Experimental Study of the Spectral Distribution of the Light Scattered from Flexible Macromolecules in Very Dilute Solution

Chi Wu,* Kam Kwong Chan,† and Ke-Qing Xia‡
Departments of Chemistry and Physics, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Received July 29, 1994; Revised Manuscript Received November 14, 1994

ABSTRACT: Spectral distributions (SD) of the light scattered from three high molecular weight polystyrene standards in dilute solution over a wide range of scattering angles (5.7°–154°) were precisely determined from a series of carefully executed light scattering experiments. At x = 1, the SD have only one narrow peak, where x = (qRg)², with q being the scattering vector and Rg the radius of gyration of the polymer coil. As expected, this peak is purely due to translational diffusion and has a line width Γₚₑₚₓleccion = Dq², with D being the diffusion coefficient of polymer. In the intermediate range of 1 < x ≤ 15, the SD have two peaks. We have identified that the normalized line width Γₚₑₚₓleccion(Dq²) of the second peak is associated with the internal motions and follows the plot of [1 + 2Γq(Dq²)] versus x, wherein Γₚₑₚₓleccion is the line width associated to the nth-order internal motion with n = 1 in 1 < x < 3; n = 2 in 3 < x < 6; n = 3 in 6 < x < 10; and n = 4 in 10 < x < 15. Thus, we can obtain Γₚₑₚₓleccion from Γₚₑₚₓleccion(Dq²) = [1 + 2Γq(Dq²)]. These measured Γₚₑₚₓleccion values agree with the predicted values according to the non-free-draining bead-and-spring model. However, the same model also predicts that, for 3 < x < 15, the contribution from [1 + 2Γq(Dq²)] should be dominant in the SD. This contradiction between the theory and observation leads us to believe that some of the energy-favored internal motions are not observable in dynamic LLS at particular x, which is related to the observation length scale (1/q). For x > 15, the two peaks merge into one broad peak. The plot of [Γₚₑₚₓleccion(q²)] versus xᵢⁿ for this peak approached a plateau value which is lower than a theoretically predicted value, where (W, b, T, and η₁ are the z-average line width, the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

Introduction

As one of the fundamental problems in polymer physics, the dynamics of flexible polymer chains in dilute solution has been theoretically investigated and experimentally examined for a number of years.1–6 It has been shown that the relaxation processes associated with internal motions of flexible polymer chains in dilute solution will add additional broadening to the spectral distribution of the scattered light.7 Quantitative predictions on the degree of this spectral broadening have been made on the basis of the bead-and-spring dynamical models with or without considering hydrodynamic interactions.8,9 But, these theories are not very successful in describing the measured spectral distributions at large values of x = (qRg)², where Rg = (Rg)² is the mean-square z-average radius of gyration and q = (4πn/λo) sin (θ/2) is the scattering vector, with n, λo, and θ being the solvent refractive index, the light wavelength in vacuo, and the scattering angle, respectively.

As stated in a recent publication,10 the study of intramolecular relaxation processes in dilute solution remains a difficult experimental challenge. In order to observe as many internal modes as possible, a long flexible polymer chain, i.e., a high molecular weight sample, has to be used. For such a polymer, there always exists a certain degree of coupling between the translational diffusion and the internal motions at the lowest accessible scattering angle (~15°) of a normal laser light scattering (LLS) spectrometer. Without a clear separation of these two types of motions, it is impossible to have a good and reliable investigation of the spectral distribution of very long polymer chains in dilute solution. Recently, Chu et al.,10 using a combina-

1 Department of Chemistry.
2 Department of Physics.
where $\omega$ is the difference between the angular frequency of the scattered light and that of the incident light, $q$ is the scattering vector as previously defined, $D$ is the translational diffusion coefficient for the center of mass of the polymer chain, and the function

$$S(q,\omega) = (1/2\pi) \int e^{-i\omega t} e^{-i q \cdot r(t)} J(q,t) \, dt$$

(1)

is the spatial Fourier transform of the segment–segment time correlation function. It arises from the interference of the scattered lights from different segments in a polymer chain with $N$ such segments. It contains all the temporal and spatial information on the internal motion of a chain with

$$S(q,t) = \langle (1/Na^2) \sum_{m=0}^{N-1} e^{-i q \cdot r_m(t) - q \cdot r_m(0)} \rangle$$

(2)

is the spatial Fourier transform of the segment–segment time correlation function. It arises from the interference of the scattered lights from different segments in a polymer chain with $N$ such segments. It contains all the temporal and spatial information on the internal motion of a chain with

In order to perform the ensemble average in $J(q,t)$, an explicit model for the internal motion of a chain is needed. By incorporating the Oseen–Kirkwood–Riseman hydrodynamic interaction into the bead-and-spring model, Perico, Piaggio, and Cuniberti (PPC) have shown

$$S(q,\omega) = P_0(x) L(\omega, q^2 D + \Gamma_0) + \sum_{a=1}^{N} P_a(x, a) L(\omega, q^2 D + \Gamma_0, \Gamma_0) + \sum_{a=1}^{N} \sum_{\beta=1}^{N} P_{\beta a}(a, x, \beta) L(\omega, q^2 D + \Gamma_0, \Gamma_0) + \cdots$$

where the functions

$$L(\omega, \Gamma) = \frac{2\Gamma}{2\pi (\omega^2 + \Gamma^2)}$$

(3)

(4)

represent the $\omega$-normalized Lorentzian distributions, with $\Gamma$ being the half-width at half-height, i.e., the line width, and the $P_a$'s ($n = 0, 1, 2, \ldots$) determine the contributions of the different Lorentzians to the spectrum of the scattered light. The zeroth-order $P_0(x)$ represents the contribution of the translational diffusion; $P_a(x, a)$, the first-order contribution of the $a$th internal mode; $P_{\beta a}(a, x, \beta)$, the second-order contribution of the $a$th and $\beta$th internal modes; and so on. When $x < 1$, the spectral distribution is measured in the long-wavelength regime and hence $P_0(x)$ is dominant in $S(q,\omega)$. As $x$ increases, the contributions from $P_1(x, a)$, $P_{\beta a}(a, x, \beta)$, and other higher-order terms become more and more important. PPC have numerically shown that $P_0(x, 1, 1)$ is the largest contribution to $S(q,\omega)$ among all Lorentzian terms associated with the internal modes.

In a dynamic laser light scattering experiment, the intensity–intensity time correlation function of the scattered light is usually measured from which $S(q,t)$, the Fourier transform of $S(q,\omega)$, is determined.

**Experimental Section**

**Sample Preparation.** Three high molecular weight and narrowly distributed polystyrene standards (Batch No. 20147-7, nominal $M_w = 6.50 \times 10^6$, $M_c/M_w = 1.06$; 20148-5, $M_w = 1.02 \times 10^7$, $M_c/M_w = 1.17$; and 20149-4, $M_w = 1.44 \times 10^7$, $M_c/M_w = 1.21$) from Polymer Laboratories Ltd., denoted hereafter as HPS-1, HPS-2, and HPS-3, and analytical grade toluene, from Riedel-de Haen Co. were used in this study. The polymer concentrations were very dilute ($\sim 30 \mu g/mL$), so that the concentration correction on the measured line-width distribution was very small ($\sim 4\%$ on the basis of the known value of the second-virial coefficient). In this concentration range and at high scattering angle, the scattering intensity was so weak that the signal-to-noise ratio could drop down to $\sim 0.9$ to as low as $\sim 0.05$. An overnight data accumulation therefore is required in order to have a good dynamic light scattering measurement. Thus, it is essential to prepare a clean solution, with all dust particles removed from the solution; otherwise, the light scattered from even one or two remaining dust particles will ruin the measured time correlation function.

**Static Laser light Scattering (Static LLs).** For a Gaussian coil in a dilute solution, the angular ($\theta$) dependence of the absolute time-averaged scattered intensity over solvent, known as the excess Rayleigh ratio $R_{ext}(\theta)$, can be expressed as

$$K C \frac{\lambda^2}{\lambda_0^2} \frac{dn}{dC} P(\theta) \frac{1}{M_c^2} + 2A_2 C$$

(5)

where $K = 4\pi n^2 (dn/dC)^2/(N_d \lambda_0^4)$ and $P(\theta) = (2\lambda^2)/x - 1 + e^{-x^2}$, with $N_d$, $dn/dC$, $n$, and $\lambda_0$ being Avogadro's number, the specific refractive index increment, the solvent refractive index, and the wavelength of light in vacuo, respectively. Again, $x = q R_g^2$. $A_2$ is the second virial coefficient. Benoit has shown that, for long polymer chains, the determination of $P(\theta)$ over a wide range of $\theta$ gives not only the weight-average molecular weight $M_w$ from the small $x$ range but also the number-average molecular weight $M_n$, and $z$-average molecular weights $M_z$ in the asymptotic portion of $P(\theta)$ at $x \gg 1$. In addition, at $x < 1$, we can determine $R_q$ from the plot of $1/p(\theta)$ versus $q^4$. $\rho_{av}(\theta)$ is a measured base line; $\beta$, a spatial coherence constant depending only on the detection optics, with its value ($0 \leq \beta \leq 1$) reflecting the signal-to-noise ratio of the actual experiment; and $g^{(2)}(q,t)$, the normalized electric field time correlation function. It can be shown that $g^{(2)}(q,t)$ is proportional to the dynamic structure factor $S(q,t)$ and $g^{(2)}(q,t)$ can be related to the line-width distribution $G(\Gamma)$ by

$$g^{(2)}(q,t) = \int_0^{\infty} G(\Gamma) e^{-\Gamma t} d\Gamma$$

(7)

A Laplace inversion of eq 7 gives $G(\Gamma)$. The inversion can be accomplished by using, for example, a CONTIN algorithm. For a monodisperse hard-sphere sample, $G(\Gamma)$ is a delta function. But, for the flexible polymer chains, even for a truly monodisperse sample, $G(\Gamma)$ is a distribution with a finite width. This is because a flexible polymer coil has a conformation distribution in dilute solution. Different conformations have different diffusion coefficients which lead to a distribution in $\Gamma$. Thus, the width of $G(\Gamma)$ consists of two parts. One is from the sample polydispersity, and the other is from the conformation distribution. This conformation broadening in $G(\Gamma)$ has been overlooked in the past. For a narrowly distributed polymer sample, at $x < 1$, $G(\Gamma)$ is a translational diffusion
We have modified the detection system by adding a pinhole was -5 times smaller than that of a normal Ar ion gas laser. The incident beam was vertically polarized with respect to the scattering plane. In our setup, the measured relative width \( \mu_{G}(\Gamma)^{2} \) was close to zero. On the other hand, the linear fitting of \( KC/R(q) \) versus \( q^{2} \) in the range of \( x \approx 1 \) gives \( M_{w}, M_{n}, M_{z} \), and \( R_{g} \) from the intercept and slope, respectively. Figure 1 shows respectively \( D(=\langle q^{2}/q^{2} \rangle) \) versus \( q^{2} \) for HPS-1 (O), HPS-2 (D), and HPS-3 (\( \Delta \)) in toluene at \( T = 20^\circ C \) and \( \theta = 5.7^\circ \) which respectively corresponds to \( x = 0.052, 0.138, \) and 0.302 for HPS-1, HPS-2, and HPS-3.

Results and Discussion

In the Range of \( x < 1 \). Figure 1 shows respectively from top to bottom three typical plots of \( KC/R(q) \) versus \( q^{2} \) from static LLS experiments for HPS-1, HPS-2, and HPS-3 in toluene at \( 20^\circ C \). As stated in the last section, the extrapolation of \( KC/R(q) \) versus \( q^{2} \) in the range of \( x < 1 \) gives \( M_{w} \) and \( R_{g} \) from the intercept and slope, respectively. Figure 1 shows that the extrapolation to \( q = 0 \) is really not necessary since our accessible lowest scattering angle is already close to zero. On the other hand, the linear fitting of \( KC/R(q) \) versus \( q^{2} \) in the range of \( x \gg 1 \) gives us \( M_{w} \) and \( M_{z} \). Such obtained \( M_{w}, M_{z}, \) and \( M_{n} \) at finite concentration were extrapolated to \( C = 0 \) by using the known \( A_{2} \) values on the basis of eq 5. All fitted values of \( M_{w}, M_{z}, M_{n}, \) and \( R_{g} \) from the static LLS are summarized in Table 1, which shows that HPS-1 and HPS-2 are fairly monodisperse and HPS-3 has a slightly broader distribution. The \( R_{g} \) values in

Table 1. Summary of Static and Dynamic LLS Results at \( x = 1 \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_{n} ) (x10^6)</th>
<th>( M_{w} ) (x10^6)</th>
<th>( M_{z} ) (x10^6)</th>
<th>( R_{g} ) (nm)</th>
<th>( D ) (X10^10)</th>
<th>( M_{w}/M_{n} ) (x10^3)</th>
<th>( M_{z}/M_{n} ) (x10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPS-1</td>
<td>6.10</td>
<td>6.33</td>
<td>6.78</td>
<td>130</td>
<td>4.43</td>
<td>1.08</td>
<td>6.09</td>
</tr>
<tr>
<td>HPS-2</td>
<td>9.80</td>
<td>10.4</td>
<td>13.4</td>
<td>210</td>
<td>3.25</td>
<td>1.12</td>
<td>10.4</td>
</tr>
<tr>
<td>HPS-3</td>
<td>16.4</td>
<td>19.8</td>
<td>24.4</td>
<td>311</td>
<td>2.25</td>
<td>1.20</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Relative errors are as follows: \( M_{n}, M_{w}, \) and \( M_{z} \), ±2%; \( R_{g} \), ±3%; \( D \), ±1%.

The incident beam was vertically polarized with respect to the internal relaxation processes to \( G(\Gamma) \) become more and more appreciable. LLS Instrumentation. A commercial LLS spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-r digital correlator) was used with a solid-state laser (ADLAS DFP525II, output power \( \approx 400 \) mW at \( \lambda = 532 \) nm) as the light source. We have modified the detection system by adding a pinhole as near the light-scattering cell as possible to reduce the angular uncertainty. With this laser and a proper alignment, all measurements were done at \( T = 20.0 \pm 0.1^\circ C \). The details of LLS instrumentation and its principles can be found elsewhere.

Figure 2 shows three typical line-width distributions \( G(\Gamma^{2}) \) obtained from the CONTIN analysis of HPS-1 (O), HPS-2 (D), and HPS-3 (\( \Delta \)) in toluene at \( T = 20^\circ C \) and \( \theta = 5.7^\circ \). This small scattering angle \( (5.7^\circ) \) corresponded to \( x = 0.052, 0.138, \) and 0.302 for HPS-1, HPS-2, and HPS-3, respectively. The z-average line-width distribution were very small \( (0.02-0.05) \) which further indicates that all polystyrene samples used in this study are narrowly distributed. In Table 1, the calculated polydispersity indexes \( (M_{w}/M_{n})_{\text{cal}} \) were estimated from the measured relative width \( \mu_{G}(\Gamma)^{2} \) by using the relation \( (M_{w}/M_{n})_{\text{cal}} \approx (1 + 4\mu_{G}(\Gamma)^{2})^{2} \). Table 1 shows that \( (M_{w}/M_{n})_{\text{cal}} \) are close to the corresponding ratio of \( M_{w} \) and \( M_{n} \) from the static LLS.

Figure 3 shows a plot of \( D(=\langle q^{2} \rangle^{1/2}) \) versus \( q^{2} \) in a regime of \( x \ll 1 \) for HPS-1 (O), HPS-2 (D), and HPS-3 (\( \Delta \)). In this small \( x \) range, \( D \) seems to be independent of \( q^{2} \). The contributions of the internal motions to the spectral distribution are insignificant, so that \( D \) approaches the 2-average translational diffusion coefficient \( D_{h} \) when \( x \rightarrow 0 \). After extrapolating to infinite dilution, we obtained \( D_{h}(\theta=0,C=0) \) which is denoted as \( D \) hereafter. The measured values of \( D \) for HPS-1, HPS-2, and HPS-3 are listed in Table 1. Also listed were \( (M_{w})_{\text{cal}} \) obtained from the measured \( D \) by using a known scaling relation: \( D = 3.64 \times 10^{-4}M_{n}^{-0.677} \) for polystyrene in toluene at \( T = 20^\circ C \). It can be seen that \( M_{w} \) from static LLS are very close to \( (M_{w})_{\text{cal}} \). We also calculated \( M_{w} \) (not listed) from \( R_{g} \) by using the scaling
relation between \( R_g \) and \( M_w \). The three \( M_w \) values from static and dynamic LLS are very close to each other. The good agreement among the \( M_w \) values from three different methods shows that the results reported in Table 1 are self-consistent and reliable, which indirectly shows that our LLS spectrometer was properly aligned and calibrated. Subsequently, the measured values of \( M_w \) \((6.33 \times 10^3, 1.04 \times 10^4, \text{and} 1.98 \times 10^7)\) were used in all analyses and calculations below.

In the Range of \( x > 1 \). Figure 4 show typical plots of \( G(\Gamma q^2) \) versus \( \Gamma q^2 \) for HPS-2 in toluene at \( T = 20^\circ C \) and at different \( x \) values; the inset shows a \( \sim 10 \) enlargement of the second (smaller) peak of the distribution in the range of \( 10^{-7} - 10^{-4} \) cm/s.

Figure 5. Plot of \( \Gamma_{peakk}(Dq^2) \) versus \( x \) for HPS-1 (\( \bigcirc \)), HPS-2 (\( \bigcirc \)), and HPS-3 (\( \bigtriangledown \)) in toluene at \( 20^\circ C \) where \( \Gamma_{peakk} \) is denoted the average line width of the second peak (the larger symbols). For comparison, we included the average line width of the first peak (the smaller symbols). The filled diamonds and circles are the experimental results respectively from refs 10 and 21.

On the other hand, \( \Gamma_{peakk}(Dq^2) \) follows an unexpected pattern, and the plots of \( \Gamma_{peakk}(Dq^2) \) versus \( x \) for all three samples are independent of the molecular mass \( M \). According to the existing theories for a flexible polymer coil in both the free-draining\(^{22}\) and non-free-draining limits,\(^{12}\) at \( x > 1 \), \( S(q,t) \) depends mainly on the first five decay rates, namely, a pure translational term plus four principle intramolecular terms. In the decreasing order of contributions to the spectral distribution, eq 3 in the time domain at \( x > 1 \) can be written as

\[
S(q,t) = P_0(x) e^{-Dq^2 t} + P_1(x,1,1) e^{-Dq^2 + 2r_1 \Gamma y} + \ldots
\]

\[
P_1(x,2) e^{-Dq^2 + 2r_2 \Gamma y} + P_1(x,1,1,1) e^{-Dq^2 + 4r_1 \Gamma y} + \ldots
\]

where the numeric values of \( P_r \) in the range of \( 1 \leq x \leq 10 \) have been calculated by PPC.\(^{12}\) On the basis of the Rouse–Zimm model,\(^2\)

\[
\Gamma_n = \frac{0.293RT\lambda'_n}{M[\eta]_n\eta_0}
\]

where \( R, T, M, \eta_0, \) and \( [\eta] \) are the gas constant, the absolute temperature, the polymer molecular mass, the solvent viscosity, and the intrinsic viscosity, respectively. \( \lambda'_n \) represents the eigenvalues in the Zimm model listed in ref 23. Using \( Dq^2 \) as a unit and replacing \( q \) with \( x \), we can rewrite eq 9 as

\[
\Gamma_n'(Dq^2) = \frac{0.293RT\lambda'_n R_g^2}{DM[\eta]_n\eta_0 x^2}
\]

\( \Gamma_n'(Dq^2) \) can be calculated from eq 10 with the known values of \( D, M, R_g, \lambda'_n, \eta_0, \) and \( [\eta] \) respectively in Table 1, in ref 23, and in the Polymer Handbook.\(^{24}\)

Substituting the well-known scaling relations for a flexible polymer coil in good solvent\(^{25,26}\) \( R_g \approx M^{a_3}, D \approx M^{-\alpha_3}, \text{and} \ [\eta] \approx M^{a_4} \) with \( \alpha_3 \approx (1 + a_3)/3 \) and \( \alpha_4 \approx a_4 \) into eq 10, we can show that the plot of \( \Gamma_n'(Dq^2) \) versus \( x \) should be independent of \( M \) for a given type of polymer, temperature, and solvent, which is exactly what we have observed in Figure 5.

By using the numeric values of \( P_r \) in ref 12 and the values of \( \Gamma_n \) calculated from eq 10, we are able to calculate the average line width (\( \Gamma_{int} \)) associated with the internal motions,\(^1\) i.e.,
\[ \Gamma_{\text{int}} = \sum_{n=1}^{N} P_{1}(x, \alpha) (Dq^{2} + \Gamma_{n}) + \sum_{n=1}^{N} \sum_{m=1}^{N} P_{2}(x, \alpha, \beta) (Dq^{2} + \Gamma_{n} + \Gamma_{\beta}) + \ldots \sum_{n=1}^{N} \sum_{m=1}^{N} \sum_{p=1}^{N} \sum_{q=1}^{N} P_{3}(x, \alpha, \beta, \gamma) + \ldots (11) \]

According to PPC’s theory, \( \Gamma_{\text{peak}}/Dq^{2} \) calculated from the second peak of the line-width distribution in Figure 4 should follow the line of \( \Gamma_{\text{int}}/Dq^{2} \) versus \( x \). However, the plot of \( \Gamma_{\text{peak}}/Dq^{2} \) versus \( x \) (the solid line) in Figure 5 shows a clear deviation between the experimental data and the calculation.

On the basis of their calculation, PPC have predicted\(^{12} \) that, in the range of \( 1 < x < 3 \), only the second term in eq 8 gives a significant contribution to \( S(q, t) \) and, at higher \( x \), the higher terms together with the second term start to contribute to \( S(q, t) \). In our experimentally accessible range of \( x \), the second term is expected to be dominant. The dotted lines in Figure 5 represent plots of \( [1 + 2\Gamma_{n}/(Dq^{2})] \) versus \( x \). It can be seen that the experimental data respectively follow the lines of \( n = 1 \) in \( 1 < x < 3 \); \( n = 2 \) in \( 3 < x < 6 \); \( n = 3 \) in \( 6 < x < 10 \); and \( n = 4 \) in \( 10 < x < 15 \). In other words, analyzing \( \Gamma_{\text{peak}}/Dq^{2} \) in Figure 4 by assuming that \( \Gamma_{\text{peak}}/Dq^{2} = [1 + 2\Gamma_{n}/(Dq^{2})] \), we are able to determine \( \Gamma_{1}, \Gamma_{2}, \Gamma_{3} \), and \( \Gamma_{4} \) in different ranges of \( x \). For \( x > 15 \), the two peaks in Figure 4 merge into one, which makes it difficult for us to get a precise \( \Gamma_{\text{peak}} \) value from the spectral distribution. So, we stop our second-peak analysis of these high \( x \) value data in order to avoid any ambiguity.

Both Chu’s and our experimental data clearly indicate that the internal motions associated with \( 2\Gamma_{n} \), i.e., \( \Gamma_{n} + \Gamma_{\alpha} \), dominate the relaxation process in a different range of \( x \), where \( n \) is the order of the internal motion. On the basis of eqs 3 and 8, this relaxation process is a self-coupling of the \( n \)-th order motion. At present, we have no explanation about why only this self-coupling internal motion was observed in dynamic LLS experiment.

Energetically, it is easier to excite the internal motions associated with \( \Gamma_{n} \) and \( 4\Gamma_{1} \) than that associated with \( 2\Gamma_{2} \). The fact that we observed \( 2\Gamma_{2} \) instead of \( \Gamma_{1} \) and \( 4\Gamma_{1} \) in the range of \( 3 < x < 6 \) might suggest that dynamic LLS’s ability to measure certain internal modes is somehow related to the observation length scale, i.e., \( 1/q \). In other words, even though there exist some internal motions which are much more favorable from an energetic point of view, we could not “see” them in dynamic LLS in a certain range of \( x \). If our speculation is right, the \( P_{3}(x) \) values in ref 12 have to be modified to take into account the nature of dynamic LLS.

In the Range of \( x > 15 \). Figure 6 shows a plot of the reduced \( z \)-average line width \( \Gamma/(q^{2}k_{B}T/\eta_{0}) \) versus \( x^{1/2} \) for HPS-1 (()), HPS-2 (()), and HPS-3 (A) in toluene at 20 °C, where \( k_{B} \) is the Boltzmann constant. As \( x \) increases, the reduced \( z \)-average line width gradually decreases and approaches a plateau. This scaling of \( \Gamma \) with \( q^{2} \) is consistent with the non-free-draining bead-and-spring model for flexible polymer chains in infinite dilute solution,\(^{22} \) which was also observed by other laboratories in the past.\(^{5,10,21} \) In general, the observed plateau values at \( 0.05 < 0.06 \) were significantly lower than the theoretical prediction (0.071 with preaveraged Oseen tensor and 0.079 without a preaveraged Oseen tensor\(^{8} \)). In Figure 6, the plateau value of \( \Gamma/(q^{2}k_{B}T/\eta_{0}) \)

is around 0.05. This consistent lower plateau value shows that, at larger \( x \), there exist some problems in the theoretically predicted \( G(\Gamma) \).

In the above discussion, we have speculated that some of the energy-favorable internal motions cannot be observed in dynamic LLS experiment. If this were true, we might be able to explain the above lower plateau value as follows: On the basis of eq 3, we know that the terms associated with the internal motions have larger line widths than that of the pure translational diffusion of the center of mass \( (Dq^{2}) \). If some of the internal motions are not contributing as expected to the measured spectrum in dynamic LLS experiment, the \( z \)-average line width calculated from the line-width distribution will be smaller than that predicted in the bead-and-spring model for flexible coils. This smaller \( z \)-average line width will in turn lead to a lower plateau value. Further study is certainly needed to verify this speculation.

Conclusions

Our dynamic laser light-scattering results have shown that, for \( x(qR_{F})^{2} > 1 \), there are two peaks in the spectral distribution. The average line width \( \Gamma_{\text{peak}} \) of the second peak associated with the internal motions does not follow theoretical predictions but a plot of \( [1 + 2\Gamma_{n}/(Dq^{2})] \) versus \( x \), where \( n = 1 \) for \( 1 < x < 3 \); \( n = 2 \) for \( 3 < x < 6 \); \( n = 3 \) for \( 6 < x < 10 \); and \( n = 4 \) for \( 10 < x < 15 \). Our speculation is that some of the internal motions, though favorable in terms of energy, are not observable in a dynamic LLS experiment at particular \( x \). This might be related to the observation length scale \( (1/q) \). The lower plateau value in the plot of \( \Gamma/(q^{2}k_{B}T/\eta_{0}) \) versus \( x^{1/2} \) may also be due to the same reason.

Acknowledgment. The partial financial support of this work by the RGC (the Research Grants Council of Hong Kong Government) Earmarked Grant 1994/95 (CUHK 299/94P, 221600260) is gratefully acknowledged.

References and Notes

(7) Kramer, O.; Frederick, J. E. Macromolecules 1972, 5, 69.


MA9411686