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Dynamics of a “Rouse” Segment As Probed by Depolarized Photon-Correlation and Viscoelasticity Measurements

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ABSTRACT: A polystyrene melt, whose molecular weight (weight-average molecular weight = 1050) is about that estimated for a Rouse segment, has been studied with depolarized photon-correlation and viscosity measurements. Theoretically the dynamic depolarized light scattering is shown to be affected by the reorientational motion of the whole polymer molecule in the long-time region and the local segmental motions in the short-time region. The elastic dumbbell model is used to describe the viscoelasticity and reorientational motion of the polymer molecule. Relaxation times $\langle\tau\rangle$ and τ_v are extracted from the depolarized light scattering and viscosity measurement results, respectively. The ratio $\tau_v/\langle\tau\rangle$, being independent of temperature as expected, is of the order of magnitude predicted from the theoretical analysis. We come to a similar conclusion supporting the above results by analyzing the depolarized photon-correlation results and the viscoelastic relaxation data in the glass−rubber transition zone of entangled polystyrene melts, which are available in literature.

1. Introduction

Slow motions in a long polymer chain, involving the whole molecule or a long section of the chain, are well described by theories developed upon using the Rouse segment as the basic structural unit.[1,2] Although by using the Rouse segment the local details of chemical structure can be ignored, the Rouse segment, with respect to its mass and length, should be different for different kinds of polymers. If the polymer chain is very long, and we are interested in only the few slowest modes of chain motions, the length of chain section assigned to a Rouse segment is not a critical issue as long as the chosen segment is much smaller than the whole chain and at the same time sufficiently long. The universal chain dynamic behavior expressed in terms of the Rouse segment is well supported by experimental results of different flexible polymers.[1,2] However, how short it can be and how it behaves dynamically, while being a fundamentally interesting problem, has rarely been studied. As shown in the Appendix, based on the information obtained from the study of the crazing phenomenon of glassy polymers[3] and the entanglement molecular weight calculated from the plateau modulus,[4,5] it can be estimated that the molecular weight of a Rouse segment for polystyrene is about 850. Here, we study a polystyrene sample, whose molecular weight is close to this value, with depolarized photon-correlation and viscosity measurements. Theoretically, the dynamics of such a system can be described in terms of the elastic dumbbell model.[6] We propose a theoretical analysis for relating the depolarized photon correlation and viscosity of a polymer whose molecule is of the Rouse segment size. The experimental results of the two very different kinds of measurements obtained for the presently studied sample are shown to support the theoretical analysis.

The depolarized Rayleigh scattering of high molecular weight polystyrene melts had been studied by Patterson et al.[7] and more recently by Brown and Nicolai[8] using photon-correlation spectroscopy. Their results are in agreement with each other, and the shapes of their photon-correlation relaxation curves are basically the same as that obtained for the presently studied sample. It has been shown that their depolarized photon-correlation relaxation reflects the reorientational motion of a Kuhn (or Rouse) segment belonging to a long chain.[9] The polystyrene samples they used were prepared in the scattering cell by thermal polymerization of dust-free monomer. Although the molecular weight and molecular weight distribution of their samples were not clearly indicated in their reports, it is clear that the samples were in a sufficiently high molecular weight region, where the glass−rubber transition temperature, T_g, as well as the dynamic rate measured by the depolarized light scattering is independent of molecular weight. However, the nature (broad molecular weight distribution and molecular weight being greater than the entanglement molecular weight) of their samples would prevent their viscoelastic properties from being studied directly in terms of a valid molecular theory[10−13] for comparison with the depolarized photon-correlation results. An assumption can be made that the depolarized light scattering results of Patterson and Brown should not be different from what can be observed from a nearly monodisperse polystyrene melt of sufficiently high molecular weight, whose viscoelastic data in the glass−rubber transition zone are available in the literature.[12] The glass−rubber transition zone, being close to the motion associated with a single Rouse segment in time scale, can be analyzed for comparison with the depolarized photon-correlation results. The conclusion reached from the comparison supports that obtained from the analysis of the experimental results of the presently studied sample, whose molecular weight is about that estimated for a Rouse segment.

2. Theoretical Considerations

a. Depolarized Rayleigh Scattering. The depolarized Rayleigh scattering spectrum $I_{\mathrm{VH}}(\omega)$ is given by the Fourier transform of the time-correlation function $C(t)$:[14]

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

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

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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 of either small molecules or polymer molecules. From the study of small symmetric top molecules,[14,15] it has been shown that depolarized Rayleigh scattering probes the collective reorientation motion rather than that associated with a single molecule, which can be determined by NMR T_1 relaxation[16] or Raman line shape measurements.[17] The collectivity can be expressed in terms of static and dynamic pair correlation between the polarizabilities associated with neighboring molecules. The static pair correlation can be measured from the total intensity measurement. In the case of chloroform,[15] the relaxation time is shown slowed down significantly by the static correlation effect, while the dynamic correlation effect is negligible. In the polymer system, the static pair correlation as determined from the depolarized intensity measurement is often expressed in terms of effective optical anisotropy δ^2 per monomer unit to account for the concentration dependence of the measured total intensity.[18] In the case of polystyrene, it has been shown that the δ^2 values of the melt[18] and the dilute solution[19] are virtually the same and are in close agreement with that calculated by Flory et al.[20] based on the rotational isomeric state model, which only considers the interactions within one single chain. This result indicates that in the polystyrene melt the segments belonging to different chains do not interact in such a way as to contribute to the static pair correlation. This may probably be generalized to polymers which do not have strong dipolar interactions among segments or a symmetry along the chain which allows the chain to crystallize at low temperatures (such as polyethylene, which shows a concentration dependence of the δ^2 value).[21,22] In general the dynamic pair correlation is much smaller than the static pair correlation.[14,15] Thus, on the basis of the above results, it should be safe to neglect the dynamic pair correlation between segments belonging to different chains.

The segmental reorientation rate affects the spectrum through the dependence of α_{yz} on reorientation angles. The segmental position $\mathbf{r}_i$ with respect to the laboratory frame can be written in terms of the position of center of mass, $\mathbf{R}_\mathrm{p}$, of the polymer molecule to which the segment belongs and the vector from the center of mass to the segmental position, $\mathbf{r}_\mathrm{pm}$. A similar modification is applied to $\mathbf{r}_j$. In other words, we have

$$\mathbf{r}_i \rightarrow \mathbf{R}_\mathrm{p} + \mathbf{r}_\mathrm{pm}$$

$$\mathbf{r}_j \rightarrow \mathbf{R}_{\mathrm{p}'} + \mathbf{r}_{\mathrm{p}'\mathrm{m}'}$$

With these modifications and by neglecting the correlation (both static and dynamic) between segments not belonging to the same molecule as explained above, $C(t)$ can be written as

$$C(t) = \sum_p \sum_m \sum_{m'} \langle \alpha_{yz}{}^{p,m}(t)\, \alpha_{yz}{}^{p,m'}(0) \exp[i\mathbf{q}\cdot(\mathbf{R}_\mathrm{p}(t) - \mathbf{R}_\mathrm{p}(0))]\rangle \tag{2}$$

using the fact that the studied polymer molecule is much smaller than the scattering wavelength, i.e., $\mathbf{q}\cdot\mathbf{r}_\mathrm{pm} \ll 1$. We also assume that the translational motion of the center of mass of a polymer chain is independent of the segmental reorientation. Then eq 2 can be rewritten as

$$C(t) = \sum_p C_\mathrm{p}(t)\, T_\mathrm{p}(t) \tag{3}$$

where

$$C_\mathrm{p}(t) = \langle \sum_m \sum_{m'} \alpha_{yz}{}^{p,m}(t)\, \alpha_{yz}{}^{p,m'}(0)\rangle \tag{4}$$

$$T_\mathrm{p}(t) = \langle \exp(i\mathbf{q}\cdot(\mathbf{R}_\mathrm{p}(t) - \mathbf{R}_\mathrm{p}))\rangle \tag{5}$$

The characteristic time τ_r associated with the correlation function $C_\mathrm{p}(t)$ is much shorter than the time needed for the center of mass to travel the distance of a scattering wavelength. In other words, for $t \leq \tau_\mathrm{r}$, $\mathbf{q}\cdot(\mathbf{R}_\mathrm{p}(t) - \mathbf{R}_\mathrm{p}(0)) \ll 1$ and $T_\mathrm{p}(t)$ essentially remains equal to 1 as far as the correlation lifetime of $C_\mathrm{p}(t)$ (or $C(t)$) is concerned. To understand the nature of the depolarized Rayleigh scattering spectrum of the considered polymer melt is thus boiled down to carrying out analysis of the correlation function $C_\mathrm{p}(t)$. At this stage of development, the summation in eq 4 is over the chemical segments within a polymer molecule.

Assuming the polymer molecule as a Kuhn segment with a cylindrical shape, we express α_{yz} in terms of the coordinate system fixed to the Kuhn segment:

$$\alpha_{yz} = \sum_m \alpha_{yz}{}^m = i\beta[D_{-10}{}^{(2)}(\Omega) + D_{10}{}^{(2)}(\Omega)]/6^{0.5} \tag{6}$$

where Ω appearing in the rotation matrix $D^{(2)}$ denotes two angles, θ and ϕ, which define the orientation of the symmetric axis of the Kuhn segment polarizability tensor with respect to the laboratory coordinate system. The quantity β is the anisotropic part of the Kuhn segment polarizability and is defined as $\beta = (\alpha_\parallel - \alpha_\perp)$, where $\alpha_\parallel$ is the polarizability component parallel to the symmetry axis of the molecule of the assumed cylindrical shape, while $\alpha_\perp$ is the polarizability component perpendicular to the axis. As the reorientation motions of the molecule and the chemical segments within a molecule take place, β and the orientation angle Ω will be modulated in time. We assume that the rates of reorientation of the whole molecule and the chemical segments differ widely in time scales so that, during the reorientation of the molecule (the Kuhn segment), the chemical segments in it move as though the principal axes of the polarizability tensor of the Kuhn segment were fixed in their instantaneous orientation. In this approximation, the correlation function of eq 4 can be written as

$$C_\mathrm{p}(t) = (1/6)\langle\beta(t)\,\beta(0)\rangle\langle[D_{-10}{}^{(2)}(t) + D_{10}{}^{(2)}(t)] \times [D_{-10}{}^{*(2)}(0) + D_{10}{}^{*(2)}(0)]\rangle \tag{7}$$

The time dependence of β in eq 7 is due to the motions of chemical segments which fluctuate rapidly with respect to the principal axes of the coordinate frame fixed to the whole molecule. Assuming that the correlation function is real and that all orientations of a single molecule are equally probable at the initial time, one can average over orientation at the initial time. Using the spherical harmonic addition theorem, eq 7 can be reduced to

$$C_\mathrm{p}(t) = (1/15)\langle\beta(t)\,\beta(0)\rangle\langle P_2[\hat{u}(t)\cdot\hat{u}(0)]\rangle \tag{8}$$

where $\hat{u}(t)$ is the unit vector representing the direction of the symmetry axis of the molecule at time t.

Following a derivation, which is essentially the same as that made previously for a polymer molecule in a solution, one can obtain from eq 8[9,23,24]

$$C_p(t) = [Sf_s(t) + R]\langle P_2[\hat{u}(t)\cdot\hat{u}(0)]\rangle \quad (9)$$

where $f_s(t)$ is the normalized time-correlation function that reflects the motions associated with the local chemical bonds and the relaxation strength S depends on the details of the bond angles and steric interactions among the chemical bonds. R is a constant and is related to how anisotropic the Kuhn segment (i.e., the whole molecule here) is.

b. Elastic Dumbbell Model. Because the molecular weight of the studied sample is about that estimated for a Rouse segment, we shall model the polymer molecule as an elastic dumbbell. Based on describing the Brownian motions of the molecule in terms of the Smoluchowski equation, the model gives the stress relaxation modulus as[6]

$$G(t) = (\rho RT/M)\exp(-t/\tau_v) \quad (10)$$

where ρ is the density of the polymer melt and M the molecular weight and the relaxation time τ_v is given as

$$\tau_v = \zeta\langle b^2\rangle/(12kT) \quad (11)$$

with $\langle b^2\rangle$ being the mean squared bond length of the dumbbell and ζ being the friction constant experienced by each bead. Corresponding to eq 10, the zero shear viscosity is given as

$$\eta = \rho RT\tau_v/M \quad (12)$$

Thus from the viscosity data we can calculate the relaxation time τ_v through eq 12.

Equivalently the Brownian motions of the elastic dumbbell can be described in terms of the Langevin equation, which are given as[1]

$$\zeta d\mathbf{R}_1/dt = -(3kT/\langle b^2\rangle)(\mathbf{R}_1 - \mathbf{R}_2) + \mathbf{f}_1 \quad (13a)$$

$$\zeta d\mathbf{R}_2/dt = -(3kT/\langle b^2\rangle)(\mathbf{R}_2 - \mathbf{R}_1) + \mathbf{f}_2 \quad (13b)$$

where $\mathbf{R}_1$ and $\mathbf{R}_2$ are the position vectors of the two beads in the elastic dumbbell and $\mathbf{f}_1$ and $\mathbf{f}_2$ are the fluctuation forces acting on the two beads, respectively, and satisfy

$$\langle f_{i\alpha}\rangle = 0, \quad \langle f_{i\alpha}(t)\, f_{j\beta}(t')\rangle = 2\delta_{ij}\delta_{\alpha\beta}\zeta kT\,\delta(t-t') \quad (14)$$

From eqs 13 and 14, one can show that

$$\langle \mathbf{b}(t)\cdot\mathbf{b}(0)\rangle = \langle b^2\rangle\exp(-t/\tau_1) \quad (15)$$

or

$$\langle \hat{u}(t)\cdot\hat{u}(0)\rangle = \exp(-t/\tau_1) \quad (16)$$

with

$$\tau_1 = \zeta\langle b^2\rangle/(6kT) \quad (17)$$

where $\hat{u}$ is a unit vector along the bond axis of the dumbbell. From a different viewpoint, we can assume that the reorientational motion of the molecule be described in terms of the rotational diffusion model.[25] Then, the second-order correlation function is given as

$$\langle P_2[\hat{u}(t)\cdot\hat{u}(0)]\rangle = \exp(-t/\tau_2) \quad (18)$$

with the correlation time τ_2 being related to the correlation time of the first-order correlation function (eq 16) as

$$\tau_2 = \tau_1/3 \quad (19)$$

Using eq 17 for τ_1, eq 19 gives

$$\tau_2 = \zeta\langle b^2\rangle/(18kT) \quad (20)$$

Equation 18 describes the slow reorientation motion observed by the depolarized Rayleigh scattering (see eq 9). By comparing eqs 11 and 20, the relaxation time calculated from the viscosity value (eq 12) and that measured from the depolarized Rayleigh scattering are theoretically related as

$$\tau_v/\tau_2 = 1.5 \quad (21)$$

The elastic dumbbell model is actually an oversimplification of the contributions of the molecular motions to viscosity. The viscosity of the presently studied low molecular weight polymer should receive a significant contribution from the local segmental motions, which is often termed as a kind of internal viscosity or as a limiting high-frequency viscosity η'_∞.[2] Due to the lack of a transducer rigid enough, η'_∞ of a polymer *melt* is often not obtainable. However, we can assume that the situation in a polymer melt is similar to the relative magnitude of intrinsic viscosity values at zero and limiting high frequencies, $[\eta']_0$ and $[\eta']_\infty$, of polymer solutions. The very high frequency $[\eta']_\infty$ values of polystyrene/Aroclors solutions were measured by Moore et al. at 23.0, 40.0, and 98.94 MHz.[26] The $[\eta']_\infty$ data of Moore fell between 4 and 5 (cm^3/g); while the $[\eta']_0$ values measured by Schrag et al.[27] at very low molecular weights indicated that the $[\eta']_0$ value at the molecular weight of the presently studied sample should be about 7 (cm^3/g). On the basis of these results, we can estimate that the high-frequency viscosity contribution to the zero shear viscosity of the studied sample can be about 64%. Thus, the apparent τ_v value calculated from the measured viscosity value could be larger than that, which could be assigned to an elastic dumbbell motion by a factor of about 2.8. In other words, the τ_v/τ_2 ratio given by eq 21 should be considered as the lower limit, when the τ_v value calculated directly from the viscosity value using eq 12 is compared to τ_2 obtained from the depolarized photon-correlation spectroscopy. The apparent τ_v/τ_2 ratio could be as large as 4.2.

3. Experimental Section

The studied polystyrene sample is a TSK standard.[28] It has a general structure of $CH_3(CH_2)_3(CH_2CHC_6H_5)_nH$, a weight average molecular weight of 1051, and molecular weight distribution of $M_w/M_n = 1.13$. It is estimated in the Appendix that the molecular weight associated with a Rouse (or Kuhn) segment is close to the molecular weight of the studied sample. The glass−rubber transition temperature (T_g) was measured with DSC to be 11.4 °C. The dust-free sample for the light scattering measurements was prepared by using the centrifugal method at elevated temperatures (>100 °C). The sample was first heated in an oven and insulted before it was put into the centrifugal rotor and then centrifuged at about 16000*g* for 30 min. Because of the high viscosity of the sample, it was necessary to repeat the process many times, before the sample was observed to be free of dust.

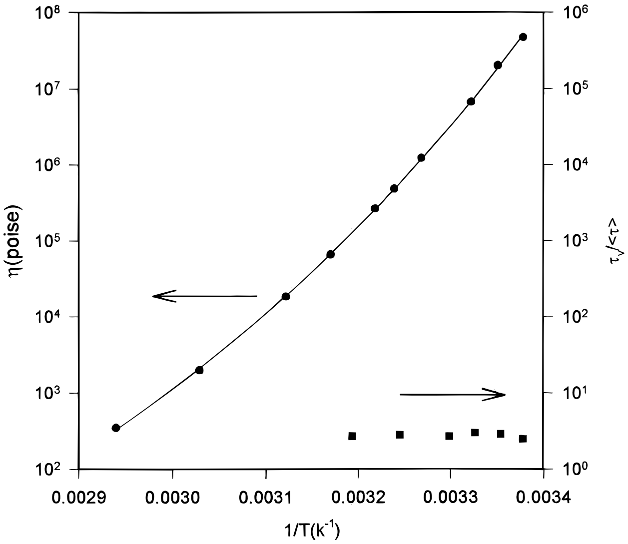

Figure 1. Upper part: Zero shear viscosity of the studied polystyrene sample (M_w = 1051) as a function of reciprocal temperature. The solid line is the best fitting of the Fulcher and Tammann-Hesse equation to the experimental data points (●). Lower part depicts the temperature independence of the ratio of the relaxation times, $\tau_v/\langle\tau\rangle$ (■, see the text).

The dynamic depolarized Rayleigh scattering is measured with the light scattering goniometer and correlator (256 channels) manufactured by Malvern Instruments Inc. The light source is provided by an argon ion laser operating at 488 nm. The depolarized scattering component is measured at the 90° scattering angle with a Glan-Thompson polarizing prism (extinction ratio of 1:10^{-6}). The polarization direction parallel to the optical table is adjusted by minimizing the scattering intensity of a polystyrene (molecular weight = 355 000)/cyclohexane solution at 35 °C.

The zero shear viscosities of the studied polymer melt were measured with a Rheometrics dynamic spectrometer (manufactured by Rheometrics, Inc.) in the low-frequency region, where the measured values were independent of frequency.

4. Analyses of the Experimental Results

a. Viscosity. As shown in Figure 1, the measured zero shear viscosity data from 22.9 to 67 °C can be correlated in terms of the Fulcher and Tammann-Hesse (FTH) equation (a modified form of the Williams–Landel–Ferry (WLF) equation)[2] given as

$$\eta = (5.03 \times 10^{-7}) \exp[2419.6/(t°\mathrm{C}+52.15)]$$

Using eq 12, the τ_v values are calculated from the viscosity values at several temperatures for comparison with the relaxation time measured from the depolarized photon-correlation spectroscopy as shown in Table 1.

b. Depolarized Photon-Correlation Spectroscopy. The depolarized photon-correlation spectra measured from 22.9 to 40 °C can be superposed on one another very well. The superposability is illustrated in Figure 2 using the spectrum at 22.9 °C as the reference. This indicates that, in the measurement window, the observed light scattering dynamic processes maintain their relative strengths and rates. This is similar to what is observed in dynamic viscoelastic behavior in a rheologically simple case. The measured photon-correlation spectra can be well analyzed in terms the so-called Williams–Watts (WW) function[29] (the stretched exponential):

$$\phi(t) = A \exp[-(t/\tau_0)^{\beta}] \qquad (22)$$

Table 1[a]

τ, °C	τ_v	τ_p	$\langle\tau\rangle$	β	τ_v/τ_p	$\tau_v/\langle\tau\rangle$
22.9	2.0	0.61	0.79	0.408	3.3	2.5
25	0.89	0.23	0.30	0.409	3.9	2.9
27.5	0.33	0.092	0.12	0.410	3.6	3.0
30	0.13	0.038	0.049	0.409	3.4	2.7
35	0.023	0.0064	0.0083	0.405	3.6	2.8
40	0.0051	0.0015	0.0019	0.400	3.4	2.7

[a] τ_v is the relaxation time calculated from the zero shear viscosity of the studied sample using eq 12 (the density of the sample was measured to be 1.0044 at 23 °C; because the potential errors from other sources could be larger than the variation of ρT with temperature in the narrow temperature range considered here, the same ρT value is used to calculate the τ_v values at the different temperatures shown in the table); the peak and average relaxation times, τ_p and $\langle\tau\rangle$, calculated from their respective values at 22.9 °C and the involved shifting factors (see the test) are virtually identical to those obtained from directly fitting the Williams–Watts function with the parameter β to the photon-correlation data.

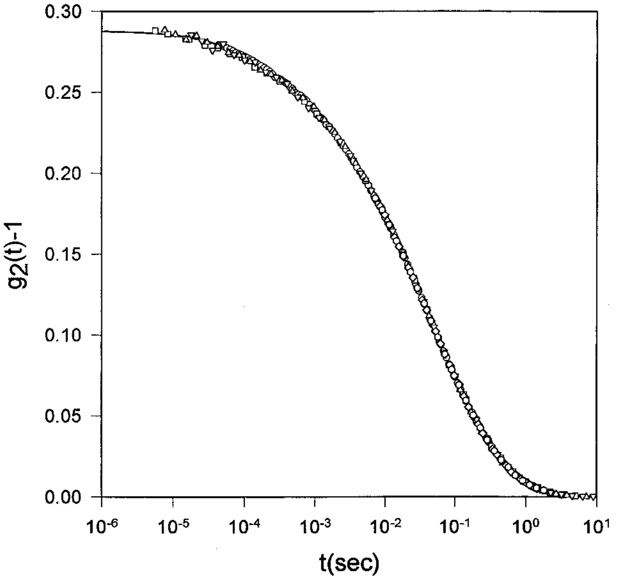

Figure 2. The superposition of the measured photon-correlation curves, $g_2(t) - 1$, onto the calculated curve obtained from fitting eq 24 (the MSVD analysis) to the data at 22.9 °C: (○), 22.9 °C; (□), 25 °C; (△), 27.5 °C; (▽), 30 °C; (◇), 35 °C; and (⬡), 40 °C.

The obtained best β values at different temperatures are near 0.4 as listed in Table 1. These β values are very similar to those obtained by Patterson et al.[7] and Brown and Nicolai[8] for high molecular weight polystyrene melts above 100 °C. In contrast to eq 18, which has a single relaxation time, eq 22 has a certain relaxation time distribution, which can be expressed as

$$\phi(t)/A = \int_0^{\infty} H(\tau) \exp(-t/\tau)\, d\tau = \int_{-\infty}^{\infty} \tau H(\tau) \exp(-t/\tau)\, d(\ln \tau) \qquad (23)$$

The distribution function $\tau H(\tau)$[30] calculated using the τ_0 and β values obtained from fitting eq 22 to the experimental results at 22.9 °C is shown in Figure 3 as a function of ln τ. The single-exponential form of eq 18 and its relaxation time τ_2 (eq 20) are obtained on the basis of applying the elastic dumbbell model as well as the rotational diffusion model. This relatively simple consideration does not indicate a distribution of relaxation time of any breadth. The relaxation time distribution of the depolarized scattering as well described by eq 22 can arise from the segmental motions contrib-

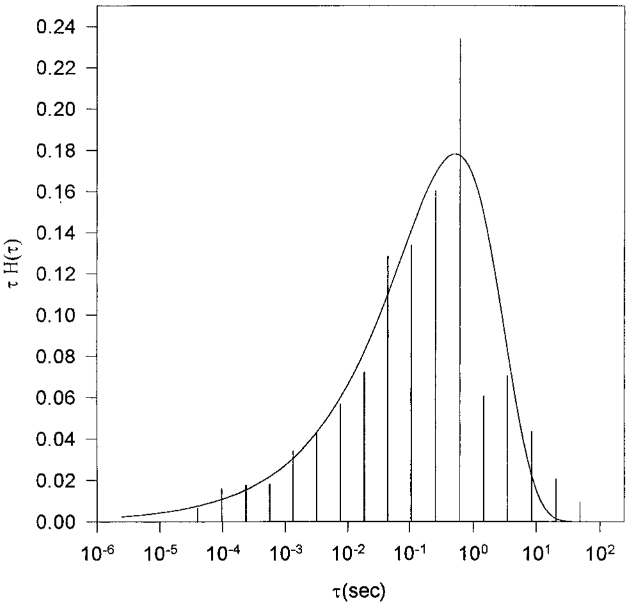

Figure 3. Distribution $\tau H(\tau)$ of the relaxation times of the studied sample at 22.9 °C. The continuous curve is calculated for the Williams–Watts function with $\beta = 0.408$ and $\tau_0 = 0.25$ (values obtained from the best WW function fitting); the vertical lines represent the distribution from the MSVD analysis.

uting to the internal viscosity and related to the relaxation function $f_s(t)$ in eq 9; and the separation of the correlation functions for the segmental motions and the reorientational motion of the whole molecule may not be as distinct as assumed in deriving eq 9. These factors may be the main reasons for a continuous distribution of relaxation times as shown in Figure 3. We have also made a multiexponential singular-value decomposition (MSVD)[31] analysis to the measured photon-correlation function. In this approach, $\phi(t)$ is approximated as

$$\phi(t) = \sum_i p_i \exp(-t/\tau_i) \qquad (24)$$

In the analysis the relaxation times are equally spaced in the logarithmical scale (i.e., $\log \tau_{i+1} - \log \tau_i =$ a constant). The distribution $\{p_i\}$ is shown together with the distribution function $\tau H(\tau)$ of the WW equation in Figure 3. Except for some fluctuations as often expected in the MSVD analysis, the two distributions are very similar and have the peak at about the same position. These two distributions are also very similar to those obtained by Brown (see Figure 2 of ref 8).

Corresponding to eq 22 an average relaxation time $\langle\tau\rangle$ can be defined as

$$\langle\tau\rangle = \int_0^\infty \tau H(\tau)\,\mathrm{d}\tau = \int_0^\infty (\phi(t)/A)\,\mathrm{d}t = (\tau_0/\beta)\Gamma(1/\beta) \qquad (25)$$

where Γ is the gamma function. For the obtained β value, the average relaxation time $\langle\tau\rangle$ is about 30% greater than the peak relaxation time τ_p shown in Figure 3. Since the reorientation motion of the molecule (the dumbbell) should be the major slow mode of motion, at the least for the order of magnitude, we can treat either τ_p or $\langle\tau\rangle$ as τ_2 of eqs 18 and 20 to calculate τ_v/τ_p or $\tau_v/\langle\tau\rangle$ for comparison with the theoretical prediction of $\tau_v/\tau_2 = 1.5 \sim 4.2$. Using $\langle\tau\rangle$ as τ_2 is consistent with subtituting eq 18 for $\phi(t)/A$ in eq 25.

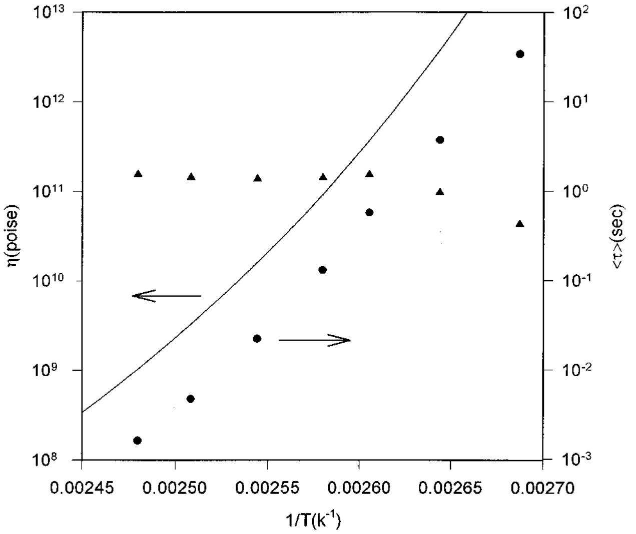

Figure 4. Average relaxation time $\langle\tau\rangle$ (●), as determined from depolarized photon-correlation spectroscopy by Patterson et al., and zero shear viscosity η (line) of a nearly monodisperse polystyrene sample ($M_w = 189\,000$) determined by Plazek and O'Rourke as a function of reciprocal temperature. Also shown is the temperature independence of the ratio $\langle\tau\rangle/\eta$ (▲), whose vertical coordinate is from 10^{-15} to 10^{-10}.

In Table 1, we list the τ_p and $\langle\tau\rangle$ values at different temperatures. The τ_p and $\langle\tau\rangle$ values at a given temperature were obtained by applying the shifting factor involved in the superposition shown in Figure 2 to the τ_p and $\langle\tau\rangle$ values of 22.9 °C. The $\langle\tau\rangle$ value obtained this way was virtually identical to that obtained by directly fitting the WW equation (eq 22) to the measured correlation function at each temperature shown. As listed in Table 1, the best β values obtained from the fittings are very much the same at different temperatures. As can be observed in Table 1 and shown in Figure 1, the obtained ratios of $\tau_v/\langle\tau\rangle$ and τ_v/τ_p are, as expected, independent of temperature and fall in the estimated range of 1.5–4.2. In contrast to the temperature independence of the relaxation time ratios, the viscosity and the relaxation time $\langle\tau\rangle$ (or τ_p) decrease by a factor of 400 ± 3% from 22.9 to 40 °C. These results support strongly the close relation between the depolarized photon-correlation relaxation times and the viscosity of the bulk as analyzed in the theoretical section.

As mentioned above, the polystyrene samples studied by Patterson and by Brown, because of their broad molecular weight distributions, could not be easily studied directly for their viscoelastic properties. However, we can assume that their depolarized photon-correlation results should not be different from what can be observed from a nearly monodisperse polystyrene melt of sufficiently high molecular weight ($>10M_e$). Then, the viscoelastic results of the nearly monodisperse polystyrene samples already available in literature can be used to calculate the relaxation time τ'_v associated with a single Rouse segment situated in a long chain for comparison with the relaxation time $\langle\tau\rangle$ extracted from the depolarized light scattering by Patterson et al.[7] (The results obtained by Brown and Nicolai[8] are essentially the same as those of Patterson et al.)

We can model the polymer molecule as a chain of freely jointed Kuhn segments. Physically, the Kuhn segment represents the size of a domain along a chain, within which the chemical segments are correlated dynamically and statically. If only the static correlation is considered, each Kuhn segment can be viewed as having the same order of volume as the so-called correlation volume defined as[18]

$$V_c = 4\pi \int f_\theta(r) r^2 \, dr \tag{26}$$

with

$$f_\theta(r) = \langle (3 \cos \theta_{ij} - 1)/2 \rangle \tag{27}$$

where θ_{ij} is the angle between the axes of the scattering units i and j, which are at a distance r apart. Using the property that the Kuhn segments are freely jointed (namely, no correlation among different Kuhn segments) and following a slightly different argument, an equation identical to eq 9 had been derived for an entangled polymer system,[9] with $\langle P_2[u(t)\cdot u(0)]\rangle$ for describing the reorientation motion of a Kuhn (or Rouse) segment belonging to a long freely jointed chain (or a Gaussian chain) and similar meanings as described for the other terms.

As to the viscoelastic properties, we can make use of the the viscoelastic spectrum in the glass–rubber transition zone, which can be modeled as the Rouse motions on an entanglement strand with two entanglement ends fixed[11,12,32,33] (assumed as fixed, because the motions occur in the short-time region). It is well-known that a stress relaxation spectrum of a nearly monodisperse polymer melt shows three characteristic regions: the glass–rubber transition zone, the plateau zone, and the terminal zone.[1,2] The line shapes of such characteristic spectra of a series of polystyrene samples over a wide molecular weight range have been quantitatively analyzed in terms of a proposed general theory,[11–12] which contains four dynamic processes: the Rouse process of an entanglement strand, $\mu_A(t)$; the chain slippage through entanglement links to equilibrate the segmental density along the primitive chain contour, $\mu_X(t)$; the primitive chain contour length fluctuation, $\mu_B(t)$; and the reptational motion corrected for the chain length fluctuation effect, $\mu_C(t)$. An important result of the spectrum shape analyses is that the friction factor extracted from the comparison of theory and experiment is independent of molecular weight as expected if the theory is valid. As a natural consequence of the successful spectrum shape analyses, the theory also explains the molecular weight dependence of the zero shear viscosity and the steady state compliance and their respective transition points, often denoted as M_C and M_C'. Furthermore, the value of the diffusion proportional constant ($K_d = DM^2$, where D is the diffusion constant and M the molecular weight) calculated from the friction factor obtained from the viscoelastic data analyses is in quantitative agreement with those obtained from diffusion measurements.[34] Thus, this obtained friction factor provides an important quantitative information source for the chain dynamics; we can use it to calculate the rates of the different dynamic processes. Because of its proximity to the motion associated with a single Rouse segment in the time scale, the $\mu_A(t)$ process, which describes the stress relaxation in the glass–rubber transition zone, is of particular interest to us here. Observed for both the polystyrene melt[12] and the concentrated solution[35] systems in the high molecular weight region, the friction factor in the $\mu_A(t)$ process (denoted as K') was found to be independent of molecular weight and about 3.3 times larger than the friction factor in the other three relaxation processes (denoted as K). A full description of this effect may be found in refs 12 and 35.

The spectrum in the glass–rubber transition can be analyzed in terms of the $\mu_A(t)$ process, which is given as[11,12,35]

$$\mu_A(t) = \sum_p \exp(-t/\tau_A{}^p) \tag{28}$$

with

$$\tau_A{}^p = K'\pi^2 M_e{}^2/[24(N_e + 1)^2 \sin^2(\pi p/2(N_e + 1))] \tag{29}$$

where $\tau_A{}^p$ is the relaxation time of the pth mode of the Rouse process, N_e is the number of Rouse (or Kuhn) segments per entanglement strand, and M_e is the entanglement molecular weight, which can be determined from the plateau modulus ($M_e = 4\rho RT/5G_N$) and is 13 500 for polystyrene.[4,5] Because of the presence of some fast glassy relaxation process (which should be related to the internal viscosity or η'_∞) in the short-time region of the measured glass–rubber transition viscoelastic spectrum, the high mode region of the Rouse process as given by eqs 28 and 29 cannot be directly compared with the measured spectrum (see Figures 4–13 of ref 12). However, the friction factor K' in eq 29 can be well determined from matching the calculated spectrum with that measured in the low Rouse mode region. The results of the best matching are illustrated for a series of polystyrene samples at different molecular weights (Figures 4–13 of ref 12). As mentioned above, the obtained K' value is 3.3 times larger than the friction factor K occurring in the $\mu_X(t)$, $\mu_B(t)$, and $\mu_C(t)$ processes. The K value at 127.5 °C can be taken to be 5.4×10^{-9}; this value represents the average of four sources of viscoelastic data[11,12,36,37] and four sources of diffusion data[38–41] with a standard deviation of only 11%.[5,34] The details of the relations between K and the results of viscoelasticity and diffusion measurements can be found in ref 34. Using $N_e = 16$ (which is consistent with the calculation of the molecular weight for a Rouse segment as shown in the Appendix) and $K' = 5.4 \times 10^{-9} \times 3.3 = 17.8 \times 10^{-9}$, we can calculate the relaxation time of the highest Rouse mode $\tau_A{}^{16} = 4.7 \times 10^{-3}$ s, which is equivalent to the relaxation time τ'_v associated with a single Rouse segment belonging to a long chain. By interpolation, Patterson's depolarized light scattering data give $\langle\tau\rangle = 3.5 \times 10^{-3}$ s at 127.5 °C. Thus, for high molecular weight samples, $\tau'_v/\langle\tau\rangle = 1.3$, or $\tau'_v/\tau_p = 1.7$, which is very close to the estimated relaxation time ratio (see eq 21) and is about half of the $\tau_v/\langle\tau\rangle$ ratio of the presently studied Rouse segment size polymer (see Table 1). It is reasonable to have such a difference between the two results, if we consider the contribution of the internal viscosity or viscosity at limiting high frequency η_∞ to η in the very low molecular weight case as explained above. The relaxation time ratio $\tau'_v/\langle\tau\rangle$ for a high molecular weight sample is obtained on the basis of the viscoelastic information associated with the lowest modes of the Rouse motions of an entanglement strand, where the segmental motions responsible for η'_∞ are not expected to have an effect. In the case of the presently studied melt sample, it appears that the relative contribution of η'_∞ to η is not as much as that of $[\eta']_\infty$ to $[\eta']_0$ in the polystyrene solution case.

To confirm the relation between dynamic depolarized Rayleigh scattering and viscoelastic relaxation, the temperature dependence of the relaxation times, $\langle\tau\rangle$, obtained by Patterson et al. and that of the zero shear viscosity, η, of a sufficiently high molecular weight polystyrene sample obtained by Plazek and O'Rourke[36] can be compared as shown in Figure 4. In the figure, the two curves (the solid line for the zero shear viscosity; the filled circles for $\langle\tau\rangle$) run parallel with each other. This becomes more apparent by showing the ratio, $\langle\tau\rangle/\eta$, in Figure 4. From 110 to 130 °C, $\langle\tau\rangle/\eta$ is clearly independent of temperature. Below 110 °C the η values shown in Figure 4 do not exactly correspond to the measured. They are calculated from the Fulcher and Tammann-Hesse equation fitted to the experimental data obtained above 110 °C. Thus, their accuracy may be questionable. This may explain the slight drop of the $\langle\tau\rangle/\eta$ values below 110 °C. The temperature independence of $\langle\tau\rangle/\eta$ above 110 °C indicates clearly that the relaxation time observed by depolarized photon correlation is closely related to viscoelastic relaxation and is in agreement with the temperature independence of $\tau_v/\langle\tau\rangle$ of the presently studied system shown in Figure 1.

5. Discussion

In the analysis of relating depolarized photon-correlation and viscoelasticity results, we have used a Gaussian chain or a freely jointed linkage of Kuhn segments interchangeably as the model for the polymer chain.[1] In the the presently studied polystyrene sample of $M_w = 1050$, the whole molecule is regarded as basically equivalent to a single Kuhn (or Rouse) segment. The reorientation motion of the whole molecule is reflected in the long-time region of the depolarized photon-correlation spectrum. In the case of an entangled polymer, each Kuhn segment physically represents a domain along the chain, whose dynamics as a whole is similarly observed by depolarized photon-correlation spectroscopy. This process, as observed by depolarized photon-correlation spectroscopy, is often referred to as the so-called α process, which is known to be closely related to the glass−rubber transition and slows down greatly as the temperature of the sample approaches its glass−rubber transition temperature. When the Rouse segment (or the elastic dumbbell) is used in a viscoelastic model, an entropic force constant is automatically attached to its connector, which is mainly valid in a mobile liquid state. Thus, as T_g is approached, the large slowdown of the α motion or the reorientational motion of a Kuhn segment may lead to the *stiffening* of a Rouse segment. Consequently while the viscosity of the polymer rises sharply at T_g, the consistency of the polymer changes from being rubber-like to being glasslike.

6. Conclusion

We have presented a theoretical analysis linking the depolarized photon-correlation relaxation times with the viscosity data of a polystyrene melt, whose molecular weight is only about that estimated for a Rouse segment. Firstly, the dynamic depolarized light scattering is shown related to the second-order time-correlation function describing the reorientational motion of the whole molecule in the melt state. Then the elastic dumbbell model is used to describe the viscoelasticity and the first-order correlation function for the reorientational motion of the polymer molecule. Finally the linkage between the first-order and the second-order correlation functions describing the molecular reorientational motions is made by assuming the rotational diffusion model. The experimental results of viscosity and depolarized photon correlation of the studied sample support such an analysis in both the agreements of the magnitude of the obtained relaxation times and their temperature dependence.

A similar conclusion has be reached from comparing the depolarized photon-correlation and viscoelastic data in the high molecular weight region which are available in the literature. In doing this, we have also shown that useful dynamic information can be obtained from the characteristic viscoelastic spctrum in the glass−rubber transition zone.

In this study, the agreements between the theoretical analyses and the experimental results support that the molecular weight of a section of polystyrene chain, which can be properly assigned as a Rouse segment, is about that estimated in the Appendix.

In the past, the depolarized photon-correlation spectroscopy and viscoelasticity of a polymer *melt* were often studied separately. It is shown in this study that the combination of these two very different probing methods aided with the theoretical analyses for linking them can lead us to a greater in-depth understanding of polymer chain dynamics in melt. It sheds light on the α motion and its close relation to the glass−rubber transition. Whether the presented theoretical analyses can be applied to polymers other than polystyrene remains to be seen.

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Appendix. The Estimation of a Rouse (or Kuhn) Segment

It is well recognized that it takes quite a few linked chemical segments to form a statistical Kuhn segment. Here we consider a polymer that has a molecular weight much higher than its entanglement molecular weight and thus consists of many Kuhn segments. In the melt state, the polymer molecule can be well treated as a Gaussian chain and the Kuhn segment can be considered as equivalent to a Rouse segment. It is clear that such a model describes the rubber-elasticity nature of a polymer melt. In the glassy state, the polymer losing its rubber-elasticity nature, it is more proper to regard the Kuhn segment as a stiff segment and model the polymer molecule as a freely jointed chain made up of the Kuhn segments. In the freely jointed chain model, the directions of different Kuhn segments including the nearest neighbors are completely uncorrelated. We shall assume that the number of Kuhn segments, N_e, between two adjacent entanglements of distance a apart while in equilibrium is sufficiently large, so that the relation

$$a^2 = N_e b^2 \tag{A-1}$$

holds in both the melt state and the glassy state, where b is the length of each Kuhn segment or the average length of each Rouse segment $(=\langle b^2\rangle^{0.5})$.

From the study of the crazing phenomenon of glassy polymers, Donald and Kramer[3] related the extension strain λ_c caused by crazing to the ratio of the length of a fully extended entanglement strand to that before being extended (i.e., in the equilibrium state). Then,

$$\lambda_c = N_e b/a = N_e b/(N_e b^2)^{0.5} = N_e^{\,0.5} \tag{A-2}$$

For polystyrene, $\lambda_c \approx 4$ gives $N_e \approx 16$. Then the molecular weight associated with each Kuhn segment or Rouse segment of a polystyrene polymer can be calculated from the estimated N_e value and its entanglement molecular weight ($M_e = 13\,500$)[4,5] to be about 850, which is close to the weight-average molecular weight (1050) of the presently studied polystyrene sample.

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