Laser Light-Scattering Characterization of a Polymer Mixture Made of Individual Linear Chains and Clusters

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ABSTRACT: The characterization of a polymer mixture made of individual linear chains and clusters is often hindered by the presence of a small amount of high molecular weight clusters. Here, an analytical method combining both static and dynamic laser light scattering (LLS) was utilized to characterize such polymer mixtures. The LLS method was carefully verified by using a set of polymer mixtures made of two polystyrenes, in which the two polystyrenes have a very large difference in their molecular weights and the higher molecular weight polystyrene was used as an imitation of the clusters. We have successfully applied this LLS method in the study of PES-C (phenolphthalein poly(ether sulfone)), a newly developed high-performance thermoplastic resin. The PES-C sample contains about 6% high molecular weight clusters by weight. The large clusters can be removed by a filter with a smaller pore size. The average molecular weight of the clusters is ~15 times higher than that of the linear PES-C chains. The PES-C linear chain has a random coil conformation in chloroform at room temperature, while the structure of the clusters seems to be more compact. This LLS method should also be very useful in the study of aggregation or association in a polymer or colloid system as long as the large “clusters” are reasonably stable in time.

Introduction

A small amount of high molecular weight polymer clusters might sometimes be produced in a given polymerization due to chain transfer or branching, e.g. cross-linking in the epoxy curing process.1 When this happens, the final product will be a polymer mixture of individual linear chains and clusters. This small amount of high molecular weight clusters can greatly affect the rheological properties and its ultimate applications. However, the high molecular weight clusters are often overlooked in some conventional analytical methods,2 such as in size exclusion chromatography, because the amount of the clusters is too small to be detected in terms of weight or number. On the other hand, this small amount of the clusters has a larger scattering power and leads to a false apparent weight-average molecular weight $M_{w,app}$ in static laser light scattering (LLS).

According to the LLS theory,3,4 the weight-average molecular weight $M_w$ can be related to the excess absolute time-averaged scattered intensity over solvent (known as the Rayleigh ratio $[R_g(q)]$) by

$$
\frac{KC}{R_g(q)} = \frac{1}{M_w} \left( 1 + \frac{1}{3}(R_g^2q^2) + 2A_2^2 \right)
$$

where $K = 4\pi n^2(\partial n/\partial C)^2/(N_A \lambda_0^4)$ with $N_A$, $n$, and $\lambda_0$ being Avogadro’s number, the solvent refractive index, and the wavelength of light in vacuo, respectively; $C$ is the total polymer concentration (g/mL); $q = (4\pi/\lambda_0) \sin(\theta/2)$ with $\theta$ being the scattering angle; $(R_g^2)_{av}$ (written as $R_g^2$) is the z-average radius of gyration; and $A_2$ is the second virial coefficient. If there exist some clusters with a high weight-average molecular weights, $M_w$ can be an apparent weight-average molecular weight $M_{w,app}$ and

$$M_{w,app} = \frac{\int_0^\alpha M_w(M) dM}{\int_0^\alpha M_w dM} = \frac{\int_0^\alpha MC(M) dM}{\int_0^\alpha C dM} = \frac{\int_0^\alpha M_w dM}{\int_0^\alpha C dM} + \frac{\int_0^\alpha M_w dM}{\int_0^\alpha C dM} = M_wX_L + M_wX_H = M_wX_L + M_wX_H
$$

where the subscripts “L” and “H” denote low molecular weight linear polymer chains and high molecular weight clusters, respectively; $\alpha$ is the cutoff molecular weight between the linear chains and clusters; $f_w(M)$ [$=C(M)$] represents the weight distribution; $\int_C C dM$ and $\int_C C dM$ are the concentrations ($C_L$ and $C_H$) of the linear chains and clusters, respectively; $X_L$ ($=C_L/C$) and $X_H$ ($=C_H/C$) are the weight fractions; and $X_L + X_H = 1$.

Equation 2 clearly shows that if $M_{w,H} > M_{w,L}$, the $M_w$ measured from static LLS will be seriously distorted by the presence of a very small amount of high molecular weight clusters. Therefore, it is very important to have a reliable analytical method for the characterization of lower molecular weight linear chains in the presence of high molecular weight clusters.

It is the study of phenolphthalein poly(ether sulfone) (PES-C) that brought us into this kind of “chain-and-cluster” mixture. PES-C is a new kind of high-performance thermoplastic resin that has recently been developed to substitute for poly(ether ether ketone) (PEEK) because the process of PES-C is much easier in comparison with that of PEEK. The previous static LLS studies of a similar system showed that the $M_w$ of PES-C is higher than the expected value of 100 000 for polymers made from polycondensation,5 which implies the existence of some unexpected high molecular weight...
species in PES-C. Moreover, the high glass transition temperature of PES-C also leads us to believe the existence of some high molecular weight clusters in PES-C. In order to prove it, we adopted a method of combining both static and dynamic LLS to characterize PES-C. This LLS method has recently been used to characterize a block ionomer in the presence of small amounts of ionomer aggregates. Before using this LLS method, first we would like to prove the feasibility of applying this method to the characterization of a polymer mixture made of individual linear chains and clusters.

Basic Principles

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

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

(3)

where $A$ is a measured baseline, $\beta$ 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. For a polydisperse sample, $g^{(1)}(t,q)$ is related to the line-width distribution $G(\Gamma)$ by

$$g^{(1)}(t,q) = \int_{0}^{\infty} G(\Gamma) e^{-\Gamma t} d\Gamma$$

(4)

where the line width $\Gamma$ usually depends on both $C$ and $\theta$. This dependence can be expressed as:

$$\Gamma q^2 = D_0 q^2 (1 + k_4 C)(1 + f R_g^2 q^2)$$

(5)

where $D$ is the diffusion coefficient, the superscript "0" and subscript "4" denote $C = 0$ and $q = 0$, respectively, $f$ is a dimensionless constant, and $k_4$ is the diffusion second virial coefficient. $G(\Gamma)$ in eq 4 can be obtained from the Laplace inversion of the measured time correlation function. Further, $G(\Gamma)$ can be converted into $G(D)$. On the basis of eqs 1 and 4, at $t = 0$ and $C = 0$, we have

$$g^{(1)}(0,q) = \int_{0}^{\infty} G(\Gamma) d\Gamma \propto R_g(q) \propto M_w C$$

(6)

It shows that the integrated area (A) under $G(\Gamma)$ (or $G(D)$) is proportional to the excess scattered intensity over solvent. For a polymer mixture of linear chains and clusters, if there exist two distinct peaks in $G(D)$, denoted as $G_L(D)$ and $G_H(D)$, the area ratio $A_L$ of these two peaks can be written as:

$$A_L = A_H \left[ \int_{0}^{R_g} G_L(D) dD \right] / \left[ \int_{0}^{R_g} G_H(D) dD \right] = M_w L C L / M_w H C_H = M_w^L x_L L / M_w H^{R_H}$$

(7)

where as before the subscripts "L" and "H" denote low molecular weight linear chains and high molecular weight clusters, respectively, and $\gamma$ is the cutoff translational diffusion coefficient between $G_L(D)$ and $G_H(D)$. On the basis of eqs 2 and 7, a combination of $M_{w,app}$ from static LLS and $A_L$ from dynamic LLS will lead to $M_w,CL$ and $M_w,CH$. In principle, by knowing any one of the four parameters ($M_w,CL$, $M_w,CH$, $x_L$, and $x_H$), we will be able to determine the remaining three parameters.

Experimental Section

Samples. Three narrowly distributed polystyrene standards ($M_w/M_n < 1.05$) from Polymer Laboratories Ltd., were used without further purification. Static LLS results confirmed that the weight-average molecular weights of these polystyrene standards are $1.20 \times 10^5$, $3.00 \times 10^5$, and $5.94 \times 10^5$, respectively. Three polymer mixtures were made from two of these three polystyrene standards with different macroscopic weight ratios, so that the ratios of the scattered light intensity between the two polystyrenes in the mixture were $1:1$, $1:2$, and $1:3$. These mixtures are denoted as MX-11, MX-12, and MX-21 hereafter. In these mixtures, polystyrene with a higher molecular weight acted as the "cluster". The data for these mixtures, such as $M_w,CL$, $M_w,CH$, $x_L$, and $x_H$, are listed in Table 1.

Phenolphthalein poly(ether sulfone) (PES-C) with the following chemical structure

was kindly supplied by the Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Academia Sinica, China. PES-C was made from a one-step polycondensation of phenolphthalein with 4,4'-dichloro-1,1'-sulfonyldibenzene in the presence of dry K$_2$CO$_3$. A high molecular weight PES-C fraction was used in this study. The synthesis details of PES-C can be found elsewhere. Analytical grade chloroform (Merck) was used as a solvent without further purification.

LLS Instrumentation. A commercial LLS apparatus (ALV/Sp-125 equipped with an ALV-5000 multi-channel digital time correlator) was used with a solid-state laser (ADLAS DPY42511, output power $400\text{ mW at } \lambda = 532\text{ nm}$) as the light source. The incident beam was vertically polarized with respect to the scattering plane. In our setup, $\beta$ in eq 3 was $-0.9$, a rather high value for an LLS spectrometer capable of doing both static and dynamic LLS simultaneously. Due to this high $\beta$ value, we were able to carry out dynamic LLS in very dilute solutions with a good signal-to-noise ratio, so that the concentration correction was reduced to the minimum. After some proper modifications, the present LLS spectrometer was capable of doing both static and dynamic LLS continuously in the scattering angle range 5.7–154°.

Results and Discussion

Figure 1 shows a typical Zimm plot of PEB-C in chloroform at $\theta = 25^\circ C$. The concentration of PEB-C ranges from 0.373 to 1.86 mg/mL. According to eq 1, the extrapolations of $C = 0$ and $q = 0$ lead to $M_w$, listed as $M_w^\theta$ in Table 1. In addition, the slopes of plots of $(KC/R_g(q))_{q \rightarrow 0}$ vs $q^2$ and $(KC/R_g(q))_{C \rightarrow 0}$ vs $C$ lead to $B_k = 27.3$ nm and $A_L = -2.58 \times 10^{-4}$ (mol/mL$^2$) respectively. The negative value of $A_L$ indicates that chloroform is a poor solvent of PES-C. $M_w$ is higher...
than the expected value for a polymer made from polycrystalline. In a previous static LLS study of a similar system,5 no explanation was given to the unexpected higher value of $M_w$.

Figure 2 shows a typical translational diffusion coefficient distribution $G(D)$ of PES-C in chloroform at $T = 25 \, ^\circ\text{C}$ and $\theta = 20\, ^\circ\text{C}$.

Figure 3 shows plots of the average hydrodynamic radius ($R_h$) versus $q^2$ for the low molecular weight PES-C chains (○) and high molecular weight clusters (□).

Table 1. Mixing Details of Three Polystyrene Mixtures and the LLS Results of These Polystyrene Mixtures and PES-C$^{a,b}$

<table>
<thead>
<tr>
<th>sample</th>
<th>$10^{-5}M_w^{m}$</th>
<th>$10^{-5}M_w^{h}$</th>
<th>$x_1^{m}$</th>
<th>$A^c_t$</th>
<th>$10^{-5}M_x^{m}$</th>
<th>$10^{-5}M_x^{h}$</th>
<th>$A^c_r$</th>
<th>$10^{-5}M_r^{m}$</th>
<th>$10^{-5}M_r^{h}$</th>
<th>$10^{-5}M_{r,s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX-11</td>
<td>3.00</td>
<td>59.4</td>
<td>0.954</td>
<td>1.05</td>
<td>5.60</td>
<td>5.60</td>
<td>1.02</td>
<td>2.95</td>
<td>6.06</td>
<td>60.6</td>
</tr>
<tr>
<td>MX-12</td>
<td>1.19</td>
<td>59.4</td>
<td>0.963</td>
<td>0.53</td>
<td>3.34</td>
<td>3.32</td>
<td>0.52</td>
<td>1.27</td>
<td>59.4</td>
<td>15.5</td>
</tr>
<tr>
<td>MX-21</td>
<td>1.19</td>
<td>59.4</td>
<td>0.991</td>
<td>2.10</td>
<td>1.75</td>
<td>1.73</td>
<td>2.05</td>
<td>1.19</td>
<td>57.4</td>
<td></td>
</tr>
<tr>
<td>PES-C</td>
<td>1.03$^c$</td>
<td>0.936$^d$</td>
<td></td>
<td></td>
<td>2.00</td>
<td>1.01</td>
<td>3.32</td>
<td>1.07</td>
<td>15.5</td>
<td>57.4</td>
</tr>
</tbody>
</table>

$^a$ $M_w$ is the weight average molecular weight, $x_1$ is the weight fraction of low molecular weight polymer, and $A_t$ is the ratio of the light intensity scattered from high molecular weight polymer to that from low molecular weight polymer, where the superscripts "m" and "c" denote low and high molecular weight polymers, respectively.

$^b$ Relative errors: $M_w \pm 2\%$, $x_1 \pm 1\%$, $A_t \pm 3\%$.

$^c$ The static LLS result from the PES-C solution after removing the clusters by a 0.1-μm filter.

$^d$ It was determined by using a very precise differential refractometer described in the text.
solution even after 6 weeks of standing at room temperature. These larger species could be either the aggregates made of the linear PES-C chains or the highly branched polymer clusters formed during polymerization. However, we believe that they are polymer clusters. A possible way to form the larger clusters could be the opening of the ester ring in phenolphthalein. This ring opening will lead to branching along the PES-C backbone chain or even possible cross-linking between different PES-C chains. The existence of these larger polymer clusters partially explains why the viscoelastic and mechanical properties of PES-C are similar to those of PEEK even though the expected interactions among the PES-C chains are much less than those among the PEEK chains because the introduction of the phenolphthalein side groups along the PES-C backbone chain prevents a close chain packing. The investigation of the structural detail of the PES-C clusters is ongoing, which is however not the problem we intend to address here.

After removing the larger clusters from the PES-C solution by filtration, we characterized the linear PES-C chains remaining in the solution by static LLS. We found $M_w = 1.03 \times 10^5$, listed in Table 1 as $M_{w,L}$, $(R_g) = 17.4$ nm, and $A_2 = -4.0 \times 10^{-4}$ (mol/mL)/g$^2$. The value of $(R_g)/(R_w) \sim 1.34$ shows that the PES-C chain has a random-coil conformation in chloroform at 25 °C, which has also been observed in a previous intrinsic viscosity study of a similar system. This coil conformation is expected because there are two very flexible ether linkages (−O−) in each repeating unit of PES-C. The fact that PES-C is a mixture of individual linear chains and clusters triggered us to use the described LLS procedure to reexamine the previous results obtained from Figure 2. Before using it, we decided to check its validity and limitation in the characterization of such a polymer mixture. We used three two-polystyrene mixtures as model systems, wherein the polystyrene with a higher molecular weight acted as the cluster.

Figure 5 shows typical diffusion coefficient distributions of the polystyrene mixture MX-11 at two different scattering angles (○, $\theta = 14^\circ$ and □, $\theta = 17^\circ$). The two relaxation processes related to the low and high molecular weight polystyrenes are well separated. The peak with a higher (D) shows the polystyrene with a lower molecular weight $(M_{w,L})$, and the peak with a lower (D), the polystyrene with a higher molecular weight $(M_{w,H})$. The narrow widths of the two peaks confirm that the polystyrenes used in this study were narrowly distributed. The positions of the two peaks are basically independent of the scattering angle in the range 9−20°, but the area ratio $A_r (=A_L/A_H)$ slightly varies.

Figure 6 shows the ratio of the area under the two peaks in Figure 5 as a function of $q^2$, where $A_L$ and $A_H$ are the areas under $G(D)$ of the low and high molecular weight polystyrenes in the mixture, respectively.

$$A = \int_0^\infty G(D) \, dD \propto R_v(q) \propto \frac{M_w C}{1 + \frac{1}{3}(R_g)q^2 + 2A_2 M_w C} \quad (8)$$

so that for a polymer mixture of low molecular weight linear chains and high molecular weight clusters the area ratio $(A_r)$ should be

$$A_r = \frac{A_L}{A_H} = \frac{M_{w,L} C_L}{M_{w,H} C_H} \left[ 1 + \frac{1}{3}(R_g)q^2 + 2A_2 M_{w,H} C_H \right]$$

$$= \frac{M_{w,L} C_L}{M_{w,H} C_H} \left[ a L (R_g)q^2 + \frac{1}{3} a L (R_g)C_L + a H (R_g)q^2 + a H C_H \right] \quad (9)$$

where $a L = 1 - 2A_2 M_{w,L} C_L$ and $a H = 1 + 2A_2 M_{w,H} C_H$. The plot of "$A_r$ vs $q^2$" is a straight line when $(R_g)q^2 \ll 1$. This is why the accessible small angle range used in this study is vital, since $(R_g)q^2$ is usually quite large for clusters with a high average molecular weight. On the basis of eq 9, the intercept in Figure 6 should be very close to $(M_{w,L} C_L)/(M_{w,H} C_H)$ since $a _L a_H = 1$ for a very dilute solution; and the slope can be directly related to $(R_g)q^2$ since $(R_g)q^2 \gg (R_g)^2$.

A combination of $(A_r)_{q^2 \gg 1} = (M_{w,L} C_L)/(M_{w,H} C_H)$ from dynamic LLS with $M_{w,app}$ from static LLS leads to $M_{w,L} x_L$ and $M_{w,H} x_H$. As previously stated, by knowing any one of the four parameters $(M_{w,L}, x_L, M_{w,H},$ and $x_H)$, we will be able to calculate the other three. However, it would be difficult to accurately determine $x_H$ or $M_{w,H}$ because the amount of the high molecular weight
polymer clusters is usually very small. Therefore, a more practical way is to determine either $M_{w,L}$ or $x_L$. Actually, to measure $x_L$ rather than $M_{w,L}$ is experimentally preferred due to the higher accuracy and less difficulty. On the basis of this consideration, we used the values of $x_L$ from the preparation of the higher molecular weight mixtures to calculate both $M_{w,L}$ and $M_{w,H}$.

Table 1 summarizes all calculated values of $M_{w,L}$ and $M_{w,H}$ for the three polystyrene mixtures. A comparison of each pair of the corresponding values of $M_{w,L}$ and $M_{w,H}$ and $M_{w,H}$ for each of the three mixtures shows that the LLS method adopted here works reasonably well for the polystyrene mixtures wherein the high molecular weight polystyrene was used to imitate the large "clusters". The agreement between the measured and calculated weight-average molecular weights gives us confidence to use this method to characterize PES-C. However, it should be stated that if the amount of high molecular weight clusters is too small, i.e., $x_H < 1$ or $x_L \sim 1$, the errors introduced in the determination of $x_H$ or the calculation of $M_{w,H}$ from the $x_L$ value would be rather large. Fortunately, we can see in Figure 2 that the amount of the clusters in PES-C (i.e., the area under the peak with a lower value of $D$) is not too small.

Figure 7 shows a plot of $A_t$ vs $q^2$ for PES-C in chloroform at $T = 25^\circ$C, where $A_t$ represents the experimental data and the line represents the fitting of $A_t = 1.01 + 5.60 \times 10^{-11}q^2$. The method of combining the weight-average molecular weight $M_w$ from static laser light scattering (LLS) and the area ratio ($A_t$) under the translational diffusion coefficient distribution ($D(D)$) peaks from dynamic LLS is useful for the characterization of a polymer mixture made of individual chains and clusters. Using this method, we have accomplished the characterization of a recently developed high-performance thermoplastic resin: phenolphthalein poly(ether sulfone) (PES-C). We found that PES-C consists of $\sim$94% (by weight) linear polymer chains and $\sim$6% large polymer clusters. The weight-average molecular weight $M_w$ of the linear PES-C chains is $\sim$100 000 and the $M_w$ of the clusters is $\sim$15 times higher. The existence of these high molecular weight clusters might partially explain the high glass transition temperature and other viscoelastic properties of PES-C. The linear PES-C chains have a typical coil conformation in chloroform at room temperature, while the PES-C clusters seem to have a more compact structure in the solution. It is expected that the LLS method used here will be particularly useful in the characterization of association/aggregation in a given polymer or colloidal system.

Conclusions

The method of combining the weight-average molecular weight $M_w$ from static laser light scattering (LLS) and the area ratio ($A_t$) under the translational diffusion coefficient distribution ($D(D)$) peaks from dynamic LLS is useful for the characterization of a polymer mixture made of individual chains and clusters. Using this method, we have accomplished the characterization of a recently developed high-performance thermoplastic resin: phenolphthalein poly(ether sulfone) (PES-C). We found that PES-C consists of $\sim$94% (by weight) linear polymer chains and $\sim$6% large polymer clusters. The weight-average molecular weight $M_w$ of the linear PES-C chains is $\sim$100 000 and the $M_w$ of the clusters is $\sim$15 times higher. The existence of these high molecular weight clusters might partially explain the high glass transition temperature and other viscoelastic properties of PES-C. The linear PES-C chains have a typical coil conformation in chloroform at room temperature, while the PES-C clusters seem to have a more compact structure in the solution. It is expected that the LLS method used here will be particularly useful in the characterization of association/aggregation in a given polymer or colloidal system.
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References and Notes


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