Laser Light-Scattering Study of Novel Thermoplastics.
2. Phenolphthalein Poly(ether sulfone) (PES-C)

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ABSTRACT: Five narrowly distributed fractions of phenolphthalein poly(ether sulfone) (PES-C) were studied in CHCl₃ by both static and dynamic laser light scattering (LLS) at 25 °C. The dynamic LLS showed that the PES-C samples contain some large polymer clusters as in previously studied phosphonlein poly(ether ketone) (PEK-C). These large clusters can be removed by a 0.1-µm filter. Our results showed that $R_g^2 = (3.35 \pm 0.13) \times 10^{-2} M_w^{0.52 \pm 0.03}$ and $D = (2.26 \pm 0.02) \times 10^{-4} M_w^{-0.54 \pm 0.03}$ with $R_g^2$, $M_w$, and $D$ being the average radius of gyration, the weight-average molecular weight, and the z-average translational diffusion coefficient, respectively. A combination of static and dynamic LLS results enabled us to determine $D = (2.45 \pm 0.04) \times 10^{-4} M_w^{-0.55 \pm 0.05}$, where $D$ and $M_w$ correspond to monodisperse species. Using this scaling relationship, we have successfully converted the translational diffusion coefficient distribution into the molecular weight distribution for each of the five PES-C fractions. The weight-average molecular weights obtained from dynamic light scattering have a good agreement with that obtained from static laser light-scattering measurements.

Introduction

High-performance thermoplastics with excellent heat resistance are currently receiving considerable interest as advance materials. Among them are poly(aryl ether ketones), well-known in the form of poly(ether ketone) (PEEK) and poly(ether ketone) (PEK). They have been used as matrix resins for advanced composite materials for aircraft and automobiles because of their high mechanical strength, excellent thermal stability, and good chemical resistance. However, poly(aryl ether ketones) have several limitations in preparation, molding, and processing and low thermo-oxidative stability. Also, these polymers are only soluble in strong acids or solvents with a boiling point higher than their melting points, mainly due to their insoluble crystalline structures. So far, few studies on dilute solution properties of PEEK have been done because PEEK can only be dissolved in concentrated H₂SO₄, HSO₃Cl, and CH₃SO₃H. Previously, we have studied a thermoplastic: phenolphthalein poly(ether ketone) (PEK-C) which has viscoelastic properties similar to those of PEEK but is soluble in various common solvents, such as chloroform (CHCl₃). In this paper, we will show the characterization of another novel thermoplastic phenolphthalein poly(ether sulfone) (PES-C) which was recently developed in the Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Academia of Sinica, China. It is a linear aromatic polymer with the following chemical structure:

PES-C not only has outstanding physical and mechan-

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extrapolation of $KC$ determine the values of $A, D,$ and $\tau$.

Typical static Zimm plot of PES3 in CHCl$_3$ at $25^\circ$C,

![Figure 1](image)

Figure 1. Typical static Zimm plot of PES3 in CHCl$_3$ at $25^\circ$C, where $C$ ranges from $2.0 \times 10^{-3}$ to $5 \times 10^{-3}$ g/mL.

multi-functional digital time correlator was used with a solid state detector (ADLAS DPY 425I, output power $\approx 400$ mW at $\lambda = 532$ nm) as the light source. The primary beam is vertically polarized with respect to the scattering plane. The detail of the LLS instrumentation and theory can be found elsewhere.

The angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio, $R_w(q)$, of a dilute polymer solution at concentration $C$ (g/mL) and scattering angle $q$ was measured, and $R_w(q)$ is related to the weight-average molecular weight $M_w$, the scattering vector $q$, and $C$ as

$$
\frac{KC}{R_w(q)} = \frac{1}{M_w}(1 + \frac{1}{3}(R_g^3q^2) + 2A_2C
$$

where $K = 4\pi^2(n^2d^2dn/dc^2)/(N_A\lambda^4)$ and $q = (4\pi n_0/\lambda)\sin(\theta/2)$ with $N_A$, $dn/dc$, $n_0$, and $\lambda_0$ being the Avogadro number, the specific refractive index increment, the solvent refractive index, and the wavelength of light in vacuum, respectively. $A_2$ is the second virial coefficient, and $(R_g^3)_{\theta}$ is the root-mean-square $z$-average radius of gyration of the polymer. By measuring $R_w(q)$ at a set of $C$ and $q$, we are able to determine $M_w$, $R_w$, and $A_2$ from a Zimm plot which incorporates $q$ and $C$ extrapolation on a single grid.

In static light scattering, it is very important to have a precise value of differential refractive index increment $dn/dc$ because the measured $M_w$ is proportional to $(dn/dc)^{-2}$. A novel and high precision differential refractometer was used to measure the $dn/dc$ of PES-C. The measured $dn/dc$ of PES-C in CHCl$_3$ at $25^\circ$C and $\lambda = 532$ nm is 0.204 mL/g.

In dynamic LLS, a precise intensity-intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode was measured, which has the following form

$$
G^{(2)}(t,q) = \langle I(t+\tau)I(0) \rangle = \Delta I^2[1 + \beta G^{(1)}(t,q)/\tau^2]
$$

where $\Delta I$ is a measured base line, $\beta$ is a parameter depending on the coherence of the detection, $t$ is the delay time, and $G^{(1)}(t,q)$ is the normalized first-order electric field time correlation function.

**Result and Discussion**

Figure 1 shows a typical static Zimm plot of PES3 in CHCl$_3$ at $25^\circ$C. On the basis of eq 1 we were able to determine the values of $M_w$, $R_w$, and $A_2$ from the extrapolation of $[KC/R_w(q)]_{q\rightarrow\infty}$, $[KC/R_w(q)]_{q=0}$ vs $q^2$, and $[KC/R_w(q)]_{R_g<\infty}$ vs $C$, respectively. The results are summarized in Table 1. The positive values of $A_2$ show that CHCl$_3$ is a reasonably good solvent for PES-C at room temperature. For samples PES4 and PES5, $R_g$ is too small to be accurately determined. Even for PES2 and PES3, the errors associated with their $R_g$ values are large, so that they can be read only as a reference. Nevertheless, the scaling of $R_g$ with $M_w$ shows that $R_g \propto M_w^{0.52-0.53}$, which indicates that the PES-C chain in CHCl$_3$ at $25^\circ$C might have a random coil conformation.

If modeling PES-C as a wormlike chain, we estimate the persistence length, $\ell$, on the basis of $R_g = 12\ell/3(L/\ell) - 1 + (2L/\ell^2)[1 - \exp(-L/\ell)]^{1/2}$ where $L = nL_w$ is the contour length, with $L$ being the projected length of the segment between two ether linkages and $n = (M_w/M_0)$ being the number of the segments. In the case of PES-C, the average values of $L_0$ and $M_0$ are $\sim 1.1$ nm and $\sim 266$ g/mol, respectively, from its chemical structure. Strictly speaking, $n$ should be $M_w/M_0$. The value of $\ell$ estimated from five PES-C samples is $\sim 1$ nm in CHCl$_3$ at $25^\circ$C, which leads to a value of $C_{\ell} \approx 13$ using the formula $C_{\ell} = (2L/\ell^2) - 1$, where $L_0$ is the average bond length. In comparison with PEK-C, PES-C is more flexible, which may be related to the difference between the sulfone and ketone groups.

Figure 2 shows a typical plot of the measured intensity-intensity time correlation function of PES3 in CHCl$_3$ at $\theta = 20^\circ$ and $T = 25^\circ$C. For a polydisperse sample, $G^{(1)}(t,0)$ is related to the line width distribution $G(\Gamma')$ by

$$
G^{(1)}(t,0) = \langle E(t,0)E^*(0,0) \rangle = \int_0^\infty G(\Gamma')e^{-\Gamma \tau}d\Gamma
$$

The computer program CONTIN was used in this work to convert $G^{(2)}(t,0)$ to $G(\Gamma')$. The line width $\Gamma$ usually depends on both $C$ and $q$. This dependency can be expressed as

$$
\Gamma = D(1 + k_dC)(1 + f(R_g^2)q^2)
$$

where $D$ is the translational diffusion coefficient at $C = 0$ and $q = 0$; $k_d$ is the diffusion second virial coefficient. The value of $\Gamma$ generally increases as the molecular weight decreases. The values of $D$, $f$, and $k_d$ can be calculated from $I(\Gamma)/I(q^2)/I(0)$ and $I(0)/I(q^2)$ vs $q^2$ and $I(0)/I(q^2)$ vs $C$, respectively.

Figure 3 shows the typical translational diffusion coefficient distributions of PES-C in CHCl$_3$ at $25^\circ$C after the solution was clarified with a 0.5-μm filter (“0”) and a 0.1-μm filter (“1”), respectively. When a 0.5-μm filter was used, the distribution has two peaks. The large peak with a higher average diffusion coefficient corresponds to single linear PES-C chains, while the small peak with a lower average diffusion coefficient indicates the presence of some large species in the PES-C solution. At first, we thought that these large species are the aggregates of PES-C in CHCl$_3$, but later we found that these large species can be removed by a 0.1-μm filter and the large species did not reappear in the solution even after 15 days. This leads us to speculate that these large species are polymer clusters formed during the polymerization.

Figure 4 shows the translational diffusion coefficient distribution $G(D)$ of five PES-C samples in CHCl$_3$ at $T = 25^\circ$C, $C = 0$, and $q = 0$. From $G(D)$, we were able to calculate the $z$-average translational diffusion coefficient $D = \int_0^\infty G(D)dD$ and, further, the average hydrodynamic radius $R_h$ by replacing $D$ in the Stokes–Einstein equation with $D$, i.e., $R_h = k_BT/(6\eta D)$, where $k_B$, $T$, and $\eta$ are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. The values of $D$, $R_h$, and $R_h/(R_0)$ of five PES-C samples are also listed in Table 1. The ratio $(R_h/R_0)$ is in the range 1.5–1.8, normally observed for a flexible polymer.
Table 1. Summary of Static and Dynamic Laser Light Scattering Results for Five PES-C Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>(10^{-4}M_w) (g/mol)</th>
<th>((R_g)_{12}) (nm)</th>
<th>(10^4A_2) (mol-cm²/g²)</th>
<th>(10^4\langle D\rangle) (cm²/s)</th>
<th>(R_h) (nm)</th>
<th>(R_g/R_h)</th>
<th>(10^{-4}M_w)calcld (g/mol)</th>
<th>((M_w/M_n)_{LALS})</th>
<th>((M_w/M_n)_{GPC})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES1</td>
<td>8.52</td>
<td>13</td>
<td>3.9</td>
<td>53.9</td>
<td>7.46</td>
<td>1.7</td>
<td>8.48</td>
<td>1.33</td>
<td></td>
</tr>
<tr>
<td>PES2</td>
<td>6.15</td>
<td>~10</td>
<td>4.5</td>
<td>65.0</td>
<td>6.20</td>
<td>~1.6</td>
<td>6.04</td>
<td>1.32</td>
<td>1.68</td>
</tr>
<tr>
<td>PES3</td>
<td>5.01</td>
<td>~10</td>
<td>8.6</td>
<td>70.0</td>
<td>5.75</td>
<td>~1.6</td>
<td>5.24</td>
<td>1.21</td>
<td>1.65</td>
</tr>
<tr>
<td>PES4</td>
<td>4.15</td>
<td>&lt;9</td>
<td>82.0</td>
<td>4.71</td>
<td>4.11</td>
<td>1.17</td>
<td>4.48</td>
<td>1.17</td>
<td>1.47</td>
</tr>
<tr>
<td>PES5</td>
<td>2.50</td>
<td>&lt;9</td>
<td>103</td>
<td>3.91</td>
<td>2.48</td>
<td>1.17</td>
<td>2.48</td>
<td>1.17</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Figure 2. Typical measured intensity–intensity time correlation function of PES3 in CHCl₃ at \(\theta = 20°\) and \(T = 25 °C\).

Figure 3. Translational diffusion coefficient distribution \(G(D)\) of PES3 in CHCl₃ at \(T = 25 °C\), where the symbols “C” and “D” respectively represent the clarification of the PES-C solution with a 0.5-µm filter and a 0.1-µm filter.

Figure 4. Translational diffusion coefficient distributions of five PES-C samples in CHCl₃ at \(T = 25 °C\), where the solutions were clarified with a 0.1-µm filter.

Figure 5. Double logarithmic plot of \(D\) vs \(M_w\), where the solid line represents the least-squares fitting of \(D\) (cm²/s) = 2.26 × 10^{-4}M_w^{-0.54} and the dotted line, the calibration of \(D\) (cm²/s) = 2.45 × 10^{-4}M_w^{-0.55}, where \(D\) and \(M\) correspond to monodisperse species and \((\alpha_D)\) were obtained from \(D\) and \(M_w\) rather than \(D\) and \(M\) for monodisperse species. The value of \((\alpha_D)\) also indicates that the PES-C chain has a coil conformation in CHCl₃ at \(T = 25 °C\). In principle, we can use the scaling relationship between \(D\) and \(M\) to transfer \(G(D)\) into a molecular weight distribution (MWD) by using the following procedure. From dynamic LLS, by the definition of \(g^{(1)}(t)\), when \(t \to 0\),

\[
[g^{(1)}(t)]_{t \to 0} = (E(t)E^*(0))_{t \to 0} = \int_0^{\infty} G(\Gamma) d\Gamma \propto I
\]

while from static LLS, when \(C \to 0\) and \(q \to 0\), the net scattering intensity is given by

\[
I \propto \int_0^{\infty} f_w(M) M dM
\]

A comparison of eqs 5 and 6 leads to

\[
\int_0^{\infty} G(\Gamma) d\Gamma \propto \int_0^{\infty} f_w(M) M dM \propto \int_0^{\infty} G(D) dD
\]

This equation can be written as

\[
\int_0^{\infty} G(D) d(\ln D) \propto \int_0^{\infty} f_w(M) M^2 d(\ln M)
\]

where \(d(\ln D) \propto d(\ln M)\) since \(D = k_D M^{-\alpha_D}\), which further leads to,

\[
f_w(M) \propto \frac{G(D)D}{M^2} \propto \frac{G(D)D^{1+2(\alpha_D)}}{M^2}
\]

From \(f_w(M)\), we can calculate \(M_w\) by its definition,

\[
(M_w)_{calcld} = \frac{\int_0^{\infty} f_w(M) M dM}{\int_0^{\infty} f_w(M) M dM} = \frac{k_D^{1+2(\alpha_D)} \int_0^{\infty} G(D) dD}{\int_0^{\infty} G(D) dD}
\]

Our previous studies\(^{19,20}\) have shown that using \((\alpha_D)\) instead of \(k_D\) and \(\alpha_D\) can introduce a large error in the final MWD. Therefore, we have to use the measured
Table 1. The values of $M_\text{w}$ from static LLS as constraints to find $k_D$ and $\alpha_0$ from G(D) on the basis of eqs 9 and 10. The detail of this method has been reported before. Here, we determined that $\alpha_0 = 0.55$ and $k_D = 2.45 \times 10^{-4}$. This pair of $k_D$ and $\alpha_0$ values defines the calibration between $D$ and $M$ for PES-C in CHCl$_3$ at $T = 25 ^\circ$C, shown in Figure 5 by the dotted line which slightly deviates from the fitting of $\langle D \rangle = (k_D)M_w^{-(\alpha_0)}$. With the values of $k_D$ and $\alpha_0$, we are ready to convert the G(D)s in Figure 4 to their corresponding MWDs.

Figure 6 shows five differential weight distributions $f_w(M)$ of the PES-C samples. From each $f_w(M)$ we were able to calculate the weight-average molecular weight ($M_w^{\text{calc}}$) and polydispersity index ($M_w/M_n$) from GPC, which are listed in Table 1. The values of $M_w/M_n$ show that the distribution of the PES-C samples after clarifying with a 0.1-µm filter is fairly narrow. It should be noted that the existence of a small amount of large species in PES-C was not observable in previous gel permeation chromatography (GPC), because GPC is less sensitive to their corresponding $M_n$.

Conclusion

A combination of static and dynamic laser light-scattering studies of five phenolphthalein poly(ether sulfone) (PES-C) samples shows that the PES-C chain in CHCl$_3$ at $T = 25 ^\circ$C has a random coil conformation with a persistence length of ~1 nm and $C_m \approx 13$, and CHCl$_3$ is a fairly good solvent for PES-C at room temperature. A calibration between the translational diffusion coefficient ($D$) and molecular weight ($M$) has been determined, namely, $D = (2.45 \times 10^{-4})M^{-0.25}$. Using this calibration we have determined not only weight-average molecular weights of five PES-C samples but also their molecular weight distributions. The established calibration between $D$ and $M$ together with the values of $\alpha_0$ will enable us to characterize PES-C with only one concentration in the future.

References and Notes

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References and Notes

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