Scientific
Research

Effects of Side-Chain on Conformational Characteristics of Poly(3,5-Dimethyl-Phenyl-Acrylate) in Toluene at 40°C

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ABSTRACT

The intrinsic viscosity [η] of poly(3,5-dimethyl-phenyl-acrylate) (35PDMPA) solutions were evaluated throughout the measurements of the flow times of toluene and polymer solutions by classical Huggins, and Kraemer's methods using a Cannon-Ubbelohde semi-micro-dilution capillary viscometer in a Cannon thermostated water bath at 40°C ± 0.02°C. The values of Huggins' constant estimated ranged from 0.2 to 0.4 which were within expectations. The intrinsic viscosities and molecular weight relationship was established with the two-parameter classical models of Staudinger-Mark-Houwink-Sakurada and Stockmayer-Fixman. Conformational parameter C_∞ and σ indicated 35PDMPA be semi flexible. Also, the rigidity of 35PDMPA was confirmed by Yamakawa-Fuji wormlike theory modified by Bohdanecký. The molecular parameters were estimated and compared. The results showed that 35PDMPA behaves like a semi-rigid polymer in toluene at 40°C rather than a random coil flexible macromolecule.

Keywords: Intrinsic Viscosity; Poly(3,5-Dimethyl-Phenyl-Acrylate); Conformational Parameters; Rigidity Factor; Kuhn Statistical Length

1. Introduction

The influence of temperature and side chain groups on the physical properties of polyethylene chains is well documented [1]. In the case of polyacrylates, interests have focused on the changes induced by altering the length of alkyl ester group [2] or identity of the ester linkage such as phenyl with alkyl substituent in various positions [3]. One way to evaluate and analyze the properties of such polymers is at least to correlate the dependence of their equilibrium configuration to their structure. Among the 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_∞) [4] and or application of the wormlike model based on Yamakawa-Fuji theory [5] and its simplified form by Bohdanecký [6]. Neither the RIS nor the wormlike model has been applied to evaluate the influence of side chain on unperturbed dimensions of 35PDMPA. This paper presents experimental findings pertaining to dilute

solution properties of 35PDMPA in toluene at 40°C.

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 were found that explored the empirical relationships between coil dimensions of synthetic polymers with their intrinsic viscosity [1-7]. The most frequently used relationship between intrinsic viscosity, [η], and the weight-average molecular mass, M_w, is the Mark-Houwink-Kuhn-Sakurada (MH) Equation:

$$[\eta] = K_\alpha M_w^\alpha ; \tag{1}$$

where, the parameter α is a measure of the thermodynamic power of solvent and K_α is a measure of coil volume for an unperturbed condition or ideal solvent called θ-condition for random coil polymers. Numerous researchers [1-8] have demonstrated the validity of the MH equation applied to random coiled polymers for molecular weights ranging in 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 ran-
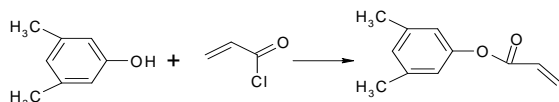
dom coil flexible polymer molecules, the value of α would be between 0.50 and 0.80. For non-flexible and rigid (worm-like or rod-like) macromolecules higher values of α larger than or equal to unity have been observed. Thus, the numerical value of α provides information concerning polymer conformation as well.

In this work, the viscosity of 35PDMPA samples are treated according to the Huggins' [9] and Kraemer's [10] relationship to evaluate the intrinsic viscosity of the polymer samples; the constant of each method has been determined and related to the nature of the polymer solvent system. The intrinsic viscosity, in conjunction with the molecular mass data of 35PDMPA solutions, is treated according to the theories of intrinsic viscosity of random flexible and worm-like polymers developed by Yamakawa-Fuji and simplified by Bohdanecký.
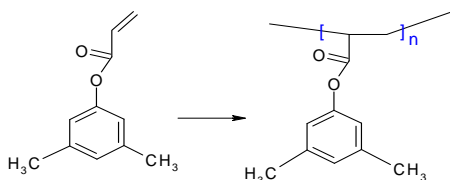
2. Experimental

2.1. Monomer

3,5-dimethyl-phenyl-acrylate (35DMPA) was obtained by the reaction of corresponding phenol and acryloyl chlorideat low temperature (in an ice bath)using triethylamineas a base to trap HCl produced and hexanes as solvent (**Scheme 1**). Acryloly chloride and 3,5-dimethylphenol are slightly soluble in hexanes but 35DMPA is miscible in hexanes. It was purified by re-distillation under reduced pressure (~7 torr). The monomer was characterized by NMR and IR.

Scheme 1. Reaction of preparing the monomer.

2.2. Polymer

Poly(3,5-dimethy-phenyl-acrylate), (35PDMPA) was synthesized by bulk polymerization of 35DMPA under nitrogen atmosphere in a sealed flask using 2,2'-azo-bis-iso-butyro-nitrile (~0.02 % of monomer) as the radical initiator at 333 K (**Scheme 2**). The obtained polymer dissolved in dichloromethane, re-precipitated in hexanes three times, and deride under vacuum (~2 torr) at 298 K. The sample was fractionated using dilute (~1%) toluene solution with hexanes as precipitants [11].

Scheme 2. Reaction of preparing the monomer.

2.3. Molecular Mass Characterizations

To estimate molar mass of 35PDMPA two methods were used: absolute method, light-scattering and relative method, size exclusions. Absolute methods are classified by the type of average they yield such as colligative techniques, for example, membrane osmometry measures number average, light scattering yields weight average, and ultracentrifuge determines *z*-average molar mass. The absolute methods require extrapolation to infinite dilution for rigorous fulfillment of the requirements of theory. Relative methods require calibration with the samples of known molar masses and include viscosity, vapor pressure osmometry and size exclusion chromatography (SEC) [12-14].

A Viscotek GPCMAX 303 with a two angle light scattering detector, a refractive index detector, and two Viscotek universal bed size exclusion columns, all housed in a thermo stated oven at 30°C was used to evaluate weight average (M_w), number average (M_n), and polydispersity of the samples [15].

2.4. Viscosity Measurements

The intrinsic viscosity of a polymeric solution is defined as

$$[\eta] = \lim\left(\frac{\eta - \eta_1}{\eta_1 C}\right)_{C \to 0} = \lim\left(\frac{\ln(\eta / \eta_1)}{C}\right)_{C \to 0}$$
$$= \lim\left(\frac{\eta - \eta_1}{\eta_1 C}\right)_{\eta_{sp} \to 0} \quad (2)$$

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

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

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

where η_1, is the viscosity of the pure solvent, and η is the viscosity of the solution at zero shear conditions. **Table 1** shows the values of $[\eta]$, k_H and $k_K + k_H$ solutions of 35DMPA in toluene at 40°C [16].

The dilute solution viscosities were measured with a semi-micro Cannon-Ubbelohde capillary dilution viscometer, thermostated in a water bath at 40°C (313.2 ± 0.02 K) where solvent flow times (t_1) were at least 110 s. Linear least-squares fit of specific viscosity and inherent viscosities versus concentration were used to obtain the intrinsic viscosity as a common intercept. **Figure 1** shows the plot of viscosity number versus concretization for eleven samples of polymer.

Table 1. Values of intrinsic viscosity [η], k_H, and $k_H + k_K$ of 35PDMPA in toluene at 40°C.

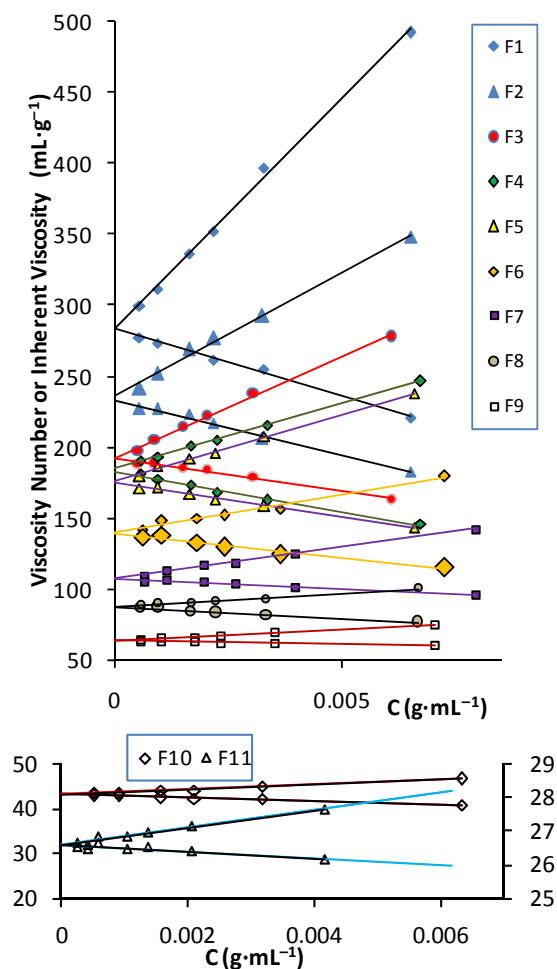| Sample	k_H	$<[\eta]>$	$k_H + k_K$
F1	0.407	282.9	0.525
F2	0.312	272.6	0.457
F3	0.388	192.0	0.516
F4	0.267	183.8	0.438
F5	0.308	174.9	0.465
F6	0.272	139.2	0.451
F7	0.389	107.1	0.519
F8	0.237	87.63	0.454
F9	0.377	63.41	0.511
F10	0.27	43.45	0.482
F11	0.364	26.60	0.502

Figure 1. Estimation of limiting viscosity number by plot of variation of viscosity number $(t - t_1)/ct_1$ versus concentration of samples of 35PDMPA in toluene at 313.15 K.

3. Results and Discussion

Figure 1 shows the variation of $(t - t_1)/t_1 C$ and $(\text{Ln } t/t_1)/C$ versus C (g/mL); the data fit well into a straight line with a common intercept which is the value of intrinsic viscosity and from the slopes Huggins' (k_H) and Kraemer's (k_K) constants were estimated.

3.1. Huggins (k_H) and Kraemer (k_K) Constants

The values of Huggins' constant k_H can be used as an index to describe polymer solvent and polymer-polymer interactions [17,18]. For flexible, linear, nonpolar or not very polar vinyl polymers in good solvents the values of k_H usually lie between 0.3 to 0.4. The values of k_H for 35PDMPA and toluene solution range 0.27 - 0.41 which are within the expected scope. **Figure 2** shows the variation of k_H and k_K versus molar mass of polymer. The values are scattered from 0.27 to 0.41. The list square fitted to the data shows a positive slope: as molar mass increasing the k_H also increases.

The equality of Equations (2) and (3) demands that the $k_H + k_K = 1/2$, which has been confirmed in this work.

3.2. The Intrinsic Viscosity and Molar Mass

Figure 3 shows the double logarithmic graph of intrinsic viscosity and molar mass at 40°C. The molecular weight dependence of [η] are expressed in the values of K_α and α of MH. Several factors contribute to enhance the exponent α. [19]. Among them are: 1) chain stiffness, 2) excluded volume, and 3) 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 [17], and temperatures under theta condition where the values of α are found to be less than 0.5. Besides 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), $\alpha = 0$.
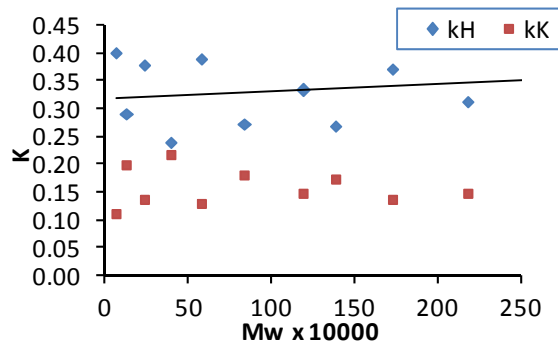

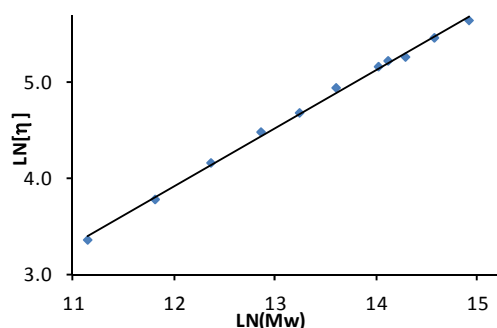**Figure 2. Variation of Huggins' and Kreamer's constatants versus viscosity number.**

Figure 3. Double logaritmic graph of intrinsic viscosity and molar mass of 35PDMPA in toluene at 40˚C.

Figure 3 shows the treatment of viscosity data in the light of MH double logarithmic plot. The K_α and α of the plot are summarized in **Table 2**. According to the values of **Table 2**, the solvation capacity of toluene increases as temperature increases from 25˚C to 40˚C.

3.3. Unperturbed Dimensions

The unperturbed dimensions of a linear flexible polymer are obtained either by light scattering over an angular range or dilute solution viscometric of macromolecules in ideal solvent so called Θ-conditions. The square of end-to-end dimensions $\langle R_{00}^2 \rangle$ for a random distribution of n particle with bond length of l is expressed as nl^2. The expansion of a covalently bonded polymer chain is restricted by valence angles θ between each chain atom, $\langle R_{00}^2 \rangle$ modified to allow for short-range interactions called $\langle R_{0f}^2 \rangle$:

$$\langle R_{0f}^2 \rangle = nl^2 \frac{(1-\cos\theta)}{(1+\cos\theta)} \quad (5)$$

For C-C backbone polymers such as 35PDMPA*l*the bond length is 1.54 Å, and n is the total number of backbone bonds. For the simplest case of an all carbon backbone chain such as polyethylene, $\cos(109.5) \sim -1/3$ so that the Equation (5) becomes

$$\langle R_{0f}^2 \rangle = nl^2 \frac{(1-\cos 109.5)}{(1+\cos 109.5)} = 2nl^2 \quad (6)$$

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 [20]. This feature in Equation (6) causes further modifications:

$$\langle R_o^2 \rangle = nl^2 \frac{(1-\cos\theta)(1-\cos\langle\phi\rangle)}{(1+\cos\theta)(1+\cos\langle\phi\rangle)} \quad (7)$$

where $\cos\langle\phi\rangle$ is the average cosine of the angle of rotation of the bonds in the backbone chain. The parameter

Table 2. The slopes and intercepts, K_α and α, of the double logarithmic plot of [η] and Mw in toluene at 25˚C and 40˚C.

t˚C	K_α	α
40	0.0320	0.612
25	0.0472	0.5894

of $\langle R_o^2 \rangle$ is the average mean square of the unperturbed dimension, which is the main characteristic parameter of a polymeric chain.

For a 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 as:

$$K_\theta = \Phi_0 \left(\frac{\langle R_0^2 \rangle}{M} \right)^{3/2} \quad (8)$$

where Φ_0 is the Flory universal constant; it depends on molecular mass of the polymer and the type of polymer with the best experimental value of 2.51×10^{23} to 2.87×10^{23} when the intrinsic viscosity is expressed in mL/g [21].

3.4. Unperturbed Dimension by Stockmayer-Fixman Method

The unperturbed dimensions of a polymer in a thermodynamically good solvent usually are estimated by extrapolation methods using a number of plots based on theoretical or semi-theoretical equations developed for this purpose, for example, applications of the excluded volume equations between the molecular weight and intrinsic viscosities in good solvents. Stockmayer-Fixman (SF) proposed one such relationship for treating data covering the usual range of molecular weights encountered in experiments.

$$[\eta]M^{-1/2} = K_\theta + 0.51\Phi_0 BM^{1/2} \quad (9)$$

The constant K_θ is the intercept; it is equal to the K_{MH} at the theta conditions [22]. The plot of $[\eta]M^{-1/2}$ against $\langle M_w \rangle^{1/2}$ according to the Equation (9) for 35PDMPA in toluene illustrated in **Figure 4**. The value of K_θ in toluene at 40˚C was estimated by fitting a straight line into a data point using the least square method. These findings are summarized in **Table 3** for 35PDMPA at 25˚C, and 40˚C. As can be seen, the values of K_θ decreased as the temperature increased and the quality of solvent improved. This was not within expectations.

Based on Equation (9) the plot of $[\eta]/Mw^{1/2}$ versus $M^{1/2}$ should be linear only for long enough chains ($n > 10^3$) where the function of excluded volume z approaches its limit. As **Figure 4** shows the two low-molecular-weight samples did not meet these conditions since their $n < 1000$. Thus, precaution is necessary to evaluate dimensional parameters based on SF under these conditions. For ideal solvent, the slope of the SF equation must
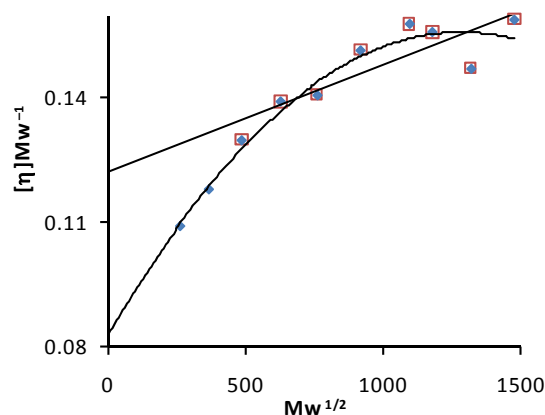
Figure 4. Stockmayer-Fixman plot, Equation (9), for 35PDMPA in toluene at 40°C.

Table 3. Values of K_θ, $\left(\langle R_0^2 \rangle / M\right)^{1/2}$, σ and C_∞ from SF plot and Bohdanecký.

Method	K_θ	$\left(\langle R_0^2 \rangle / M\right)_\infty^{1/2}$	s	C_∞
SF 25°	0.122	0.783	3.37	22.78
SF 40°	0.109	0.753	3.25	21.08
H-Mw 40°	0.124	0.786	3.39	22.98
At M∞	0.170	0.875	3.77	28.44
Bohdanecký	0.171	0.877	3.78	28.56

be zero. In a good solvent such as toluene, the slope is positive. Two different factors may contribute in determining a high value of K_θ for a polymeric chain such as 35PDMPA: the nature of the main chain and the effects of side chains and solvent. In the case of 35PDMPA, the nature of the main chain, which is composed of a simple hydrocarbon chain, may not contribute to the K_θ as the hindered voluminous side phenyl ester groups. The 3,5-dimethyl-phenyl lateral chains occupy a large volume and hinder the backbone internal rotations by establishing orientational correlations between themselves.

3.5. Evaluation of Conformational Characteristics

Reliable values of the characteristic parameters of the conformation and flexibility of polymer chains such as Flory characteristic ratio C_∞, steric factor σ, and Kuhn statistical segment length l_K are needed for the interpretation of various properties, including the rheological behavior of melts. The conformation of 35PDMPA chains currently can be characterized by the Flory characteristic ratio C_∞ or the steric factor σ. The latter two quantities are defined by the Equations (10) and (12). For more complex chains, such as 35PDMPA containing ring and heteroatom, an estimated σ is obtained from

$$\sigma^2 = \langle R_0^2 \rangle \langle R_{0f}^2 \rangle^{-1} \tag{10}$$

The mean square unperturbed end-to-end distance, $\langle R_0^2 \rangle$ can be obtained experimentally from the value of K_θ, Equation (8), which is related to the rigidity factor σ, or to the characteristic ratio C_∞, by the expression

$$\sigma = \left(\frac{\langle R_0^2 \rangle}{\langle R_{0f}^2 \rangle}\right)^{1/2} = \left(\frac{K_\theta}{\Phi_0}\right)^{1/3}\left(\frac{M_0}{2l}\right)^{1/2} \tag{11}$$

$$C_\infty = \frac{\langle R_0^2 \rangle}{\langle R_{00}^2 \rangle} = \left(\frac{K_\theta}{\Phi_0}\right)^{2/3}\frac{M_0}{2l^2} \tag{12}$$

where M_0 is the molecular mass of the monomer. The values of σ and C_∞ based on Equations (11) and (12) are also tabulated in the **Table 3**.

3.6. Wormlike Cylinder

Another method of evaluation of the characteristic parameters of 35PDMPA is by the theory for the worm-like touched-bead model [23,24]. Based on this theory, the intrinsic viscosity at theta condition depends not only on the unperturbed mean-square end-to-end distance $\langle R_0^2 \rangle$, but also on the cross-sectional dimensions of polymer-called the diameter of the bead, d_b, the small units that compose the macromolecule. The results of the theory have been expressed in a simple form convenient for use even with very short chains by Bohdanecký [25]

$$[\eta]_0 = A\eta + K_0 \cdot M^{1/2} \tag{13}$$

with: $K_0 = \Phi_{0,\infty}\left(\langle R_0^2 \rangle / M\right)_\infty^{3/2} \tag{14}$

$$A_\eta = K_0 \cdot A_0\left(d_{br}\right) \cdot M_k^{1/2} \tag{15}$$

$$d_{br} = d_b / l_K \tag{16}$$

$$l_K = \left(\langle R_0^2 \rangle / M\right)_\infty M_L \tag{17}^{[1]}$$

$$M_K = l_K \cdot M_L \tag{18}$$

$\left(\langle R_0^2 \rangle / M\right)_\infty$ is the ratio of $\langle R_0^2 \rangle$ and M is the random coil limit, and $\Phi_{0,\infty}$ is the Flory viscosity constant for random coils in the non-draining regime, $A_0(d_{br})$ is a function of the reduced bead diameter d_{br}, d_b is the bead diameter, l_K and M_K are, respectively, the length and molecular weight of the Kuhn statistical segment, and M_L is the shift factor which is usually set equal to the molecular weight per unit contour length of the chain at full extension. One of the simplest forms of description of molecular-weight dependence of the intrinsic viscosity in good solvents by theoretical and semi-empirical equa-

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[1]$L_K \equiv 2q \equiv \lambda^{-1}$.

tions is [26]

$$\alpha_\eta^3 = [\eta]/[\eta]_0 = 1 + C_\eta(n_K)z \qquad (19)$$

This is valid for $\alpha_\eta^3 < 1.5$ only [27]. It is used here because most of the α_η^3 values are in this range. The symbol α_η stands for the viscosity-radius expansion factor, n_K is the number of Kuhn segments in the chain, z is the excluded-volume variable and B reflects the polymer–solvent interaction.

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-3/2} BM^{1/2} \qquad (20)$$

The impact of chain stiffness on the onset of the excluded-volume effect becomes manifested in the chain-length dependence of the coefficient $C_\eta(n_K)$ [28-32]. This function is not known. In practice, it is usually replaced by the function $(3/4) \cdot C_\eta K(n_K)$ where $K(n_K)$ was derived by Yamakawa and Stockmayer [12] from the expansion factor $\alpha_R^2 = \langle R^2 \rangle / \langle R_0^2 \rangle$. This function is approximated by the equations:

$$K(n_K) = (4/3)\left(1 - 2.033 \cdot n_K^{1/2} + 0.875 \cdot n_K^{-1}\right)$$

for $\qquad n_K > 6 \qquad (21A)$

$$K(n_K) = n_K^{-1/2} \exp\left[6.611 \cdot n_K^{-1} + 0.9198 + 0.03516 \cdot n_K\right]$$

for $\qquad n_K < 6 \qquad (21B)$

Then, Equation (19) can be modified to

$$\alpha_\eta^3 = 1 + C_{\eta(\infty)}\acute{z} + \cdots \qquad (22)$$

where $\acute{z}$ is the scaled excluded-volume variable [24,25]

$$\acute{z} = 3/4 \cdot K(n_K)z \qquad (23A)$$

$$C_\eta(\infty) = 1.14 \qquad (23B)$$

Combining Equations (13), (19), (20), (22) and (23), yields:

$$[\eta] = \left(A_\eta + K_0 M^{1/2}\right)\left[1 + \left(\frac{3}{4}\right)C_{\eta(\infty)}\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\right.$$
$$\left. \left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-3/2} K(n_K)BM^{1/2}\right] \qquad (24A)$$

$$[\eta] = A_\eta + \left[A_\eta\left(\frac{3}{4}\right)C_{\eta(\infty)}\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-\frac{3}{2}} K(n_K)B + K_0\right]$$

$$\times M^{1/2} + K_0\left(\frac{3}{4}\right)C_{\eta(\infty)}\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-\frac{3}{2}} K(n_K)BM$$

$$(24B)^2$$

$$[\eta] = -15.64 + 0.1620 M^{1/2} + 5.691\left(10^{-6}\right)M \quad (24C)$$

Therefore, the interpretation of the intrinsic viscosity of 35PDMPA requires estimation of three characteristic parameters: cross sectional chain diameter, A_η, flexibility of the chain, K_0, and polymer–solvent interaction, B.

Polynomial regression of $[\eta]$ and $M^{1/2}$ in **Figure 5** results in Equation (24C). By comparing Equations (24B) and (24C) we get:

$$A_\eta = -15.6 \qquad (25A)$$

$$A_\eta\left(\frac{3}{4}\right)C_\eta(\infty)\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-\frac{3}{2}} K(n_K)B + K_0 = 0.162$$

$$(25B)$$

$$K_0\left(\frac{3}{4}\right)C_\eta(\infty)\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-\frac{3}{2}} K(n_K)B = 5.69E-6$$

$$(25C)$$

$$K_0 = 0.1625 \qquad (25D)$$

$$\left(\frac{3}{4}\right)C_\eta(\infty)\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-\frac{3}{2}} K(n_K)B = 6.45E-3 \text{ (25E)}$$

3.6.1. Application of Equation (24) by Plotting $[\eta]$ vs $M^{1/2}$

Equation (24) shows that the plot of $[\eta]$ vs $M^{1/2}$ should be linear over the whole range of molecular weights in theta solvents where $B = 0$. In good solvents where $B > 0$, linearity is restricted to a region where the term $B\left(\langle R_0^2 \rangle / M\right)_\infty^{3/2} K(n_K)$ is very low, such as in the case of 35PDMPA in toluene at 40°C. This implies alsothat the ratio $\left(\langle R_0^2 \rangle / M\right)_\infty$ is very high which is the case of stiff chains. Moreover, Equation (24) will be linear where $K(n_K) \sim 0$ represents short chains for both flexible and stiff polymers. At higher molecular weights the plot becomes curved upward as the function $K(n_K)$ and the value of z increases with increasing M.

Toluene at 40°C is not a theta solvent, therefore $B \neq 0$. In good solvents where $B > 0$, linearity is restricted to the condition that the term $B \cdot \left(\langle R_0^2 \rangle / M\right)_\infty^{3/2} K(n_K)$ is very

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$^2[\eta] = A_\eta + A_\eta(3/4)C_\eta(\infty)\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-\frac{3}{2}} K(n_K)BM^{1/2} + K_0 M^{1/2}$

$+ K_0 M^{1/2}(3/4)C_\eta(\infty)\left(\frac{3}{2\pi}\right)^{\frac{3}{2}}\left(\frac{\langle R_0^2 \rangle}{M}\right)_\infty^{-\frac{3}{2}} K(n_K)BM.$
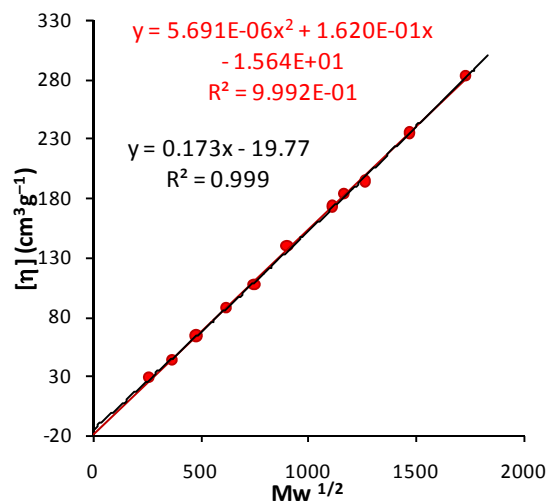
Figure 5. Plot of [η] versus Mw$^{1/2}$ for 35PDMPA in toluene at 40°C.

low such as in the case of 35PDMPA in toluene at 40°C, Equation (24E). In this case, the ratio $\left(\left\langle R_0^2\right\rangle / M\right)_\infty$ is very high which represent stiff chains. Since 35PDMPA is composed of the unit -CH$_2$-CHR- the backbone of the polymer does not introduce rigidity. Then the rigidity must be caused by the side chains effects. Hence, the excluded-volume effect also is not negligible with the lowest molecular weights.

As **Figure 5** shows, also, the plot of [η] vs $M_w^{1/2}$ for 35PDMPA homologues series fits to a straight line with $r^2 = 0.9986$.

$$[\eta] = A_\eta + K_0 M^{1/2} = -19.663 + 0.1729 M_w^{1/2} \quad (26A)$$

$$K_0 = F_{0,\infty} \left(\left\langle R_0^2\right\rangle / M\right)_\infty^{3/2} = 0.173 \quad (26B)$$

The value of K_θ calculated in this manner is only 6.4% higher than the former polynomial adjustment. **Table 4** summarizes the molecular parameters of 35PDMPA in toluene at 40°C. The molecular weight of the Kuhn statistical segment M_K is about 15 times higher than that of the chain repeating unit. This is an indication of chain stiffness of the 35DMPA in toluene at 40°C.

Most of the vinyl polymers and derivatives of poly (acrylic acid) and poly (methacrylic acid) with various side groups showed the proportionality of [η] and $M^{1/2}$ over a broad span of molecular weights as reported in reference [25]. However, they do not show semi-rigid characteristics as in the case of 35PDMPA. In the case of 35PDMPA, large size side chains increases the cross-sectional chain diameter and the orientation of side chains produce a high impediment around the polymer chain.

To verify the value of $K_{\theta,\infty}$ a plot of $[\eta] M_w^{1/2}$ vs $M_w^{-1/2}$ such as shown in **Figure 6** will be useful. The intercept of the plot $K_{\theta,\infty} = 0.170$ obtained at infinite M_w.

Table 4. Characteristics parameters of 35PDMPA. Data of other polymer also is gathering to compare PHE [25] and PDiPF [24].

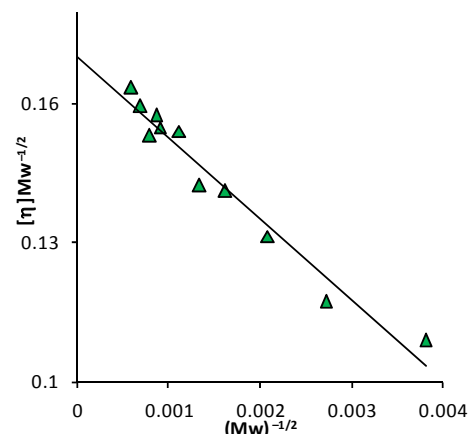| Polymer Characteristics	35PDMPA		PHE	PDiPF
	Lineal	Polynom	Ref 25	Ref 24
M_L (cm) $\times 10^{-8}$	57	57	20	134
K_θ (cm)	0.173	0.163	0.150	-
$\left(\left\langle R_0^2\right\rangle / M\right) \times 10^{16}$	0.782	0.751	0.711	-
l_K (cm) $\times 10^{-8}$	45	43	14	220
M_K	2560	2456	278	29,480
M_k/M_0	15	14	1	294
$-A$	19.77	15.64	0.000	-
$-A_0$	2.259	1.942	0.000	-
d_{br}	0.120	0.179	0.540	-
d_b (cm) $\times 10^8$	5.36	7.68	7.60	14.00

Figure 6. Plot of [η]/Mw$^{-1/2}$ versus M$^{-1/2}$. Extrapolation to infant Mw gave account for $K_{\theta,\infty}$.

$K_{\theta,\infty}$ is very close to the value of the slope of [η] and $M_w^{1/2}$ which is the value of $K_{0,\infty}$ of Equation (26B).

According to the Yoshizaki-Nitta-Yamakawa theory [23], the hydrodynamic interaction depends on the reduced bead diameter d_{br} which, in the range $0.3 \le d_{br} \le 0.8$, is related to the A_0 parameter by [33]

$$A_0 = -2.9 + 5.36 d_{br} \quad (27)$$

Table 4 shows the characteristic parameters of 35PDMPA. Also, for the sake of comparison, characteristics parameter of a very flexible chain such as bisphenol-A based poly(hydroxyethers) (PHE) from reference [25] and an stiff polymer, Poly(disopropylfumarate), (PDiPF) from reference [24] are sited. The high values of l_K and M_K of 35PDMPA suggests a semi flexible macromolecule.

3.6.2. Comments on $[\eta]/M^{1/2}$ vs $M^{1/2}$ (SF) plot [34,35]

Based on Equation (24), the plot of $[\eta]/M_w^{1/2}$ versus

$M^{1/2}$ should be linear only for long enough chains ($n <$ 10^3) where the absolute value of A_η is much lower than $K_0 M_w^{1/2}$ and the function $K(n_K)$ approaches its limit. As **Figure 4** illustrates the two low-molecular-weight samples are not met in this condition. Thus precaution is necessary to evaluate dimensional parameters based on BSF.

In the case of $A_\eta = 0$, the BSF plot can be modified to $[\eta]/M^{1/2}$ vs $K(n_K) \cdot M^{1/2}$ which should be linear and can be extrapolated to $M = 0$. This, however, is not the case of 35PDMPA in toluene that has a negative A_η value. If A_η is not equal to zero, both the original and modified SF plots are non-linear as shown in **Figure 4**. They can have a minimum if $A_\eta > 0$ or bend downward with decreasing molecular weight if $A_\eta < 0$ (such asin the case of 35PDMPA, **Figure 4**). In either case, the extrapolation to $M = 0$ based on BSF is not justified [36].

3.7. Conclusions and Remarks

As previously mentioned, 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-dimethyl-phenyl ester side chains. The 3,5-dimethyl-phenyl 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 some other polymers by several researchers. Also, it is known that the interaction of elements of polymer chains with solvent molecules could affect the probability distribution of the angles of internal rotation in the chain [37]. This observation was confirmed both theoretically and experimentally by a number of researchers [38,39] and here is confirmed by application of wormlike cylinder model.

The values of C_∞ of 35PDMPA (21 - 23) are much higher than values observed for other polyacrylates. For example, the value of C_∞ for polyphenylmethacrylate, PPMA, both theta solvents and good solvents (12.$_2$ and 13.$_3$) are larger than ones for many atactic vinyl polymers, which are in the range of $5 < C_\infty < 10$ usually found in the literature. 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 the Stockmayer-Fixman plot in which the effect of stiffness is coupled with excluded volume. And, also, it is overestimated by extrapolation to $M = \infty$. 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 ac-

counted for by the theory of flexible coils perturbed by excluded volume but has been predicted by wormlike models of stiff chains.

The value of C_∞ of 35PDMPA (29) obtained by extrapolating to $M = \infty$ using SFthe molecular weight region in which the effect of excluded volume levels is much higher than values observed for the same polymer by SF extrapolation to $M = 0$. The same effect was observed for other polymers. An example is polyphenylmethacrylate, PPMA, both theta solvents and good solvents.

4. Acknowledgements

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