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Chain dynamics of concentrated polystyrene solutions studied by depolarized photon-correlation and viscosity measurements

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Concentrated solutions of nearly monodisperse polystyrene samples in cyclohexane in the theta condition and in the entanglement-free region have been studied by means of the depolarized photon-correlation spectroscopy and viscosity measurements. It is shown that the viscoelastic behavior of the studied systems is described by the Rouse theory and that in agreement with the theoretical analysis the main polymer dynamic process probed by the depolarized Rayleigh scattering is basically the reorientational motion associated with a Rouse segment of the polymer chain, whose relaxation is independent of the scattering angle and the molecular weight. In addition to the main dynamic process, the tail region of a very fast process associated with the sub-Rouse-segmental motions can be observed, whose existence is expected from the theoretical analysis. © 1999 American Institute of Physics. [S0021-9606(99)51817-5]

I. INTRODUCTION

In a concentrated polymer fluid system, the hydrodynamic interactions among segments of the same chain are screened by the presence of other chains in the neighborhood.¹⁻³ In such a situation, the polymer dynamics and viscoelasticity are described by the Rouse theory,⁴ if the chains are not so long as to form entanglements. From the viscosity value of the solution of known molecular weight, one can calculate the relaxation time of the highest Rouse mode of motion, if the molecular weight of the Rouse segment is known.³⁻⁵ Recently it was shown that the chain dynamics of a polystyrene melt probed by the depolarized photon-correlation spectroscopy was basically the reorientational motion associated with a Rouse segment.⁶ The molecular weight, m , for a Rouse segment of polystyrene was estimated to be around 850 in close agreement with the values obtained by other methods.⁷⁻¹⁰ The reorientational time measured by the depolarized Rayleigh scattering is of the same order of magnitude as that of the motion associated with a Rouse segment calculated from the viscoelastic data using the m value.

Here we report the results of depolarized photon-correlation measurements of two concentrated solutions (at 59.832 and 60.287 wt %) of polystyrene in cyclohexane at the theta temperature (35 °C) with molecular weights differing by a factor of 2 and both below the entanglement molecular weight. Experimentally three apparent modes, well separated, have been observed. In agreement with the theoretical analysis,⁶ the main dynamic process observed in the intermediate time region is independent of the molecular weight and the scattering angle; and its reorientation time is of the same order of magnitude as the relaxation time associated with a single Rouse segment calculated from the viscosity of the solution in terms of the Rouse theory. This

shows that the motion basically associated with a Rouse segment in the polymer chain can be probed by the depolarized light scattering. In the very short time region, as expected from the previous theoretical analysis,⁶ a separate process due to the sub-Rouse-segmental motion can be observed in its tail region. It is shown that the observed slowest mode having a q^2 dependence, a characteristic of the diffusive mode, is due to the leakage of the isotropic scattering arising from the concentration fluctuation in the solution. Because the slowest mode is well separated from the true depolarized modes, its contribution to the measured photon-correlation function can be neatly removed by using the MSVD (multi-exponential singular-value decomposition) analysis.

II. THEORETICAL BACKGROUND

A. Depolarized Rayleigh scattering

In a dynamic depolarized Rayleigh light scattering, one studies the time-correlation function $C(t)$ ¹¹

$$C(t) = \langle \sum_i \sum_j \alpha_{yz}^i[\Omega_i(t)] \alpha_{yz}^j[\Omega_j(0)] \times \exp[i\mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_j(0))] \rangle, \quad (1)$$

where $\alpha_{yz}^i[\Omega_i(t)]$ is the yz component of the polarizability tensor of a chemical bond segment i (or a molecule in the case of simple liquids) at time t in a laboratory fixed coordinate system and $\Omega_i(t)$ is the orientation angle of segment i at position $\mathbf{r}_i(t)$ at time t . Equation (1) is general and is applicable to a medium containing small molecules or polymer molecules. The depolarized Rayleigh scattering probes the collective reorientation motion rather than that associated with a single molecule or chemical bond segment. The collectivity can be expressed in terms of static and dynamic pair correlation between the polarizabilities associated with neighboring molecules or segments.¹¹ In the case of polystyrene, it has been shown from the measured depolarized scattering intensities of melt and solution systems that the static correlation between segments belonging to different chains is

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basically nonexistent.¹²⁻¹⁴ And the dynamic pair correlation is in general much smaller than the static pair correlation.^{11,15} On the basis of neglecting both the static and dynamic pair correlation among segments belonging to different chains and assuming that the size of the polymer coil is much smaller than the scattering wavelength and that the collective reorientation time is much shorter than the time needed for the center-of-mass of the polymer chain to travel the distance of a scattering wavelength, $C(t)$ for a polymer melt can be expressed as⁶

$$C(t) = [Sf_s(t) + R] \langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle, \quad (2)$$

where P_2 is the second-order Legendre polynomial and $\mathbf{u}(t)$ the unit vector representing the direction of the symmetry axis of a correlate region (the whole region is regarded as a Kuhn segment or equivalently a Rouse segment) along the polymer chain at time t , and $f_s(t)$ is a normalized time-correlation function that reflects the motions associated with the local chemical bonds, which is grossly referred to as the sub-Rouse-segmental motions and the relaxation strength S depends on the details of the bond angles and steric interactions among the chemical bonds. R is a constant that is related to how anisotropic the Kuhn segment is. The relaxation time of $f_s(t)$ denoted as τ_s is much shorter than the reorientation time τ_r associated with a Rouse (or Kuhn) segment, which is defined as the characteristic time of $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$. If each Rouse segment is treated as an elastic dumbbell and undergoes a freely rotational diffusion motion, it can be shown that^{5,6,11}

$$\tau_r = \zeta' \langle b^2 \rangle / 18kT = \zeta \langle b^2 \rangle / 36kT, \quad (3)$$

where ζ' is the friction constant experienced by each bead on the elastic dumbbell, which is half the friction constant ζ for each bead on the Rouse chain ($\zeta/\zeta' = 2$, because the mass of an elastic dumbbell is equivalent to that of a Rouse segment; and the mass of the bead of the former is half that of the latter) and $\langle b^2 \rangle$ the mean-square length of a Rouse segment. The relaxation of $f_s(t)$ is often so fast that it is outside the time window of the photon-correlation spectroscopy or only its tail can be observed. In general, mainly $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ is observed in the photon-correlation measurement. For the present studied concentrated solutions of polystyrene in cyclohexane (the depolarized scattering from the solvent being very weak and relaxing very fast can be neglected), both the $f_s(t)$ and $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ processes are observed, with the former being observed only in its tail region.

B. Viscoelasticity

The viscoelastic behavior of a polymer solution can be affected by three effects: *Excluded volume*,^{3,16,17} *hydrodynamic interaction*,^{3,5,18} and *chain entanglement*.^{3,19} One can choose to study a dilute solution at the theta temperature or a sufficiently concentrated solution to eliminate the excluded volume effect. At a sufficiently high concentration, the hydrodynamic interactions among segments belonging to the same chain will be screened by the presence of the neighboring chains as well.¹⁻³ At a high concentration, however, entanglements may occur when the polymer chains are sufficiently long.

Consider a blend solution consisting of two nearly monodisperse polymer components of the same microstructure but with different molecular weights: Component one with weight fraction W_1 has the weight average molecular weight M_{w1} being just below the entanglement molecular weight M_e (determined from the plateau modulus of a high molecular weight sample, G_N ; $M_e = 4\rho RT/5G_N$), and component two with weight fraction W_2 has the molecular weight M_{w2} being much larger than M_e . In such a system, entanglements can occur only among chains of component two, if W_2 is high enough. As far as reduction of entanglement by dilution is concerned, component one serves as a solvent. It has been shown that the entanglement molecular weight denoted as M_e' of such a blend solution obeys the following equation:¹⁹⁻²¹

$$M_e' = M_e W_2^{-1}. \quad (4)$$

For a concentrated solution of polymer in a simple solvent of small molecules, Eq. (4) will be basically followed, if W_2 is regarded as the volume fraction of the polymer in the solution. Thus, Eq. (4) can be used as a guideline in preparing a concentrated polymer solution, which is free of entanglement.

The viscoelastic behavior of a polymer system free of the effects of excluded volume, hydrodynamic interaction, and entanglement is described by the Rouse theory.^{4,5} The stress relaxation modulus of the Rouse theory is given by

$$G(t) = (cRT/M) \sum_{p=1}^{N-1} \exp(-t/\tau_p), \quad (5)$$

with

$$\tau_p = K \pi^2 M^2 / [24 \sin^2(\pi p/2N) N^2],$$

for $p = 1, 2, 3, \dots, N-1$, (6)

where c is the concentration of the polymer solution in unit of g/cm^3 ; N the number of Rouse beads per polymer chain of molecular weight M ; K the frictional factor ($K = \zeta \langle b^2 \rangle / kT \pi^2 m^2$). And the zero shear viscosity of the Rouse theory is given by

$$\eta_0 = (cRT \pi^2 / 36) KM. \quad (7)$$

Thus, the frictional factor K of a polymer solution can be calculated from its viscosity value, if the concentration c and molecular weight M (treated as equal to the weight average molecular weight M_w here) are known. The obtained K value can in turn be used to calculate the relaxation times τ_p ($p = 1, 2, \dots, N-1$) of the various Rouse modes of motions through Eq. (6), if N is known. For $N \gg 1$, the relaxation time of the highest Rouse mode can be approximated by

$$\tau_v (\approx \tau_{19} \text{ in the case of } N=20 \text{ for example}) = \zeta \langle b^2 \rangle / 24kT. \quad (8)$$

The comparison of Eqs. (3) and (8) gives

$$\tau_v / \tau_r = 1.5. \quad (9)$$

It is hard to imagine that the reorientation motion of a Rouse segment in a long polymer chain can be adequately described by a freely rotational diffusion model of an elastic dumbbell

as assumed in obtaining Eq. (3). In addition, the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ relaxation observed by depolarized photon-correlation is in general not a single exponential decay, but rather often has a broad relaxation time distribution. Thus, Eq. (9) is mainly used to indicate that τ_v and τ_r have the same order of magnitude.

III. EXPERIMENT

Two nearly monodisperse polystyrene polymers: *F1* with $M_w = 9100$, $M_w/M_n = 1.02$; and *F2* with $M_w = 18100$, $M_w/M_n = 1.01$ are used to prepare solutions using cyclohexane as solvent. The trace amount of water in the solvent was removed by soaking with calcium hydride; and the solutions were prepared in a cylindrical sample cell [precision NMR (nuclear magnetic resonance) tube of 10 mm OD] in a dry box. The prepared *F1* solution (denoted as *S-F1*) and *F2* solution (denoted as *S-F2*) have a concentration of 59.832% and 60.287% by weight or of 0.552 and 0.556 g/cm³, respectively. According to the guideline given by Eq. (4), these two solutions are expected to be free of entanglement ($M_e = 13\,500$ for polystyrene^{19,21,22}). The sample cells were sealed with a flame under low vacuum. The dust-free samples for the light scattering measurements were then prepared by using the centrifugal method. The sample was first warmed to about 60 °C in the oven and insulated before it was put into the centrifugal rotor and then centrifuged at about 10 000 g for 15 h. Because the samples were quite viscous, it was necessary to repeat the process about ten times. The details of the depolarized photon-correlation measurements are the same as described before.⁶

The viscosity measurement of a concentrated polymer solution is often a problem, because of the solvent evaporation. Thus, we employ the falling ball method with both the solution sample and the ball sealed in a glass tube. In this study a small steel ball with diameter of 0.8 mm and a glass tube with inner diameter of $d = 10$ mm are used. The solutions in the glass tube were prepared in the same way as described above for *S-F1* and *S-F2* samples except for the centrifugal step. In the measurement, the whole sample tube was immersed in a thermostat with a glass window. A magnet was used to move the steel ball to the top of the tube for each run of measurement. Then the viscosity η_0 of the solution can be calculated from the time t for the ball to travel the distance, l ($= 5$ cm in the present study), between two mark lines on the glass tube according to the following equation:²³

$$\eta_0 = s[2r^2(\rho_s - \rho)gt/9l], \quad (10)$$

where ρ_s and ρ are the density of the steel ball and the solution, respectively; r the radius of the ball and g the gravitational acceleration and s the correction factor for the wall effect of the finite diameter size of the tube. The ratio of the ball diameter and the tube diameter ($2r/d = 0.08$) was chosen to be practical for the setup on the one side and on the other side small enough to require only a small correction. The correction factor s is 0.83 for the diameter ratio of 0.08.²⁴ The Deborah number De ($= 1\tau_1/tr$, τ_1 is calculated from the obtained viscosity value) is very small ($\ll 1$) for all the studied samples, which guarantees that the viscosity has

been measured in the Newtonian region. The density of each solution was determined by measuring the sample weight and the volume it occupies in the sample tube. Before the sample was prepared, the volumes of the sample tube (with the steel ball in it) at different fluid level heights and temperatures were determined by weighing the proper amounts of water in the tube. The relative error of the density determined this way arising from the uncertainty of the level height reading due to the meniscus on the liquid surface should be small, especially for our purpose, because the amount of solution contained in the glass tube is quite large (≈ 10 cm long). The viscosities of the prepared solutions were measured from 15 °C to 40 °C at the interval of 5 degrees. The time required for the ball to drop 5 cm in the solutions ranges about from 40 to 4000 s depending on the concentration, molecular weight and temperature. The viscosity values, which are used to calculate the relaxation times in this study, are obtained from averaging six such readings of time, with a standard deviation of 0.5%.

We need the viscosity data for correlating with the depolarized photon-correlation results of *S-F1* and *S-F2* samples. However, it is extremely difficult to prepare the *F1*/cyclohexane and *F2*/cyclohexane solutions for the viscosity measurements at exactly the same concentrations as those of *S-F1* and *S-F2*. However, it is much easier to prepare a solution with an accurately known concentration aimed at the close neighborhood of the concentrations of *S-F1* or *S-F2*. From the viscosity values of two solutions for each system (*F1* or *F2*) prepared this way, we can calculate the viscosity at the concentration of *S-F1* or *S-F2*; or at a certain chosen concentration common to both systems by interpolation or extrapolation. For the viscosity measurements, two solutions at concentrations: 59.618 wt % and 60.742 wt %; for the *F1*/cyclohexane system; and 58.913 wt % and 60.228 wt % for the *F2*/cyclohexane system have been prepared.

IV. VISCOSITY RESULTS

60 wt % is between the two concentrations of both sets of samples, whose viscosities have been measured. Thus, we choose to compare the viscosity values of *F1*/cyclohexane and *F2*/cyclohexane solution systems both at the concentration of 60 wt % obtained by interpolation from the measured values. As shown in Fig. 1 are the temperature dependence of the viscosity of the *F1*/cyclohexane and *F2*/cyclohexane solution systems at 60 wt % ($\log \eta_0$ vs $1/T$). At such a high concentration, it is expected that the hydrodynamic interactions have been well screened and that the viscoelastic behavior of either of the two solutions be described by the Rouse theory. Over the temperature range from 15° to 40 °C including the theta temperature (35 °C), the ratio of the viscosities of the two systems is between 2.3 and 2.4, which is about 15%–20% higher than the value 2 expected from the Rouse theory [Eq. (7)]. The slightly larger viscosity ratio than expected from the theory may be due to a small difference of the friction factor in the two systems caused by the fact that there are more chain ends in the *F1*/cyclohexane system than in the *F2*/cyclohexane system. The effect of different chain end concentrations on the viscosity ratio

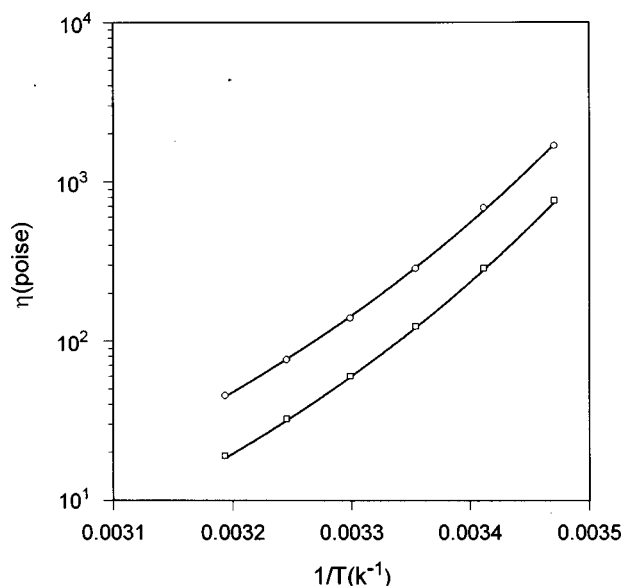


FIG. 1. The temperature dependence of the viscosity data at 60 wt % of the *F1*/cyclohexane (□) and *F2*/cyclohexane (○) systems.

should be small, because the apparent activation energies of the two systems are virtually the same: For instance at 35 °C 92 KJ/mole for the *F1*/cyclohexane system and 91 KJ/mole for the *F2*/cyclohexane system. The 15%–20% difference in the friction constant between the two systems is similarly observed for the relaxation time of the main depolarized mode as will be detailed below. Including the hydrodynamic interaction, the Rouse–Zimm theory¹⁸ gives the viscosity being proportional to $M^{0.5}$, which would give the viscosity ratio to be 1.4. Thus the viscosity results support the expectation that the hydrodynamic interaction be neglected in our studied systems, and that the polymer dynamics and viscoelasticity be described by the Rouse theory.

Based on the measured results of the prepared *F1*/cyclohexane and *F2*/cyclohexane solutions, the viscosity of *S-F1* is calculated to be 31.1 poise, and that of *S-F2* to be 80.0 poise at 35 °C. From their respective viscosity values, we calculate the relaxation times of the lowest Rouse

mode [Eqs. (5) and (6)], $\tau_1 = 1.23 \times 10^{-5}$ s for *S-F1*; and $\tau_1 = 6.2 \times 10^{-5}$ s for *S-F2*. Using the molecular weight for the Rouse segment set at $m = 900$ and 1000, which gives N close to an integer for the studied samples, yet close to the consensus value of $m = 850$ as mentioned above.^{6–10} The relaxation times of the highest Rouse mode are calculated to be, for *S-F1*: $\tau_9 = 3.11 \times 10^{-7}$ for $N = 10$; $\tau_8 = 3.86 \times 10^{-7}$ for $N = 9$; and, for *S-F2*: $\tau_{19} = 3.85 \times 10^{-7}$ for $N = 20$; $\tau_{17} = 4.76 \times 10^{-7}$ for $N = 18$. We can correct the relaxation time values of *S-F1* for the concentration difference between *S-F1* and *S-F2* and friction coefficient difference between the *F1* solution and the *F2* solution at the same concentration as explained above, so that the relaxation times of *F1* and *F2* can be compared on the same basis, (using that of *S-F2* as the comparison basis). These values of relaxation times, before and after correction, are listed in Table I along with the average reorientational time extracted from the depolarized photon-correlation function.

V. DEPOLARIZED PHOTON-CORRELATION FUNCTION

The depolarized photon-correlation function of *S-F1* and *S-F2* are very similar at two scattering angles $\theta = 45^\circ$ and 90° as shown in Figs. 2 and 3, respectively. In all these decaying curves one can easily discern three modes of motions. The two fast modes appear independent of the molecular weight and the scattering angle. This is confirmed by the detailed analysis below. The slowest mode has a q^2 dependence, a characteristic of the diffusive mode. In addition, as shown in Fig. 4, its line shape is the same as that of the isotropic scattering arising from the concentration fluctuation, whose intensity is, in general, much stronger than that arising from the density fluctuation. Thus, we suspected that it was due to the leakage from the isotropic scattering. We purposely rotate the polarization of the analyzer from the best orientation (parallel to the optical table) by a small angle to enhance the leakage to see how the correlation function will be affected. As shown in Fig. 5, the slowest mode is enhanced without changing its relaxation characteristics. This confirms our suspicion.

TABLE I. The comparison of the average relaxation time $\langle \tau \rangle_2$ of the $\langle P_2[u(t) \cdot u(0)] \rangle$ mode for *S-F1* and *S-F2* and the relaxation times of the first Rouse mode τ_1 and the highest Rouse modes: τ_8 (or τ_9 ; for *S-F1*); and τ_{17} (or τ_{19} ; for *S-F2*). Also shown are the relaxation times of *S-F1* after correcting for the small differences in concentration and friction constant to those corresponding to *S-F2*.

	$\langle \tau \rangle_2$ (MSVD) $\times 10^7$ s	τ_1 $\times 10^5$ s	τ_8 $\times 10^7$ s	τ_9 $\times 10^7$ s	τ_1 $\times 10^5$ s	τ_{17} $\times 10^7$ s	τ_{19} $\times 10^7$ s
<i>F1-45°</i>	11.7						
<i>F1-90°</i>	12.3	1.23	3.86	3.11			
<i>F2-45°</i>	15.7				6.20	4.76	3.85
<i>F2-90°</i>	14.5						
<i>F1-45°</i>	15.2						
Corrected ^a		1.60	5.02	4.04			
<i>F1-90°</i>	16.1						

^aCorrected for concentration difference [$\eta(60.2865\%)/\eta(59.8315\%) = 1.13$] and friction constant difference [$\zeta(F2)/\zeta(F1) = 1.15$ at the same concentration].

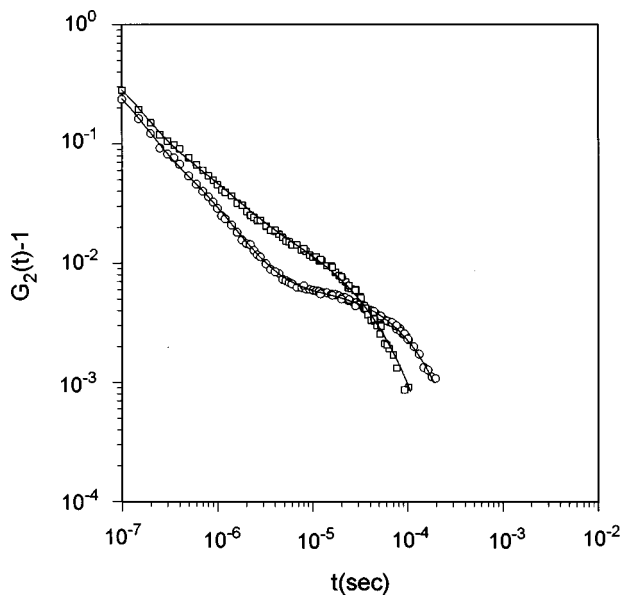


FIG. 2. The depolarized photon-correlation spectra of *S-F1* at the scattering angle $\theta=45^\circ$ (\circ) and 90° (\square). The solid lines are the calculated spectra based on the results of the MSVD fittings.

While being unable to obtain a Glan–Thompson prism with the extinction ratio better than our analyzer (10^{-6}), we resort to separating the leakage mode from the rest of the relaxation curve by applying the MSVD analysis²⁵ to the measured photon-correlation function $g_2(t) - 1 = \phi(t)^2$. In this approach, $\phi(t)$ is approximated as

$$\phi(t) = \sum_i p_i \exp(-t/\tau_i) \Delta \ln \tau, \quad (11)$$

where the relaxation times τ_i are equally spaced in the logarithmical scale (i.e., $\ln \tau_{i+1} - \ln \tau_i = \Delta \ln \tau = a$ constant, note that ϕ^2 as defined here contains the coherence factor; and

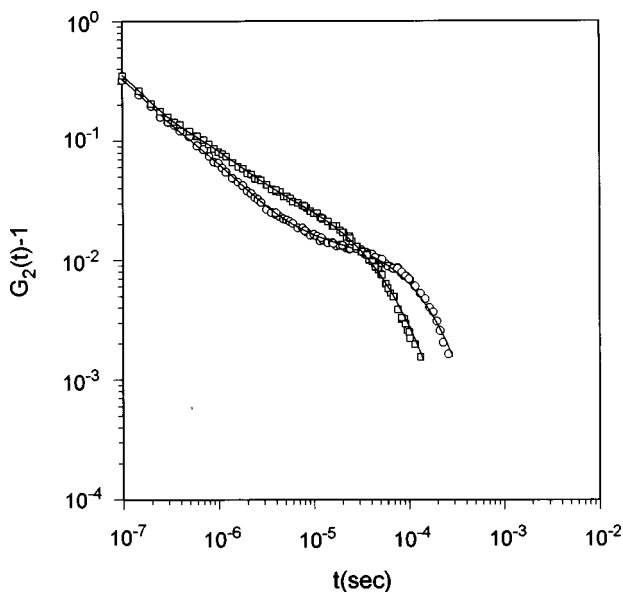


FIG. 3. The depolarized photon-correlation spectra of *S-F2* at the scattering angle $\theta=45^\circ$ (\circ) and 90° (\square). The solid lines are the calculated spectra based on the results of the MSVD fittings.

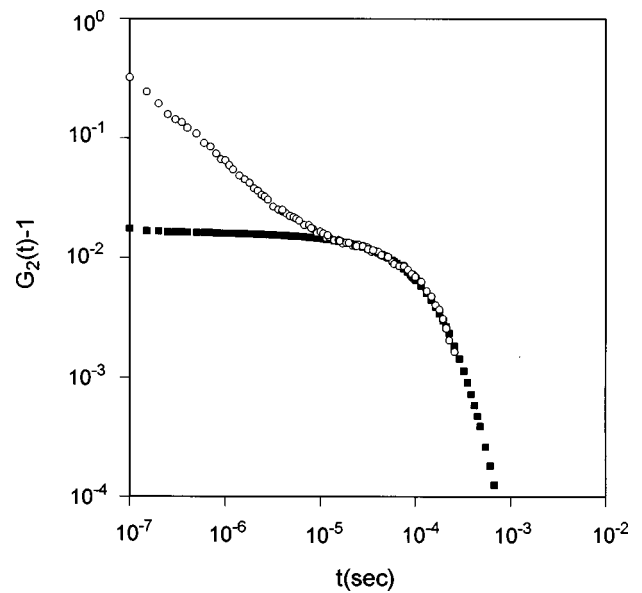


FIG. 4. The superposition of the depolarized (\circ) and polarized (\square) photon-correlation spectra of *S-F2* at $\theta=45^\circ$ in the terminal region.

that the distribution $\{p_i\}$ is not normalized). As shown in Fig. 6, the relaxation time distribution obtained from the analysis indicates that the leakage mode and the true depolarized modes are well separated. The contribution of the leakage mode to the total measured correlation function can be calculated from the distribution containing the third mode only. Then the depolarized photon-correlation function can be recovered by subtracting the leakage contribution from the measured total correlation function. The depolarized photon-correlation functions recovered from those shown in Fig. 5 are well superposed on each other as shown in Fig. 7. This shows that the different degrees of leakage from the

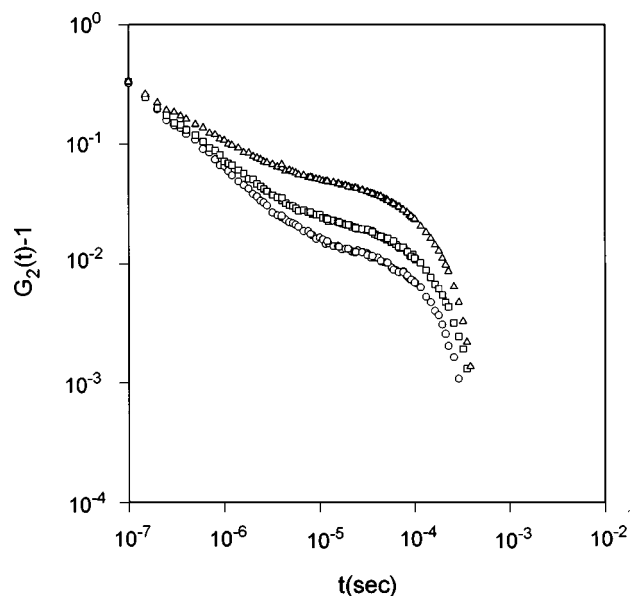


FIG. 5. The comparison of the depolarized photon-correlation spectra of *S-F2* at the scattering angle $\theta=45^\circ$ obtained with the polarization of the analyzer set at $\phi=90^\circ$ (i.e., perpendicular to that of the polarizer) (\circ); 93° (\square); and 96° (\triangle).

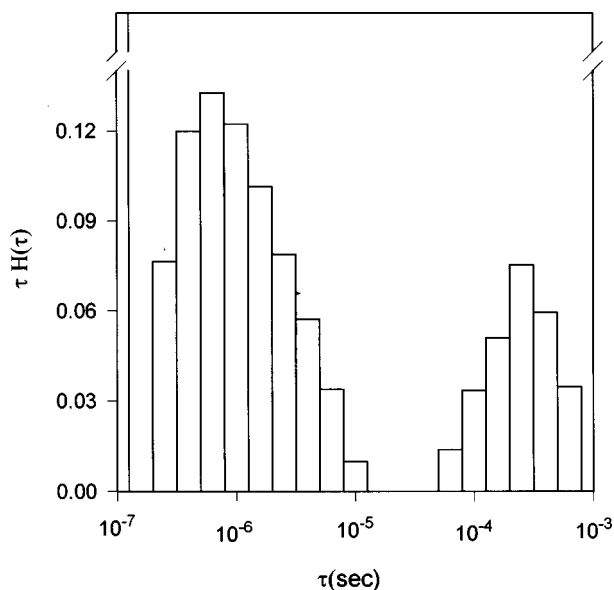


FIG. 6. Distribution $\tau H(\tau)$ of the relaxation times obtained from the MSVD analysis on the measured depolarized photon-correlation spectrum of $S-F2$ at $\theta=45^\circ$. The single peak of the first mode is excluded from the normalization of the distribution.

isotropic scattering basically have no effect on the recovered depolarized correlation function, as long as the leakage does not overshadow the depolarized mode.

We have applied the same MSVD analyses to the other measured correlation functions of $S-F1$ and $S-F2$. The calculated photon-correlation functions based on the results of the MSVD fittings are shown as the solid lines for comparison with the measured values in Figs. 2 and 3. As shown in Figs. 8 and 9 for $S-F1$ and $S-F2$, the recovered depolarized correlation functions at 45° and 90° following the procedure described above are well superposable on each other. Unlike the cases of $\theta=45^\circ$, where there is clear separation between

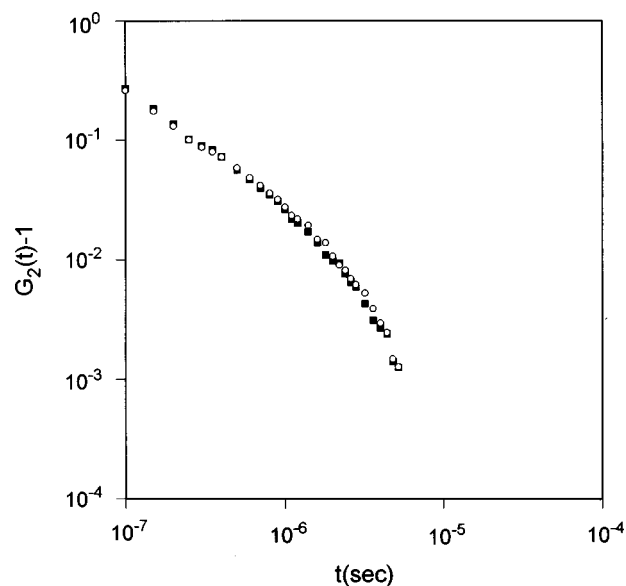


FIG. 8. The depolarized spectra of $S-F1$ at $\theta=45^\circ$ (■) and 90° (○) obtained by removing the q^2 -dependent “leakage” mode from the measured spectra.

the second and the third modes of relaxation time distribution (Fig. 6), the second and the third modes of relaxation time distribution for the cases of $\theta=90^\circ$ contact each other. For example, the relaxation time distribution of $S-F2$ at $\theta=90^\circ$ is shown in Fig. 10. In this case, the separation of the second and the third modes is made at the minimum point between the two modes in the process described above for recovering the depolarized correlation functions shown in Figs. 8 and 9. A small arbitrariness may have been exercised in this separation process; results shown in Figs. 8 and 9 indicate that the depolarized photon-correlation functions from the studied concentrated solutions are independent of the scattering angle in agreement with the theoretical analy-

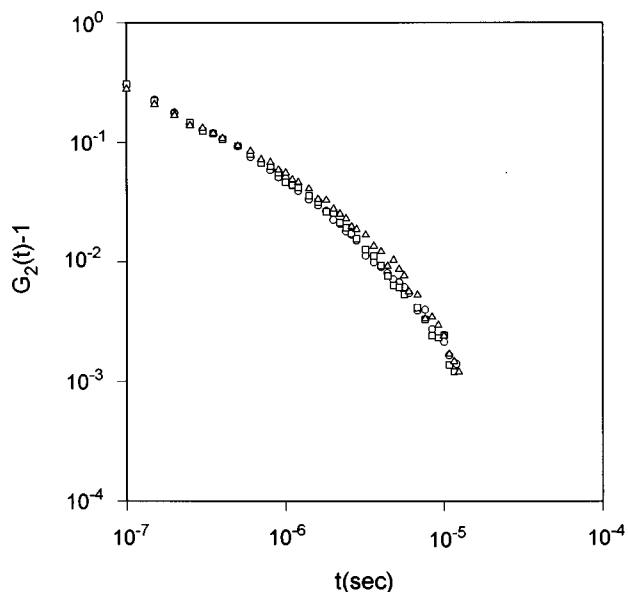


FIG. 7. The depolarized spectra obtained by removing the slowest q^2 -dependent “leakage” mode from those shown in Fig. 5 by using the MSVD analyses.

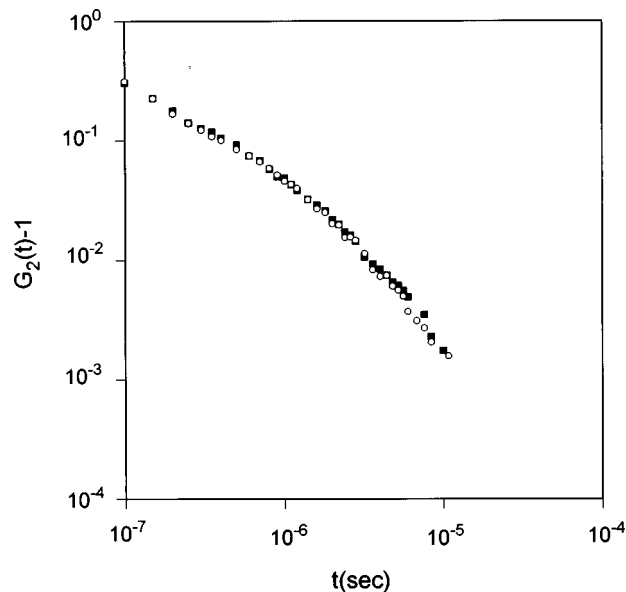


FIG. 9. The depolarized spectra of $S-F2$ at $\theta=45^\circ$ (■) and 90° (○) obtained by removing the q^2 -dependent “leakage” mode from the measured spectra.

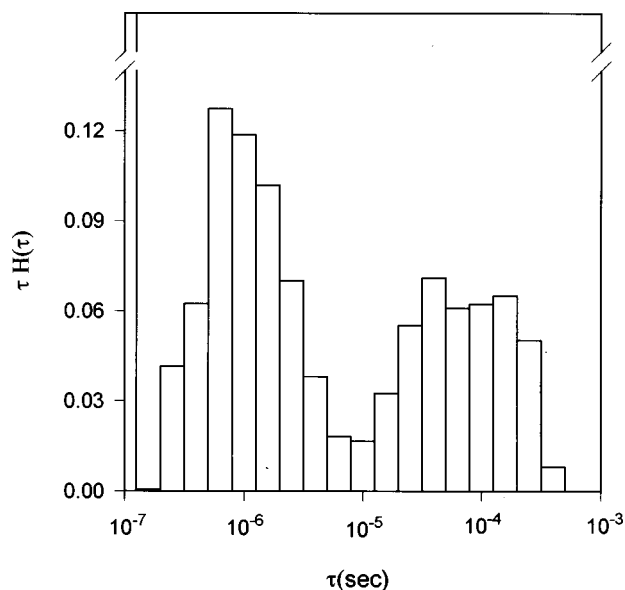


FIG. 10. Distribution $\tau H(\tau)$ of the relaxation times obtained from the MSVD analysis on the measured depolarized photon-correlation spectrum of *S-F2* at $\theta=90^\circ$. The single peak of the first mode is excluded from the normalization of the distribution.

sis. Clearly there exists a very fast mode, whose tail region only is observed in the depolarized correlation functions shown in Figs. 8 and 9. The existence of the very fast mode is confirmed by the much lower apparent coherence factors (about 0.3 in average; i.e., the average of the results of the studied two solutions *S-F1* and *S-F2* at two scattering angles 45° and 90°) of the depolarized measurements compared to those (about 0.5 in average) of the polarized photon correlations of the studied samples, which only exhibit a slow diffusive mode. (Note: The first point of our correlator is at 50 nanosecond, which, generally known containing artifacts, has been eliminated in all the analyses, including the determination of the coherence factor; and all the first points in the correlation functions shown in this paper are actually the second points of the correlator). Because only the tail region of the very fast mode is observed in the time window of the photon-correlation measurement, the full profile of the relaxation time distribution of the fast (first) mode cannot be obtained. Only a single peak for the very fast mode at $\tau = 10^{-7}$ is obtained and shown in the relaxation time distributions of Figs. 11 and 12. As shown in these figures, the relaxation time distributions for the second mode are well resolved from the first mode. The first mode should be associated with the motions of the local chemical segments, $f_s(t)$, while the second mode with $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ of Eq. (2). Although the existence of $f_s(t)$ process has long been expected based on the theoretical analysis, its present observation as a distinct mode well separated from the second mode $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ is the first that we know of. Because very limited information can be extracted from the tail region of the dynamic process, we do not expect to learn much from it now.

From the viscosity values corresponding to the *S-F1* and *S-F2* samples, we have calculated their relaxation times of the highest Rouse mode: τ_8 (for *S-F1*) and τ_{17} (for

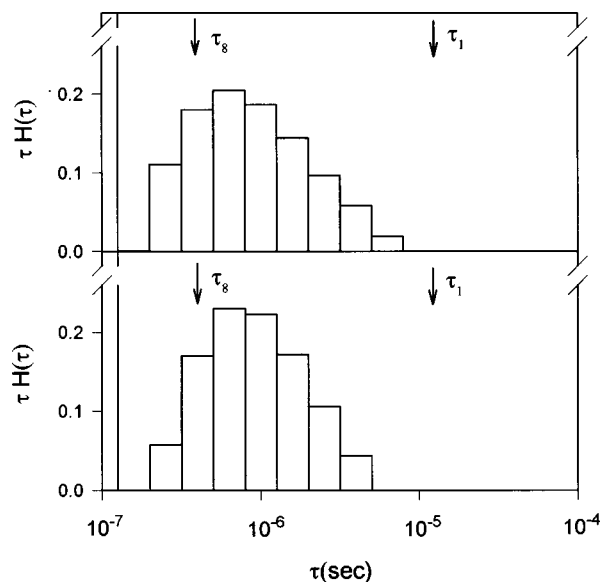


FIG. 11. The relaxation time distributions $\tau H(\tau)$ corresponding to the correlation spectra of *S-F1* shown in Fig. 8 for $\theta=45^\circ$ (lower) and 90° (upper). The arrows indicate the relaxation time of the highest Rouse mode τ_8 (left) and that of the lowest Rouse mode τ_1 (right). The single peak of the first mode is excluded from the normalization of the distribution.

S-F2) and the lowest Rouse mode: τ_1 . They are indicated by an arrow in Figs. 11 and 12. The locations of the highest Rouse modes, being close to main peak region of the relaxation time distribution of the second modes, is in agreement with the theoretical analysis [Eq. (9)]. The relaxation times of the lowest Rouse modes, being outside and behind the relaxation time distribution of the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ mode, is in agreement with the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ mode being independent of molecular weight, except for a small effect due to the

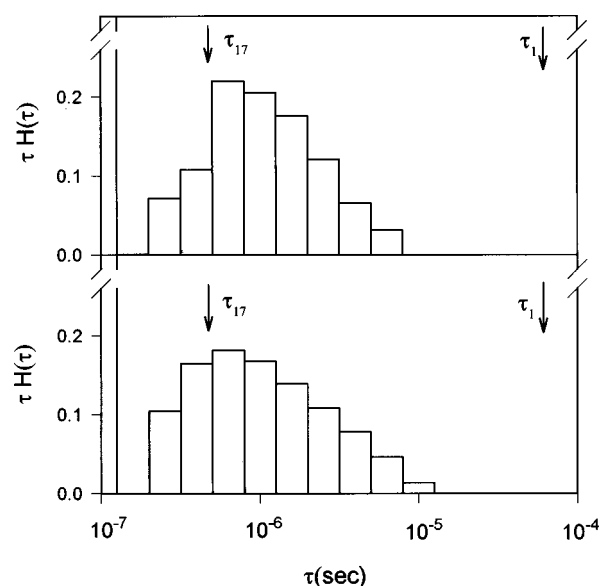


FIG. 12. The relaxation time distribution $\tau H(\tau)$ corresponding to the correlation spectra of *S-F2* shown in Fig. 9 for $\theta=45^\circ$ (lower) and 90° (upper). The arrows indicate the relaxation time of the highest Rouse mode τ_{17} (left) and that of the lowest Rouse mode τ_1 (right). The single peak of the first mode is excluded from the normalization of the distribution.

weak molecular dependence of the friction factor as further discussed below. This result clearly indicates that the depolarized light scattering does not probe the reorientational motion of the whole polymer chain molecule.

Using our viscosity data, we can correct one of the two $\langle \tau \rangle_2$ values (the average relaxation time of the second depolarized scattering mode or the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ mode) for the slight concentration difference between the two samples. As explained above, at the same concentration (in the narrow concentration range under the present study of viscosity), the friction constant in the *F2* solution system is about 15%–20% higher than that in the *F1* solution system. After the correction for these two factors, the average relaxation times $\langle \tau \rangle_2$ of *S-F1* and *S-F2* become nearly identical as shown in Table I. Equivalent to the comparison of τ_8 and τ_{17} with the relaxation time distributions of the second mode of *S-F1* and *S-F2* samples shown in Figs. 11 and 12, their values are shown together with the $\langle \tau \rangle_2$ values in Table I. From the comparison of the τ_8 and τ_{17} values with the τ_9 and τ_{19} values shown in Table I, the difference between assuming $m=900$ or 1000 is quite small.

VI. DISCUSSION AND CONCLUSION

It is shown that the main relaxation mode observed in the depolarized Rayleigh scattering of a concentrated polystyrene solution is independent of the scattering angle and the molecular weight; and can be assigned to the dynamic mode $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ given in the theoretical analysis. In agreement with the theoretical analysis the relaxation time of the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ mode is of the same order of magnitude as that of the highest Rouse mode calculated from the viscosity data in terms of the Rouse theory.

The comparison of the average relaxation time obtained by the depolarized photon-correlation spectroscopy with the relaxation time of a single Rouse segment calculated from the viscoelastic data had been made for two kinds of polystyrene melt systems recently:⁶

(a) A polystyrene melt studied has a molecular weight of 850, which is about the estimated value for a single Rouse segment. In this melt case, the $\langle \tau \rangle$ value (from the depolarized photon-correlation measurement) has the same temperature dependence as that of the zero shear viscosity measured on the same sample. The τ_v value calculated from the zero-shear viscosity value in terms of the elastic dumbbell model is of the same order of magnitude as that of $\langle \tau \rangle$ but larger by a factor of about 2.5–3. The τ_v value being greater was attributed to the contribution of the internal viscosity to the measured zero-shear viscosity. In addition, the polymer, which can be modeled as a separate elastic dumbbell, is different from a Rouse segment belonging to a long chain, whose connection of the segments can slow down the reorientational motion of the Rouse segment and increases the $\langle \tau \rangle$ value.

(b) It was shown that the temperature dependence of the average relaxation time obtained from the photon-correlation measurement for a high molecular sample prepared by thermal polymerization²⁶ is identical to that of the zero shear viscosity in the high molecular weight region.²⁷ The relaxation time of the highest Rouse mode of a high molecular

weight polystyrene melt can be calculated to be 4.6×10^{-3} s (using $m=850$) at 127.5 °C from the viscoelastic data in the transition region.^{6,19} This value is in good agreement with the average relaxation time $\langle \tau \rangle = 3.5 \times 10^{-3}$ s obtained by the depolarized photon-correlation spectroscopy.

In the present study of concentrated polystyrene solutions, the molecular weight for a Rouse segment is taken to be slightly larger than that used in the melt case (900–1000 vs 850). This may be justified by the solvent effect to enlarge the Rouse segment size somewhat. The obtained τ_8 and τ_{17} (or τ_9 and τ_{19}) values are smaller than the $\langle \tau \rangle_2$ by a factor of 3. In case (b) discussed above, such a factor was not observed. The difference can be due to resolution of the sub-Rouse-segmental motion [the $f_s(t)$ process in Eq. (2)] from the main depolarized mode (the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ process) in the present case. The two processes could not be resolved in both the (a) and (b) cases discussed above. If the obtained relaxation time distributions in (a) and (b) contain the contribution from the $f_s(t)$ process, the obtained average relaxation time $\langle \tau \rangle$ should become smaller than that containing only the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ process. It is worthwhile to mention that the relaxation time distribution of the $\langle P_2[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle$ motion in the present study (about one and half decades) is much narrower than those observed for the melt systems (> five decades). This should be related to whether the first and the second modes can be resolved or not. The more close interactions among segments in the melt system may contribute to the broader relaxation time distribution and the inseparability of the two processes.

In spite of some differences as explained and discussed above between the melt systems and the concentrated solution systems, the main conclusion of the present and the previous studies is that the main relaxation time observed from the depolarized photon-correlation spectroscopy and that of the highest Rouse mode calculated from the viscoelastic or viscosity data are of the same order of magnitude. In other words, both characterize the motion of a domain of basically the same size-scale in the polymer chain, which may be referred to as the Rouse segment.

The sub-Rouse-segmental motion $f_s(t)$ has been expected from the theoretical analysis of the dynamic depolarized light scattering from a concentrated polymeric fluid. The direct observation of the motion as a separate process in its tail region in the present study of the concentrated polystyrene solution is the first that we know of. This supports the separation of two time domains in the theoretical analysis leading to Eq. (2).

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