomer in the presence of radical initiator 2,2’-azobisisobutyronitrile (~ 0.02% of monomer) under nitrogen flow for 2 hs at 60° C. The obtained polymer was dissolved in dichloromethane, reprecipitated in hexanes three times, dried under vacuum (~5 torr) at 298 K for a week. A successive precipitational fractionation was carried out on the crude polymer by using dilute toluene solution of 35PDMPA (~2%) and hexanes as precipitants. Eleven fractions were obtained. Each sample was characterized by H-NMR and ^{13}C-NMR in $CDCl_3$ and online measurements. Fig 2 shows a 400MHz H-NMR of 35PDMPA in $CDCl_3$ and Fig 4 shows ^{13}C-NMR of the polymer. Also, NMR of polymethylacrylate in toluene included to compare the shifts.

Weight Average Molar Mass (Mw). The methods to determine molar masses are either relative or absolute. Absolute methods are classified by the type of average they yield. Colligative techniques such as membrane osmometry measures number average molecular mass. Light scattering yields weight average, and ultracentrifuge determines *z*-average molar mass 2]. The absolute methods require extrapolation to infinite dilution for rigorous fulfillment of the requirements of theory.15’[13,14] Relative methods require calibration with the samples of known molar masses and include viscosity, vapor pressure osmometry, and size exclusion chromatography.

On-Line Characterizations. The molar mass of the polymer samples is among important properties to evaluate[15] as the chain length can be a controlling factor in determining solubility, elasticity, fiber forming capacity, tear strength, and impact strength in many polymers.

Viscotek GPCMAX 303 used to estimate weight average (Mw), number average (Mn), and polydispersity I = Mw/Mn of the samples. The SEC system utilizes a laser light at 760 nm. The results of study in tetrahydrofuran at 30°C are shown in Table 1.

Intrinsic Viscosity. The intrinsic viscosity of a polymeric solution is defined as:

$$[\eta] = Lim\left(\frac{\eta-\eta_1}{\eta_1 C}\right)_{C\to 0} = Lim\left(\frac{Ln(\eta/\eta_1)}{C}\right)_{C\to 0} = Lim\left(\frac{\eta-\eta_1}{\eta_1 C}\right)_{\eta_{sp}\to 0} \qquad (2)$$

Applying the virial series the two equivalent forms known as the Huggins and Kraemer relationships rounded at second term applied to diluted polymer solutions:

$$\left(\frac{\eta-\eta_1}{\eta_1 C}\right) = [\eta] + [\eta]^2 k_H\, C \qquad (3)$$

$$\left(\frac{Ln(\eta/\eta_1)}{C}\right) = [\eta] - [\eta]^2 k_K C \qquad (4)$$

where η_1 is the viscosity of the pure solvent, and η is the viscosity of the solution at zero shear conditions.

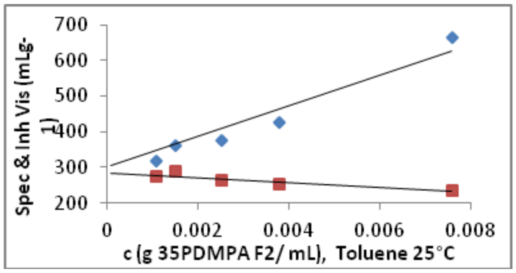
Table 1. Molecular parameters of 35PDMPA at 30°C in tetrahydrofuran obtained from Viscotek triple arrowed GPC max system.

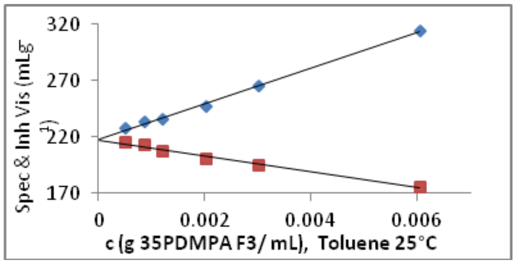
ID	VR (mL)	Mw (KDa)	Mn (KDa)	I = Mw/Mn
F1	11.45	3,948	3,081	1.28
F2	11.66	2,181	1,714	1.27
F3	11.68	1,733	1,381	1.25
F4	11.84	1,392	1,135	1.23
F6	12.25	845	730	1.16
F7	12.53	579	511	1.13
F8	12.74	397	345	1.15
F9	13.04	238	207	1.15
F10	13.40	134	115	1.16
F11	13.85	69	50	1.36
PS	12.20	118	117	1.01

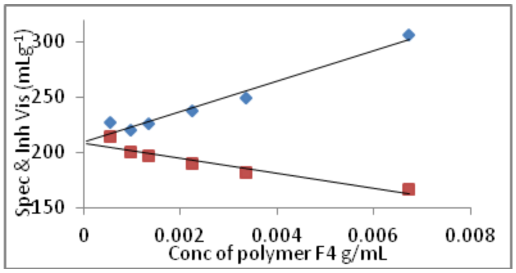
The dilute solution viscosities were measured by semi-micro Cannon-Ubbelohde capillary dilution viscometer thermostated in a water bath (298.15 and 300.15 ± 0.02 K) where solvent flow time (t_1) was at least 110 s. Microsoft Excel was used to average flow time, calculate specific viscosity, $(t-t_1)/ct_1$, and inherent viscosity, $Ln(t/t_1)/c$, then graph the above values versus concentration to fit into best fit linear least-squares lines. From the slope of the graphs K_H and from the common intercept the intrinsic viscosity was estimated as showed in Fig 4a and 4b.

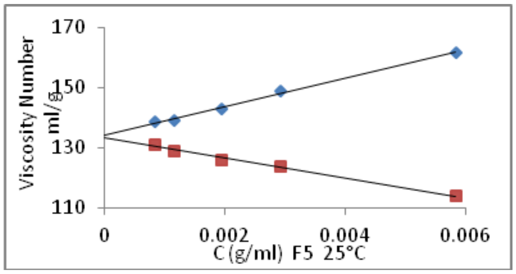
Results and Discussion

Intrinsic Viscosity. Figs 4a & 4b show the variation of viscosity number versus concentration (c) and inherent viscosity versus c in g/mL; the data fit well into a straight line; the common intercept both line is the value of intrinsic viscosity and from the slope, the Huggins and Kraemer's constants, K_H and K_K respectively, are estimated. The values of [□] obtained by Eq. (3) are the same (within their standard deviation) as those evaluated from Eq. (4), confirming the equality of the Huggins and Kraemer methods. The equality of equation (3) and (4) demands that the $K_H + K_K = 1/2$, which has been confirmed in this work. The exception arose with the value of $K_H + K_K < 0.5$ for sample F1, which has a higher polydispersity index and ultrahigh molar mass polymers as expected for a head fraction collected from precipitation fractional method.









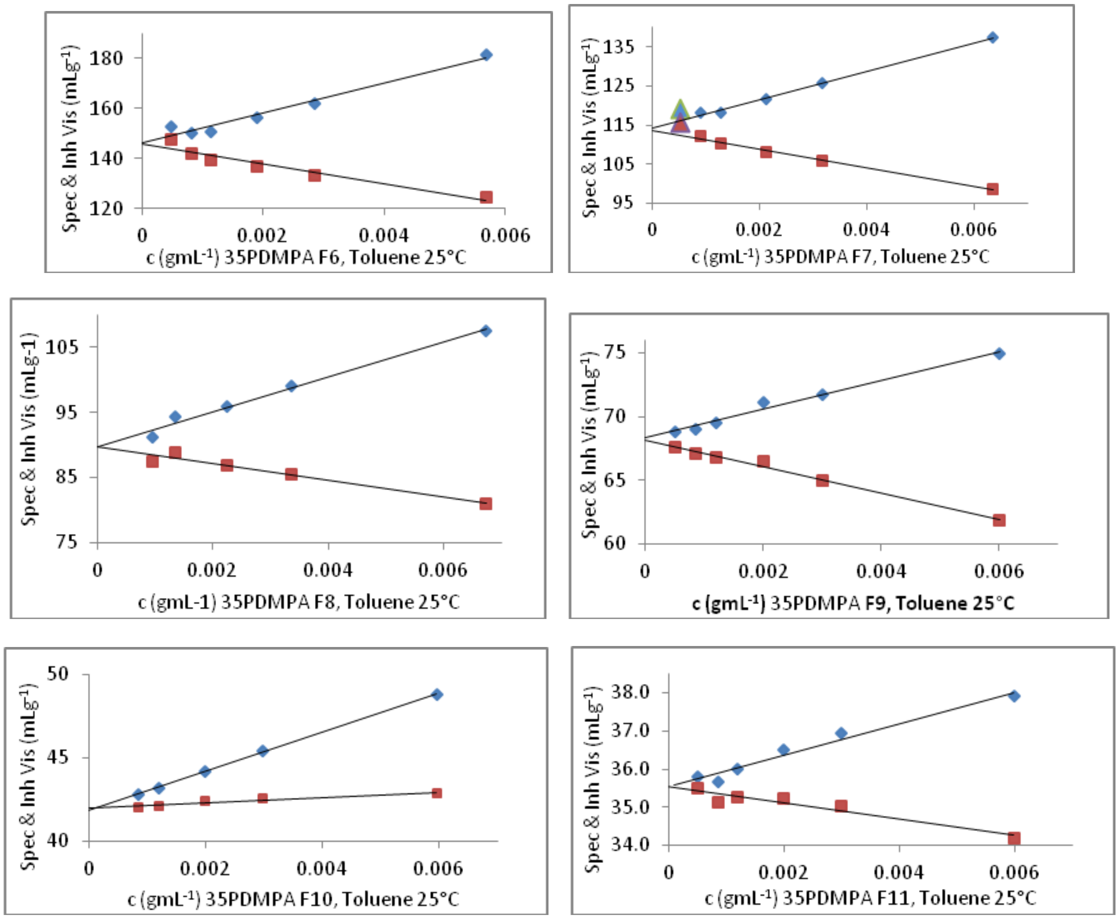
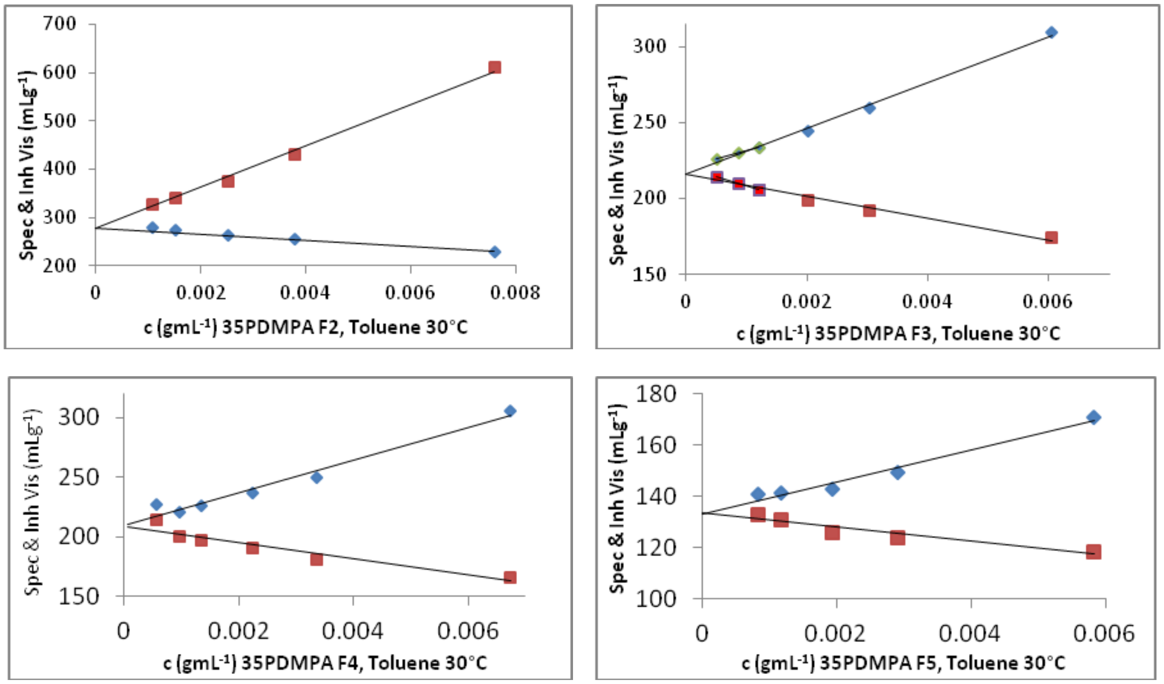


Fig 4a. Determination of limiting viscosity number by plotting the variation of viscosity number (t-t$_0$)/ct$_0$ versus concentration of samples of 35PDMPA in toluene at 298.15 K.



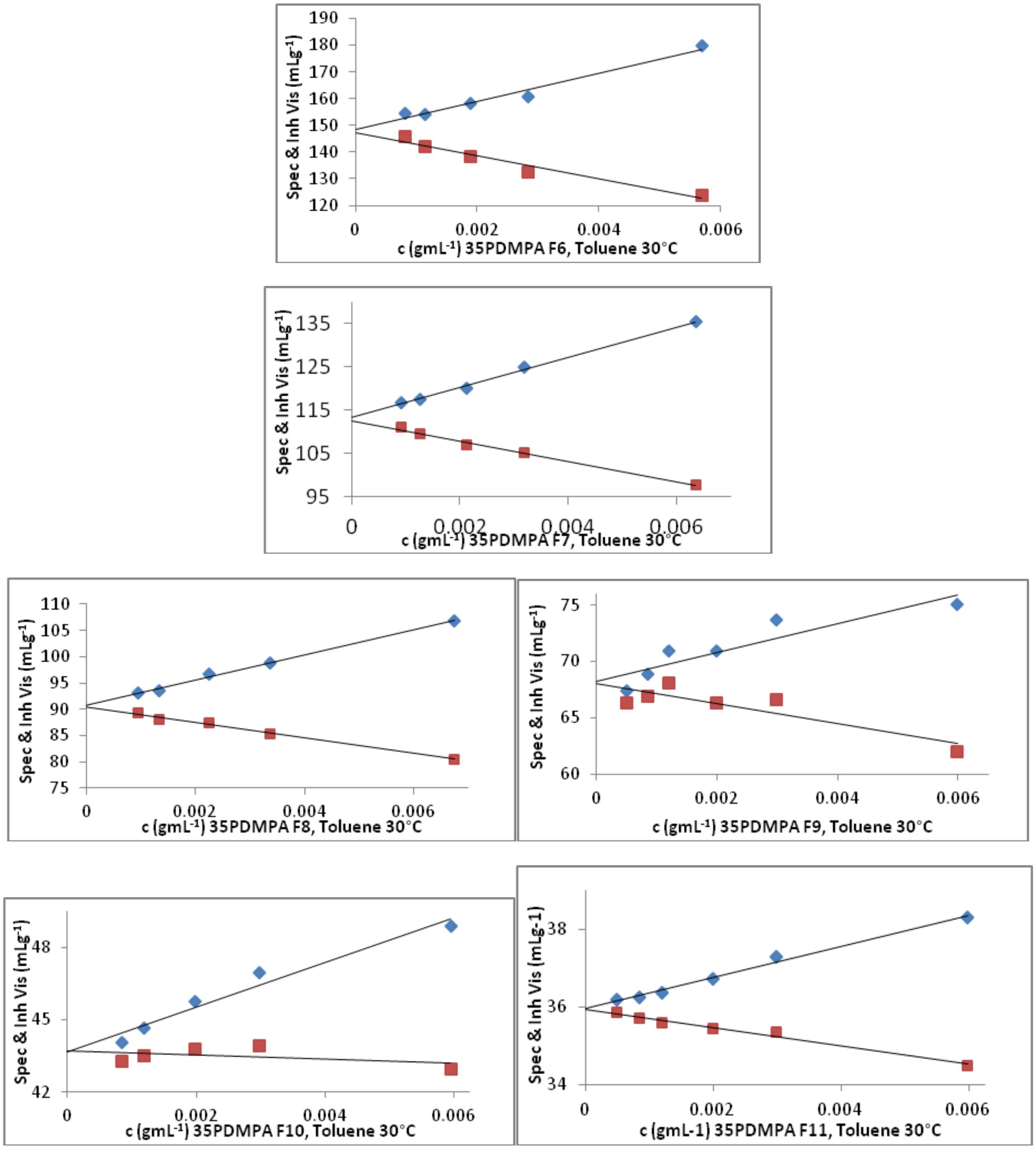


Fig 4b. Determination of limiting viscosity number by plotting the variation of viscosity number $(t-t_0)/ct_0$ versus concentration of samples of 35PDMPA in toluene at 303 K.

Huggins Constant. The values of Huggins' constant k_H, can be used as an index to describe polymer solvent and polymer-polymer interactions.[16-17] For flexible, linear, nonpolar or not very polar vinyl polymers in good solvents such as 35PDMPA in toluene the values of K_H usually lies between 0.3 to 0.4. The values of K_H for 35PDMPA in toluene solution ranged 0.2-0.4, which are within the expected range. The deviations are higher at the head and tail samples as shown in Fig 5, which is within expectations.

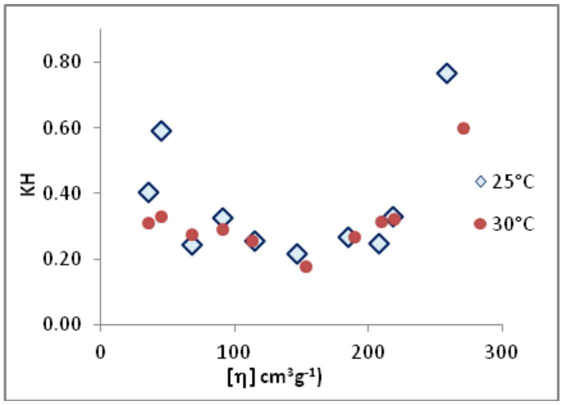


Fig 5. Variation of Huggins' constatant versus viscosity number.

3. The Intrinsic Viscosity and Temperature

The viscosity of a solution is temperature dependent and will decrease as the temperature increases as shown by the following Arrhenius equation: $\eta = Ae^{E/RT}$

The intrinsic viscosity will increase at a higher temperature if the quality of solvent is getting better due to expansion of macromolecule.

The logarithmic variation of intrinsic viscosity of 35PDMPA samples versus corresponding molecular mass, Mw, are shown in Fig 6. The analysis of chain characteristics of 35PDMPA that can be deduced from the molecular mass variation of the intrinsic viscosity at each temperature in toluene indicates that the values of [□] areslightly higher at higher temperatures in toluene. This indicates the quality of solvent is not changing significantly by increasing temperature by 5°C as shown in Fig 6.

4. The Intrinsic Viscosity and Molar Mass

The intrinsic viscosity of a macromolecule in a dilute solution is a measure of its hydrodynamic average size, form, and shape in the solution. Many studies could be found that explore the empirical relationships between coil dimensions of synthetic polymers with their intrinsic viscosity.15[-18] The most frequently used relationship between intrinsic viscosity, □ □ □ , and the weight average molecular mass, <M_w>, is MH Equation (1).

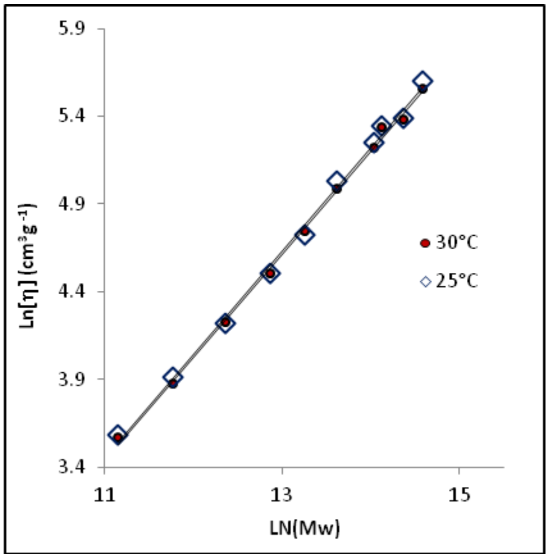


Fig 6. Double logaritmic graph of intinsc viscosity and molar mass at 25°C and 30°C in toluene

Numerous researchers**Error! Bookmark not defined.**[19] have demonstrated the validity of MH equation applied to random coiled polymers for molecular weights ranging several orders of magnitude. By increasing thermodynamic strengths of solvents, the magnitude of coefficient α would increase while the magnitude of K_α would decrease.

Generally, for the random coil flexible polymer molecules, the value of α would be between 0.50 and 0.80. Therefore, 35PDMPA with α of 0.592 at 25°C, and 0.595 at 30°C is considered to be a flexible random coil polymer. For non-flexible and rigid (worm- or rod-like) macromolecules higher values of α, larger than or equal to unity has been observed.[20] For highly branched poly(methyl methacrylate) α of 0.40 was observed[21]. Thus the numerical value of α provides information concerning polymer conformation as well.

Several factors contribute to enhance the exponent α.[22] Among them are: (a) chain stiffness, (b) excluded volume, and (c) partial drainage. It is universally accepted that the value of α that corresponds to a nondraining coil unperturbed by the excluded volume effect is 0.5; this does not include the low-molecular mass region,[16] and temperatures under theta condition where the values of α are found to be less than 0.5. In addition to the above mentioned parameters, the chain thickness is the only contributing factor that reduces the value of α; in the limit of molecules having thickness equal to length (sphere), α = 0.

Fig. 6 shows the treatment of viscosity data in the light of MH double logarithmic plot. The K_α and α of the plots are summarized in Table 2.

Table 2. The slopes and intercepts, K_α and α, of the double logarithmic Fig 6

t °C	K_α	α
25	0.0457	0.592
30	0.0447	0.595

Based on α values presented in Table 2, the interaction capacity of polymer-solvent slightly increases in the order of increasing temperature.

4. Unperturbed Dimensions

The expansion of a covalently bonded polymer chain is restricted by valence angles between each chain atom. In general this angle is θ for a homoatomic chain and the square of end-to-end dimensions $<R_{00}^2>$ expresses as nl^2, which can be modified to allow for these short-range interactions.[1]

$$< R_{0f}^2 > = nl^2 \frac{(1-\cos\theta)}{(1+\cos\theta)} \qquad (5)$$

where *l* is the bond length, 1.54 Å for C-C bond, and *n* is the total number of backbone bonds. For the simplest case of an all carbon backbone chain such as polyethylene, cos109.5 ~-1/3 so that the Eq. (7) becomes

$$< R_{0f}^2 > = nl^2 \frac{(1-\cos 109.5)}{(1+\cos 109.5)} = 2nl^2 \qquad (6)$$

This indicates that the polyethylene chain is twice as extended as the freely jointed chain model when the short-range interactions are considered. In fact, in butane and carbon chains with more atoms, steric repulsions impose restrictions-to-bond rotations.[23] This feature in equation (6) causes further modified

$$< R_o^2 > = nl^2 \frac{(1-\cos\theta)}{(1+\cos\theta)} \frac{(1-\cos<\phi>)}{(1+\cos<\phi>)} \qquad (7)$$

where <cosϕ> is the average cosine of the angle of rotation of the bonds in the backbone chain. The parameter of $<R_0^2>$ is the average mean square of the unperturbed dimension, which is the main characteristic parameter of a polymeric chain.

For the 35PDMPA chain, the unperturbed dimension may be obtained directly from the intercept of the MH plot, K_θ, in an ideal solution. The K_θ is related to the unperturbed dimension of the polymer.

$$K_\theta = \Phi_0 \left(\frac{< R_0^2 >}{M} \right)^{3/2} \qquad (8)$$

where Φ_0 is the Flory universal constant. Φ_0 depends on molecular mass of the polymer and the kinds of polymer, with the best experimental value of 2.51 x 10^{23} to 2.87 x 10^{23} when the intrinsic viscosity is expressed in mL/g.[24] Under non-ideal conditions, the well-known Flory's viscosity-molecular-mass equation is used to estimate the unperturbed dimension of macromolecules supposing the hydrodynamic draining effect is negligible and an estimate can be made of the viscosity expansion factor, α_η :

$$[\eta] = K_a M^a \alpha_\eta^3 \qquad (9)$$

$$K_v = K_\theta = \Phi_0(<R_0^2> M^{-1})^{3/2};$$
$$\alpha^5 - \alpha^3 = C_M(1-2\chi)M^{1/2};$$
$$C_M = \frac{27}{2^{5/2}\pi^{3/2}}\frac{\bar{v}^2}{N_A V_1}(<R_0^2> M^{-1})^{3/2}$$

$\bar{v}$ being the partial specific volume of polymer, V_1 the molar volume of the solvent, N_A the Avogadro's number, and Flory's χ expresses the first neighbor interaction free energy for polymer-solvent system.

The unperturbed dimensions usually are estimated by extrapolation methods using a number of plots based on theoretical or semi-theoretical equations developed for this purpose, such as applications of the excluded volume equations between the molecular weight and intrinsic viscosities in good solvents. Stockmayer and Fixman [9] approximate

$$\alpha_\eta^3 = 1 + 1.55z; \qquad z = \left(\frac{3}{2\pi}\right)^{3/2} B\left(\frac{<R_0^2>}{M}\right)^{-3/2} M^{1/2};$$
$$B = \bar{v}^2\frac{(1-2\chi)}{V_1 N_A}$$

proposed a relationship for treating data covering the usual range of molecular weights encountered in experiments.

$$[\eta]M^{-\frac{1}{2}} = K_\theta + 0.51\Phi_0 B M^{\frac{1}{2}} \qquad (10)$$

The constant K_θ is the intercept; it is equal to the HK's K_θ at the theta conditions. The plot of $[\eta]M^{-1/2}$ against $<M_w>^{1/2}$ according to the Eq. (10) for 35PDMPA in toluene is shown in Fig 7.

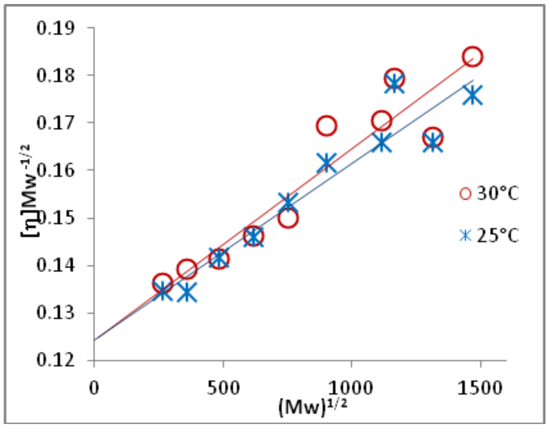


Fig 7. Stockmayer-Fixman plots (equation (10)) for 35PDMPA fractions in toluene at 25°c and 30°C.

It is apparent that all experimental data are fitting to straight lines with both lines reaching to a common intercept as observed in the Fig 7, which is within expectation. The value of □□□ and hence the values of $<R_0^2>M^{-1/2}$, σ and C_∞ in toluene at 25°C and 30°C are the same as seen in Table 3. Based on the chemical structure of main chain and the side chain the characteristic parameter of 35PDMPA is expected to be higher than PMA in toluene, and smaller than poly(3,5-dimethylphenyl methacrylate) (35PDMPMA). Data of Table 3 confirm this expectation. Two different factors may contribute in determining a higher value of □□□for a polymeric chain: the nature of the main chain and the effects of side chains. In case of 35PDMPA, the nature of the main chain, which is composed of a simple hydrocarbon chain, may not contribute to the □□ as the hindered voluminous side phenyl ester groups. The 3,5-dimethylphenyl lateral chains occupy a larger volume, hindering the backbone internal rotations by establishing orientational correlations between themselves.

Table 3. Values K_θ, $<R_0^2>M^{-1/2}$, σ and C_∞, the slope and B obtained from extrapolation according to SF.

t °C	K_θ	$<R_0^2>M^{-1/2}$	σ	C_∞	E.E23
25	0.124	0.788	3.33	22.1	2.87
30	0.124	0.788	3.33	22.2	3.10
PMA [1]	0.0951	0.721	2.17	9.43	
35PDMPMA	0.158	0.853	3.82	29.18	

For ideal solvent, the slope of Stockmayer-Fixman equation must be zero. However, as the thermodynamic power of solvent increases the slope of the SF line will also increase. As Fig 7 shows the slopes of lines fitted into experimental data at 30°C is higher than the line fitted to the data at 25°C. Hence the polymer solvent interaction parameter at 30°C is higher than 25°C due to improvement of thermodynamic quality of the solvent caused by higher temperature.

6. Chain Stiffness

σ known as the steric parameter for a freely jointed chain and for a simple chain is
$\sigma^2 = <R_0^2><R_{0f}^2>^{-1} = (1-<\cos\phi>)(1+<\cos\phi>)^{-1}$ (11).

For more complex chains such as 35PDMPA containing ring and heteroatom, an estimated σ is obtained experimentally from the value of K_θ, which is related to the rigidity factor σ, or to the characteristic ratio C_∞, by the expressions

$$\sigma = \left(\frac{<R_0^2>}{<R_{0f}^2>}\right)^{1/2} = \left(\frac{K_\theta}{\Phi_0}\right)^{1/3} \frac{M_0}{2l}^{\frac{1}{2}} \qquad (12)$$

$$C_\infty = \frac{<R_0^2>}{nl^2} = \left(\frac{K_\theta}{\Phi_0}\right)^{2/3} \frac{M_0}{2l^2} \qquad (13)$$

where M_0 = 176.2 g/mol, is the molecular mass of the monomer and l = 1.54Å lengths of C-C single bond. The values of σ and C_∞ based on Eqs (11) and (12) are also tabulated in Table 3.

The nature of the main chain of a 35PDMPA polymer may not contribute to the high value of C_∞ and σ as much as the 3,5-dimethylphenyl ester side chains. The 3,5dimethylphenyl lateral chains occupy a larger volume (thus posing steric hindrances) and more importantly, they may hinder the backbone internal rotations by establishing orientational correlations between themselves. The stiffening of the polymer chain due to the presence of large aromatic groups and long n-alkyl pendant groups has already been reported for other polymers by several researchers[14,16-18]. Also, it is known that the interactions of elements of polymer chains with solvent molecules could affect the probability distribution of the angles of internal rotation in the chain. This observation was confirmed both theoretically[25-26] and experimentally[3].

The value of C_∞ of 35PDMPA (22.1) is much higher than values observed for other polyacrylates. For example, the value of C_∞ for polyphenyl-methacrylate, PPMA, both theta solvents and good solvents (12.2 and 13.3) are larger than one for many atactic vinyl polymers, which are in range of $5 < C_\infty < 10$ usually found in the literature. Also, PPMA's C_∞ has been found to be ~50% larger than that of atatctic poly(methylmethacrylate) (8.10). [15] It should also be remarked that the value of C_∞ in good solvents probably has been underestimated as they were obtained by extrapolating to M=0 the molecular weight region of Stockmayer-Fixman plot in which the effect of stiffness is coupled with excluded volume. However, chain rigidity may be contributing to the slope so that the results obtained for K_θ and C_∞ could be inaccurate. An indication that the positive slope in this plot may include the effect of chain stiffness comes from the convergent trend observed in the curves at high molecular weights. This leveling of the slope cannot be accounted for by the theory of flexible coils perturbed by excluded volume but has been predicted by wormlike models of stiff chains. [10-12]

7. Conclusion

The treatment of viscosity data based on Huggins' and Kraemer's relationships allowed for evaluation of intrinsic viscosity of the 35PDMPA samples in toluene.

The MH relationship has accounted for the dimension of the polymer in ideal solvents and the MH's exponent has established the relative thermodynamic power of the solvents and the random coil property of 35PDMPA in solution. The application of empirical relationship of SF accounted for effects of the excluded volume-to-viscosity, and molar mass data provided additional insights to the property of 35PDMPA in solutions.

It is common to consider the equilibrium flexibility of macromolecules in a solution based on the value of the conformational parameter σ, averaging 3.3 for 35PDMPA. Such a high values of σ does not necessarily imply that the state of internal rotation of units in 35PDMA chains is truly hindered in view of the fact that the 35PDMPA chain backbone looks like a polyethylene chain but contains 3,5-dimethylphenyl-esters groups as side chains. But this means that the parameter σ is only significant for macromolecules with flexibility imparted by rotation around valence bonds without distortion of valence angles by side chain groups. Therefore, σ is unsuitable for use with many polymers, especially those containing hindered side chains such as 35PDMPA, those whose angle of rotation may be hindered by polymer-solvent interactions, and those that have cyclic structures in the chain backbone.

Acknowledgments

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