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 (Cw) [4] and or application of the wormlike model based on Yamakawa-Fujiitheory [5] and its simplified form byBohdanecký [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, Mw, is the Mark-Houwink-Kuhn-Sakurada (MH) Equation:

\[
[\eta] = K_\alpha M_w^\alpha;
\]  \hspace{1cm} (1)

where, the parameter α is a measure of the thermodynamic power of solvent and Kα 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 Kα would decrease. Generally, for the ran-
dom coil flexible polymer molecules, the value of $\alpha$ would be between 0.50 and 0.80. For non-flexible and rigid (worm-like or rod-like) macromolecules higher values of $\alpha$ larger than or equal to unity have been observed. Thus, the numerical value of $\alpha$ 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 chloride at low temperature (in an ice bath) using triethylamine as a base to trap HCl produced and hexanes as solvent (Scheme 1). Acryloy chloride and 3,5-dimethyl-phenol 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.](image)

2.2. Polymer

Poly(3,5-dimethyl-phenyl-acrylate), (35PDMPA) was synthesized by bulk polymerization of 35DMPA under nitrogen atmosphere in a sealed flask using 2,2'-azo-bisiso-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.](image)

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

$$\eta = \lim_{C \to 0} \frac{\eta - \eta_1}{\eta C} = \lim_{C \to 0} \frac{\ln(\eta / \eta_1)}{C}$$

$$= \lim_{\eta \to 0} \frac{\eta - \eta_1}{\eta C}$$

(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:

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

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

(3)

(4)

where $\eta_1$ is the viscosity of the pure solvent, and $\eta$ 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 35PDMPA 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 $[\eta]$, $k_H$, and $k_H + k_K$ of 35PDMPA in toluene at 40°C.

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

3. Results and Discussion

Figure 1 shows the variation of $(t - t_1)/t_1C$ and $(\ln v/t_1)/C$ 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 $[\eta]$ are expressed in the values of $K_\alpha$ and $\alpha$ of MH. Several factors contribute to enhance the exponent $\alpha$ [19]. Among them are: 1) chain stiffness, 2) excluded volume, and 3) partial drainage. It is universally accepted that the value of $\alpha$ that corresponds to a non-draining 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 $\alpha$ 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 $\alpha$ in the limit of molecules having thickness equal to length (sphere), $\alpha = 0$. 

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Figure 3. Double logarithmic 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 $K_\alpha$ and $\alpha$ 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 $\Theta$-conditions. The square of end-to-end dimensions $\left\langle R^2_0 \right\rangle$ for a random distribution of $n$ particle with bond length of $l$ is expressed as $n l^2$. The expansion of a covalently bonded polymer chain is restricted by valence angles $\theta$ between each chain atom, $\left\langle R^2_0 \right\rangle$ modified to allow for short-range interactions called $\left\langle R^2_{\text{eff}} \right\rangle$:

$$\left\langle R^2_{\text{eff}} \right\rangle = n l^2 \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right)$$

(5)

For C-C backbone polymers such as 35PDMPA 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

$$\left\langle R^2_{\text{eff}} \right\rangle = n l^2 \left( \frac{1 - \cos 109.5}{1 + \cos 109.5} \right) = 2 n l^2$$

(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:

$$\left\langle R^2_{\text{eff}} \right\rangle = n l^2 \left( \frac{1 - \cos \theta}{1 + \cos \theta} \right) \left( 1 - \cos \left\langle \phi \right\rangle \right)$$

(7)

where $\cos \left\langle \phi \right\rangle$ is the average cosine of the angle of rotation of the bonds in the backbone chain. The parameter $\left\langle R^2_{\text{eff}} \right\rangle$ 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, $K_{\text{MH}}$ in an ideal solution. The $K_\theta$ is related to the unperturbed dimension of the polymer as:

$$K_\theta = \Phi_0 \left( \frac{\left\langle R^2_{\text{eff}} \right\rangle}{M} \right)^{3/2}$$

(8)

where $\Phi_0$ is the Flory universal constant; it depends on molecular mass of the polymer and the type of polymer with the best experimental value of $2.51 \times 10^{-23}$ to $2.87 \times 10^{-23}$ 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.

$$[\eta] M^{-1/2} = K_\theta + 0.51 \Phi_0 B M^{1/2}$$

(9)

The constant $K_\theta$ is the intercept; it is equal to the $K_{\text{MH}}$ at the theta conditions [22]. The plot of $[\eta] M^{-1/2}$ against $M^{1/2}$ according to the Equation (9) for 35PDMPA in toluene illustrated in Figure 4. The value of $K_\theta$ 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 $K_\theta$ decreased as the temperature increased and the quality of solvent improved. This was not within expectations.

Based on Equation (9) the plot of $[\eta]/M_{\text{w}}^{1/2}$ versus $M^{1/2}$ should be linear only for long enough chains ($n > 10^6$) 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

Table 2. The slopes and intercepts, $K_\alpha$ and $\alpha$, of the double logarithmic plot of $[\eta]$ and $M_w$ in toluene at 25°C and 40°C.

<table>
<thead>
<tr>
<th>$t^\circ$C</th>
<th>$K_\alpha$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.0320</td>
<td>0.612</td>
</tr>
<tr>
<td>25</td>
<td>0.0472</td>
<td>0.5894</td>
</tr>
</tbody>
</table>
be zero. In a good solvent such as toluene, the slope is positive. Two different factors may contribute in determining a high value of $K_0$ 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 $K_0$ 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 $C_\kappa$, steric factor $\sigma$, 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 $C_\kappa$ or the steric factor $\sigma$. 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 $\sigma$ is obtained from

$$\sigma^2 = \left( \frac{\langle R_0^2 \rangle}{M} \right)^{-1}$$  \hspace{1cm} (10)

The mean square unperturbed end-to-end distance, $\langle R_0^2 \rangle$ can be obtained experimentally from the value of $K_0$, Equation (8), which is related to the rigidity factor $\sigma$, or to the characteristic ratio $C_\kappa$, by the expression

$$\sigma = \left( \frac{\langle R_0^2 \rangle}{\langle R_{00}^2 \rangle} \right)^{1/2} = \left( \frac{K_0}{\Phi_0} \right)^{1/2} \left( \frac{M_0}{2l^2} \right)^{1/2}$$  \hspace{1cm} (11)

$$C_\kappa = \left( \frac{\langle R_0^2 \rangle}{\langle R_{00}^2 \rangle} \right) = \left( \frac{K_0}{\Phi_0} \right)^{1/2} \left( \frac{M_0}{2l^2} \right)^{1/2}$$  \hspace{1cm} (12)

where $M_0$ is the molecular mass of the monomer. The values of $\sigma$ and $C_\kappa$ 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]

$$[\eta]_0 = A\eta + K_0 \cdot M^{1/2}$$  \hspace{1cm} (13)

with:

$$K_0 = \Phi_{0,0} \left( \frac{\langle R_0^2 \rangle}{M} \right)^{3/2}$$  \hspace{1cm} (14)

$$A_\eta = K_0 \cdot A_s (d_{h}) \cdot M^{1/2}$$  \hspace{1cm} (15)

$$d_{h} = d_b / l_K$$  \hspace{1cm} (16)

$$l_K = \left( \frac{\langle R_0^2 \rangle}{M} \right) M_L$$  \hspace{1cm} (17)

$$M_K = l_K \cdot M_L$$  \hspace{1cm} (18)

$\langle \langle R_0^2 \rangle / M \rangle_\kappa$ is the ratio of $\langle R_0^2 \rangle$ and $M$ is the random coil limit, and $\Phi_{0,0}$ is the Flory viscosity constant for random coils in the non-draining regime, $A_s(d_{h})$ is a function of the reduced bead diameter $d_{h}$, $d_{b}$ is the bead diameter, $l_K$ and $M_L$ are, respectively, the length and molecular weight of the Kuhn statistical segment, and $M_M$ 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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Table 3. Values of $K_0$, $\langle \langle R_0^2 \rangle / M \rangle_\kappa$, $\sigma$ and $C_\kappa$ from SF plot and Bohdanecký.

<table>
<thead>
<tr>
<th>Method</th>
<th>$K_0$</th>
<th>$\langle \langle R_0^2 \rangle / M \rangle_\kappa$</th>
<th>$s$</th>
<th>$C_\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF 25°C</td>
<td>0.122</td>
<td>0.783</td>
<td>3.37</td>
<td>22.78</td>
</tr>
<tr>
<td>SF 40°C</td>
<td>0.109</td>
<td>0.753</td>
<td>3.25</td>
<td>21.08</td>
</tr>
<tr>
<td>H-Mw 40°C</td>
<td>0.124</td>
<td>0.786</td>
<td>3.39</td>
<td>22.98</td>
</tr>
<tr>
<td>At M∞</td>
<td>0.170</td>
<td>0.875</td>
<td>3.77</td>
<td>28.44</td>
</tr>
<tr>
<td>Bohdanecký</td>
<td>0.171</td>
<td>0.877</td>
<td>3.78</td>
<td>28.56</td>
</tr>
</tbody>
</table>
The impact of chain stiffness on the onset of the excluded-volume effect becomes manifested in the chain-length dependence of the coefficient \( C_p(n_k) \) [28-32]. This function is not known. In practice, it is usually replaced by the function \( (3/4) C_p(n_k) \) where \( K(n_k) \) was derived by Yamakawa and Stockmayer [12] from the expansion factor \( \alpha^0_p = \frac{\left\langle R^2 \right\rangle}{n^2 K} \). This function is approximated by the equations:

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

for \( n_k > 6 \)  \hspace{1cm} (21A)

\[
K(n_k) = n_k^{2/3} \exp \left[ 6.611 \cdot n_k^{-1} + 0.9198 + 0.03516 \cdot n_k \right]
\]

for \( n_k < 6 \)  \hspace{1cm} (21B)

Then, Equation (19) can be modified to

\[
\alpha_p^0 = 1 + C_p(\zeta) \zeta + \ldots
\]

where \( \zeta \) is the scaled excluded-volume variable \[24,25\]

\[
\zeta = 3/4 \cdot K(n_k) z
\]  \hspace{1cm} (23A)

\[
C_p(x) = 1.14
\]  \hspace{1cm} (23B)

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

\[
[\eta] = A_{\eta} + K_0 M^{1/2} \left[ 1 + \left( \frac{3}{4} \right) C_p(x) \left( \frac{3}{2 \pi} \right)^2 \left( \frac{\left\langle R^2 \right\rangle}{M} \right)_x \right] K(n_k) BM^{1/2}
\]  \hspace{1cm} (24A)

\[
[\eta] = A_{\eta} + \left( \frac{3}{4} \right) C_p(x) \left( \frac{3}{2 \pi} \right)^2 \left( \frac{\left\langle R^2 \right\rangle}{M} \right)_x K(n_k) B + K_0
\]

\[
\times M^{1/2} + K_0 \left( \frac{3}{4} \right) C_p(x) \left( \frac{3}{2 \pi} \right)^2 \left( \frac{\left\langle R^2 \right\rangle}{M} \right)_x K(n_k) BM
\]

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 \( B \left( \frac{\left\langle R^2 \right\rangle}{M} \right)_x^{1/2} K(n_k) \) is very low, such as in the case of 35PDMPA in toluene at 40°C. This implies also that the ratio \( \left( \frac{\left\langle R^2 \right\rangle}{M} \right)_x \) is very high which is the case of stiff chains. Moreover, Equation (24) will be linear where \( K(n_k) - 0 \) 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 \( B \left( \frac{\left\langle R^2 \right\rangle}{M} \right)_x^{1/2} K(n_k) \) is very
low such as in the case of 35PDMPA in toluene at 40°C, Equation (24E). In this case, the ratio \( R^2 = 0.999 \) is very high which represent stiff chains. Since 35PDMPA is composed of the unit -CH₂-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 \([\eta]\) vs \(M_w^{1/2}\) for 35PDMPA homologues series fits to a straight line with \(r^2 = 0.9986\).

\[
[\eta] = A_0 + K_0 M_w^{1/2} = -19.663 + 0.1729 M_w^{1/2} \quad (26A)
\]

\[
K_0 = F_0 \left( \frac{\left( R_0^2 \right)}{M_w} \right)^{1/2} = 0.173 \quad (26B)
\]

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

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

According to the Yoshizaki-Nitta-Yamakawa theory [23], the hydrodynamic interaction depends on the reduced bead diameter \(d_b\) which, in the range \(0.3 \leq d_b \leq 0.8\), is related to the \(A_0\) parameter by [33]

\[
A_0 = -2.9 + 5.36d_b \quad (27)
\]

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 \([\eta]/M_w^{1/2} \text{ vs } M_w^{1/2}\)

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 $A_q$ is much lower than $K_0 M^{1/2}_w$ and the function $K(n_\theta)$ 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 $A_q = 0$, the BSF plot can be modified to $[\eta]/M^{1/2}$ vs $K(n_\theta)M^{1/2}$ 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 $A_q$ value. If $A_q$ 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 $A_q > 0$ or bend downward with decreasing molecular weight if $A_q < 0$ (such as in 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 $C_\infty$ and $\sigma$ 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 $C_\infty$ of 35PDMPA (21 - 23) are much higher than values observed for other polyacrylates. For example, the value of $C_\infty$ for polyphenylmethacrylate, PPMA, both theta solvents and good solvents. An example is polyphenylmethacrylate, PPMA, both theta solvents and good solvents.

4.4. Acknowledgements

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