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Observation of Chain Dynamics in Depolarized Light Scattering Spectra of Polymers

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ABSTRACT: A theoretical model for the chain modes' contribution to the depolarized light scattering (DLS) spectrum of polymers is developed. It is shown that the frequency dependence of the DLS susceptibility spectrum is similar to that of the shear loss modulus. Specifically, the contribution of chain modes to the DLS spectrum is composed of a series of Lorentzians (single-exponential processes) having the same amplitude. The relaxation time associated with each mode follows the Rouse prediction, but with a value equal to one-half the mechanical Rouse time. DLS spectra of poly(dimethylsiloxane) melts with different molecular weights have been analyzed in the framework of the model. Reasonable agreement on both qualitative and quantitative levels is observed. In particular, the relaxation time of the longest Rouse mode extracted from DLS spectra is consistent with that from viscosity measurements.

I. Introduction

Polymer dynamics includes many relaxation processes, starting from the fast conformational fluctuations (fast dynamics), followed by secondary and segmental relaxations, and finally the chain dynamics. Among these, chain relaxation is, of course, unique to polymers, defining their macroscopic viscoelastic behavior. The main theoretical description of the chain dynamics is based on the Rouse/Zimm model for unentangled chains and the reptation model for entangled chains.[1] Chain dynamics are traditionally analyzed using macroscopic mechanical measurements. Poly(dimethylsiloxane) (PDMS) is a prototypical flexible-chain polymer, whose thermal stability and sluggish crystallization make it an ideal subject for viscoelastic studies. Transient[2] and dynamic mechanical[3] measurements on linear PDMS have a long history, while more recently the rheology of branched PDMS has been investigated.[4] Good agreement with predictions of the Rouse model has been found in these studies.

More recently, neutron scattering experiments provided valuable microscopic information on chain relaxation.[5] In particular, analysis of neutron scattering data for PDMS melts[6] and solutions[7] also reveals good agreement with predictions of the Rouse/Zimm model even on a microscopic scale. Dielectric spectroscopy can also be used for analysis of the chain dynamics for those (few) polymers having a dipole moment accumulating parallel to the chain. However, most of the polymers do not fall into this category, and it is not possible to study their chain dynamics by dielectric spectroscopy. For example, PDMS only has a substantial dipole moment transverse to the chain, and as a result dielectric spectroscopy can be used to probe only the local segmental dynamics.[8]

Recently, chain relaxation was observed in depolarized light scattering (DLS) spectra of PDMS.[9] However, the mechanism of light scattering by chain motion is not clear. Two existing models give contradictory predictions for the DLS spectrum: (i) Ono et al.[10] calculated the DLS due to chain relaxation and found that the spectrum is identical to the Rouse/Zimm model prediction for the shear loss modulus. (ii) On the other hand, Wang et al.[11] predicted that the DLS spectrum is proportional to the mechanical loss compliance. Thus, two models predict different spectral shapes for the chain contribution to the DLS. No comparison to experimental results in the Rouse regime has been made for either model.

In this article, we present a theory that describes the chain contribution to the DLS spectrum. It predicts that the DLS susceptibility spectra in the Rouse model should be quite similar to the shear loss modulus spectrum; however, the characteristic relaxation time is expected to be one-half the usual Rouse relaxation time measured mechanically. Detailed analysis of experimental DLS spectra and viscoelastic measurements on the same PDMS samples shows quantitative agreement with the model predictions. Thus, DLS provides a new method to investigate the chain dynamics, with clear advantages: it can be used to investigate chain dynamics at high frequency for all polymers and is simpler than neutron spectroscopy. Traditional mechanical methods cover a relatively small frequency range, and dielectric spectroscopy can measure only specific polymers that have a dipole moment accumulating along the chain.

II. Theory

The general expression for the depolarized (VH) light scattering intensity at frequency ω with scattering wave

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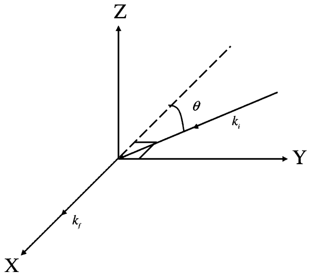
Scheme 1. Scattering Geometry II[a]



[a] The XY plane is the scattering plane. k_i and k_f is the incoming and the final wave vectors, respectively, and θ is the scattering angle. This geometry is used in connection with the molecular theories.[12]

vector **k** for the simple geometry of the experiment is given by

$$I_{\mathrm{VH}}(\mathbf{k},\omega) = A\langle|\delta\epsilon_{\alpha\beta}|^2\rangle_{\mathbf{k}\omega} \tag{1}$$

where α and β are the respective polarizations ($\alpha \neq \beta$) of the incident and scattered light (e.g., for the so-called geometry II (Scheme 1) in terms of ref 12, α is z and β is y), $\delta\epsilon_{\alpha\beta}$ is the local fluctuation of the dielectric tensor, and A is a constant. Since we are interested in the frequency dependence of $I_{\mathrm{VH}}(\mathbf{k},\omega)$, the exact value of this constant, as well as some others to follow, is unessential for our purposes. The right-hand side of eq 1 is determined by the space and time Fourier transform of the dielectric susceptibility correlation function

$$\langle|\delta\epsilon_{\alpha\beta}|^2\rangle_{\mathbf{k}\omega} = \int\int \mathrm{d}(t-t')\,\mathrm{d}(\mathbf{r}-\mathbf{r}') \times \langle\delta\epsilon_{\alpha\beta}(\mathbf{r},t)\langle\delta\epsilon_{\alpha\beta}(\mathbf{r}',t')\rangle \mathrm{e}^{i\mathbf{k}(\mathbf{r}-\mathbf{r}')-i\omega(t-t')} \tag{2}$$

The theory of depolarized light scattering in polymer melts and solutions was considered in refs 10−11 (see also ref 12 for a review), but the results are controversial. Reference 10 considered the forward DLS from dilute solution of optically anisotropic flexible macromolecules, the latter described by Rouse dynamics. It was found that the spectrum is the sum of equally weighted Lorentzians, corresponding to multiple Rouse modes. Such a spectrum corresponds to the light scattering susceptibility $\chi''(\omega) \propto I(\omega)/[n(\omega)+1] \propto \omega^{1/2}$, having the same power law as for the shear modulus $G''(\omega)$ in the Rouse regime (where $n(\omega)+1 = [1-\exp(-h\omega/kT)]^{-1}$ is the temperature Bose factor). In ref 11, the depolarized light scattering in a viscoelastic polymer liquid was analyzed. It was shown that, with some approximations, when the chain segmental reorientational rate is fast, the DLS spectrum becomes the sum of the reorientational and imaginary parts of the dynamic shear compliance, $J''(\omega)$. The latter in the Rouse regime is $J''(\omega) \propto G''(\omega)/(|G''(\omega)|^2 + G''(\omega)|^2)$. Thus, these two models predict significantly different spectral shapes for the chain contribution to DLS. This difference may be connected to one of the approximations used in ref 11, namely, the photoelastic, or Pockel's, constant p, which was assumed to be frequency independent. However, if the Pockel's constant is allowed to relax (e.g., refs 13−15), the resulting spectrum would be different.

Let us consider the depolarized light scattering spectrum in the regime of Rouse dynamics. We assume that segments of the polymeric chain are characterized by a polarizability tensor that has a rotational symmetry for the segments. The anisotropic part of the polarizability tensor, $\alpha_{\alpha\beta}$, can be written in the form

$$\alpha_{\alpha\beta} = B\left(a_\alpha a_\beta - \frac{1}{3}a^2\delta_{\alpha\beta}\right) \tag{3}$$

where B is a constant and **a** is a segment vector. The constant B is proportional to $\alpha_\parallel - \alpha_\perp$, where $\alpha_\parallel$ and $\alpha_\perp$ are the respective polarizability along and perpendicular to the segment.[1] The contribution of the segment polarizabilities to the dielectric susceptibility can be represented to a first approximation by the sum

$$\delta\epsilon_{\alpha\beta}(\mathbf{r},t) \propto \sum_n \delta(\mathbf{r}-\mathbf{R}_n(t))\alpha_{\alpha\beta}(n,t) \tag{4}$$

where $\mathbf{R}_n(t)$ is the radius vector of the end of the nth segment at a time t and $\alpha_{\alpha\beta}(n,t)$ is its current polarizability tensor. After substituting eq 3 into eq 4, one has

$$I_{\mathrm{VH}}(\mathbf{k},\omega) \propto \int \mathrm{d}(t-t')\mathrm{e}^{-i\omega(t-t')}\sum_{n,m}\langle\alpha_{\alpha\beta}(n,t)\,\alpha_{\alpha\beta}(m,t')\mathrm{e}^{i\mathbf{k}(\mathbf{R}_n-\mathbf{R}_m)}\rangle \tag{5}$$

Since in our case $\alpha \neq \beta$, we omit the second term in eq 3, and taking into account that $\mathbf{a}_n = \mathbf{R}_{n+1} - \mathbf{R}_n$, we write for long chains (changing sums over n and m to integrals)

$$I_{\mathrm{VH}}(\mathbf{k},\omega) \propto \int\int\int \mathrm{d}n\,\mathrm{d}m\,\mathrm{d}(t-t')\mathrm{e}^{-i\omega(t-t')} \times \left\langle \frac{\partial R_{n\alpha}(t)}{\partial n}\,\frac{\partial R_{n\beta}(t)}{\partial n}\,\frac{\partial R_{m\alpha}(t')}{\partial m}\,\frac{\partial R_{m\beta}(t')}{\partial m}\,\mathrm{e}^{i\mathbf{k}(\mathbf{R}_n-\mathbf{R}_m)}\right\rangle \tag{6}$$

Experimental depolarized light scattering spectra of bulk polymers and neat liquids do not have a recognizable k dependence. In refs 11 and 16, the authors argued this property of DLS could be ascribed to the smallness of the correlation length l_c in comparison with the inverse value of the light scattering wave vector k^{-1}, so that $kl_\mathrm{c} \ll 1$. Following this argument, we neglect the exponential term inside the angle brackets in eq 6. Strictly speaking, this corresponds to the case of forward scattering, but as explained, it should also approximately describe the more general k geometry.

In the Rouse model, the respective dynamical equation is diagonalized by the transformation from the vector $R_\alpha^{(n)}(t)$ to $\mathbf{X}_\mathrm{p}$, the time-dependent amplitudes of the "Rouse modes" of the polymer chain:

$$\mathbf{R}_n(t) = \mathbf{X}_0(t) + 2\sum_{p=1}^{\infty}\mathbf{X}_\mathrm{p}(t)\cos\left(\frac{p\pi n}{N}\right) \tag{7}$$

where N is the number of units in the chain. After substitution of $\mathbf{R}_n(t)$ from eq 7 into eq 6, and integrating over n and m, one has

$$I_{\mathrm{VH}}(\omega) \propto \int \mathrm{d}(t-t')\mathrm{e}^{-i\omega(t-t')}\sum_{p,q=1}^{\infty}p^2q^2\langle X_{p\alpha}(t)\,X_{p\beta}(t)\,X_{q\alpha}(t')\,X_{q\beta}(t')\rangle \tag{8}$$

Application of the Gaussian factorization approximation for the four-point correlation function in eq 8 results in products of two-point correlation functions:

$$\langle X_{p\alpha}(t)\, X_{p\beta}(t)\, X_{q\alpha}(t')\, X_{q\beta}(t')\rangle \cong \langle X_{p\alpha}(t)\, X_{p\beta}(t)\rangle\langle X_{q\alpha}(t')\, X_{q\beta}(t')\rangle + \langle X_{p\alpha}(t)\, X_{q\alpha}(t')\rangle\langle X_{p\beta}(t)\, X_{q\beta}(t')\rangle + \langle X_{p\alpha}(t)\, X_{q\beta}(t')\rangle\langle X_{p\beta}(t)\, X_{q\alpha}(t')\rangle \quad (9)$$

In the Rouse model, the time correlation function of the mode amplitudes is an exponential:

$$\langle X_{p\alpha}(t)\, X_{q\beta}(t')\rangle = \frac{T}{k_{\mathrm{p}}}\,\delta_{\alpha\beta}\delta_{pq}\,\exp(-|t - t'|/\tau_{\mathrm{p}}) \quad (10)$$

Here

$$k_{\mathrm{p}} = \frac{6\pi^2 T p^2}{N b^2} \quad (11)$$

and $\tau_{\mathrm{p}} = \tau_1/p^2$, $\tau_1 = \zeta N^2 b^2/3\pi^2 T$ is the Rouse relaxation time for the pth mode, ζ is a friction coefficient, and b is the segment length. With this expression for the two-point correlation function, the first and the third terms on the right-hand side of eq 9 are equal to zero because, for the depolarized scattering, they are nondiagonal in vector indices α and β. The second term is equal to $(T/k_p)^2\delta_{pq}\exp(-2|t - t'|/\tau_{\mathrm{p}})$. Substituting this expression to eq 8, one gets

$$I_{\mathrm{VH}}(\omega) \propto \sum_p^{\infty}\int \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t}\exp(-2|t|/\tau_{\mathrm{p}}) = 2\sum_p^{\infty}\frac{\tau'_{\mathrm{p}}}{1 + \omega^2 {\tau'_{\mathrm{p}}}^2} \quad (12)$$

where $\tau'_{\mathrm{p}} = \tau_{\mathrm{p}}/2$. For the light scattering susceptibility, $\chi''(\omega) = I_{\mathrm{VH}}(\omega)/(n(\omega) + 1) \approx \omega I_{\mathrm{VH}}(\omega)/T$, approximating the sum in eq 12 by an integral, square root behavior is obtained:

$$\chi''(\omega) \propto \int \mathrm{d}p\, \frac{\omega\tau'_{\mathrm{p}}}{1 + \omega^2 {\tau'_{\mathrm{p}}}^2} \propto \omega^{1/2} \quad (13)$$

Therefore, the DLS susceptibility spectrum has the same frequency dependence in the Rouse regime as that of the shear loss modulus,[1] in agreement with the results from ref 10. However, the relaxation time of each mode from DLS is expected to be one-half of that from mechanical measurements under the same conditions.

III. Experimental Section

Methyl-terminated PDMS was purchased from Gelest with typical polydispersity ~ 1.5−2.0.[17] DLS spectra were measured using a Raman spectrometer (JY T64000) for frequencies down to ~300 GHz and a tandem Fabry-Perot interferometer (Sandercock model) for lower frequencies. All measurements were done at 400 K. A detailed description of the measurements can be found in ref 9. PDMS samples with molecular weights equal to 162, 550, 1250, and 116 500 Da were measured using a backscattering geometry (scattering angle $\Theta = 180°$). Additionally, the spectra of PDMS samples with molecular weight 550 and 116 500 Da were measured with right angle ($\Theta = 90°$) and near forward ($\Theta \approx 10°$) scattering geometries to verify the scattering wave-vector dependence of the DLS spectrum.

Torsional creep viscosities were measured on two PDMS samples (550 and 1250 Da) over a range of temperatures, using a Plazek constant stress instrument.[18] A parallel plate geometry was employed, with sample diameter = 50 mm and a gap of 1−1.5 mm. Strain rates were in the range from 0.007 to 2 s^{-1}. To minimize degradation and eliminate bubbles, the sample was degassed while mounted in the rheometer, which was then backfilled with nitrogen. Temperature control was ±0.1 deg.

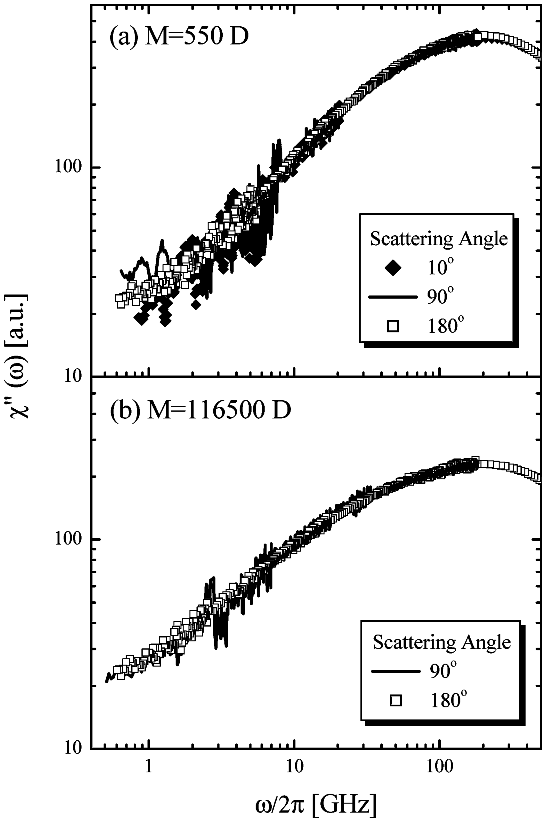


Figure 1. (a) DLS susceptibility spectra of PDMS 550 at different scattering angles: (◆) 10°, (—) 90°, (□) 180°. (b) DLS susceptibility spectra of PDMS 116 500 at different scattering angles: (—) 90°, (□) 180°.

IV. Results and Discussion

IV.1. Dependence of the DLS Spectrum on Scattering Wave Vector. DLS spectra of PDMS measured at different scattering wave vectors are presented in Figure 1 as the imaginary part of the susceptibility, $\chi''(\omega)$. The scatter of the data, due to the limited statistics, increases at lower frequencies. The susceptibility presentation allows direct comparison of the scattering data to dielectric $\epsilon''(\omega)$ or mechanical $G''(\omega)$ loss spectra.[19] For our analysis, it is essential to know the relaxation times (characteristic frequencies) at this temperature. The local segmental relaxation frequency ν_α ($= \omega/2\pi$) estimated for PDMS ($M = 92\,000$ Da) from quasi-elastic neutron scattering experiments is ~50 GHz at $T = 400$ K.[9,20] The longest Rouse relaxation time for PDMS with $M = 6462$ Da at 373 K is estimated from neutron spin echo (NSE) experiments, $\tau_1 = 2\langle R_g^2\rangle/\pi^2 D_R$ ~ 30 ns (both R_g and D_R are available in ref 6). This corresponds to a characteristic frequency for the longest Rouse mode, $\nu_1 = (2\pi\tau_1)^{-1}$ ~ 0.005 GHz. Therefore, the low-frequency tail of the scattering spectra falls in the regime of chain relaxation, i.e., $\nu_1 < \nu < \nu_\alpha$. Note that the segmental relaxation time (frequency) depends on molecular weight up to a certain M (~10^4 Da),[21] while the longest chain (Rouse) relaxation time (frequency) scales with molecular weight as $\tau_1 \propto M^2$, for

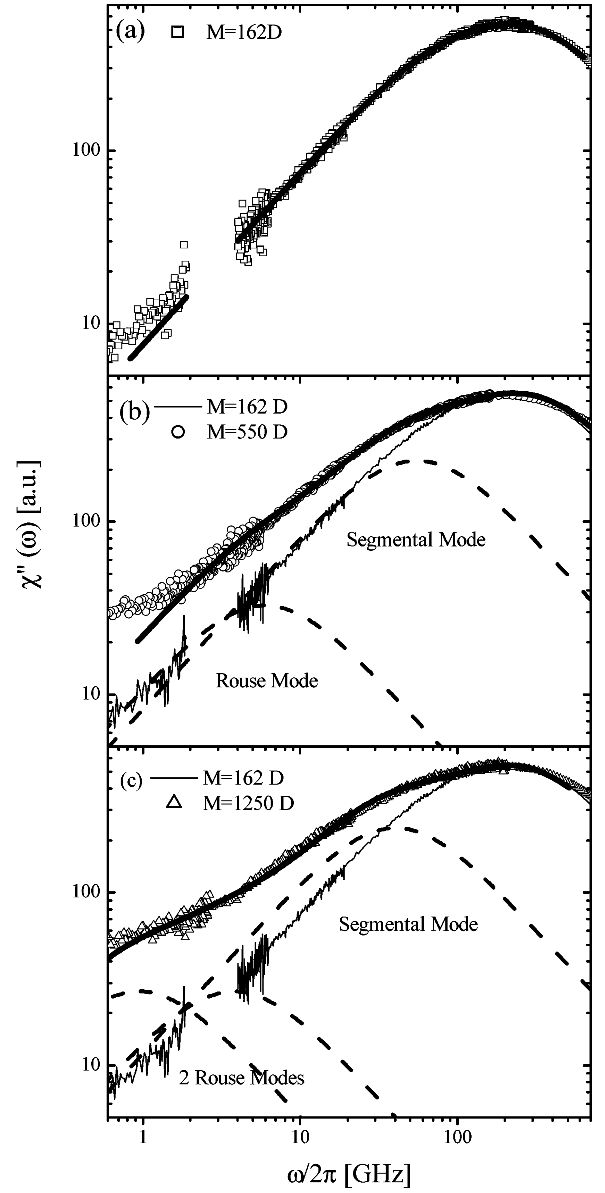


Figure 2. DLS susceptibility spectra of (a) PDMS 162 (□), (b) PDMS 550 (○), and (c) PDMS 1250 (△). Thick lines represent the fitting results; dashed lines represent the component relaxation processes as noted; thin lines in (b) and (c) represent the spectrum of PDMS 162, used for comparison.

molecular weights less than the entanglement molecular weight.

The spectra in Figure 1 for neither sample show any significant dependence on the scattering wave vector. This result confirms that the DLS spectrum is insensitive to k in the frequency range studied. In the light scattering experiment, k is very small, and thus the length scale probed is large compared to the spatial extent of the segmental and internal chain modes. Hence, the simplification used in the model (neglecting the exponential term in eq 6) is justified. Of course, a k dependence of the light scattering can exist in polymer solutions due to scattering caused by the concentration fluctuation associated with chain translational motions.[12]

IV.2. Analysis of DLS Spectrum: Rouse Modes Contribution. Figure 2 shows the DLS spectra of PDMS with molecular weight 162, 550, and 1250 Da. The spectrum of the former shows behavior typical for small molecule: The low-frequency tail increases as $\chi''(\omega) \propto \omega$. This spectrum can be approximated by a sum of two Lorentzians

$$\chi''(\omega) = \chi''_{\text{micro}}(\omega) + \chi''_{\text{seg}}(\omega) = \frac{A_1\omega\tau_{\text{m}}}{1+(\omega\tau_{\text{m}})^2} + \frac{A_2\omega\tau_{\text{seg}}}{1+(\omega\tau_{\text{seg}})^2} \quad (14)$$

the first representing a microscopic process and the second reflecting segmental relaxation. It is known that at high temperatures these two relaxation processes—a microscopic (fast) process and an α-relaxation (slow) process—exist in all liquids. The latter is called segmental relaxation in polymers. The local segmental relaxation usually has an extended, high-frequency tail and cannot be described by a single Lorentzian function. However, this stretching is usually insignificant at very high temperatures. $T = 400$ K is much higher than T_g, which varies with the number-average molecular weight (in daltons) as[21] $T_g(K) = 147.0 - 5064/M_n$. Characteristic relaxation times of the two dynamic processes, obtained from the fit to eq 14, are presented in Table 1.

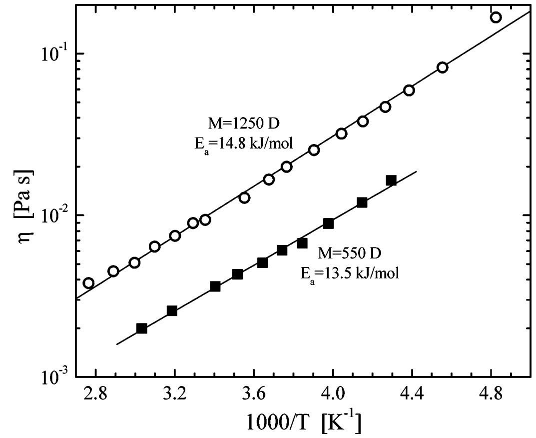


Figure 3. Zero-shear-rate viscosities for PDMS with M = 1250 Da (○) and 550 Da (■). The activation energies calculated from the respective slopes are indicated.

Table 1. Relaxation Times from DLS Spectra and Viscosity Measurements

				τ_1 (ps)	
M	τ_{m} (ps)	τ_α (ps)	τ'_1 (ps)	DLS[a]	η_0
162	0.66 ± 0.05	2.0 ± 0.2			
550	0.57 ± 0.05	2.9 ± 0.2	27 ± 3	54 ± 6	103 ± 9
1250	0.57 ± 0.05	3.9 ± 0.2	168 ± 13	336 ± 26	604 ± 11

[a] After adjustment by the required factor of 2 (see text).

In section II, we showed that the DLS susceptibility spectrum for chain relaxation should have the same frequency dependence as a loss modulus in the Rouse regime. Specifically, the susceptibility spectrum is a sum of a series of single-exponential relaxation modes of equal amplitudes (eq 13). Figure 2 reveals an additional contribution near the lower frequency tail, for PDMS with $M = 550$ and 1250 Da. In ref 9, it was shown that the stretching of the low-frequency tail increases with molecular weight, approaching $\omega^{0.5}$ behavior at high molecular weight. According to ref 9, the molecular weight associated with the smallest Rouse mode in PDMS is estimated to be ~560 Da. Therefore, we expect that the spectrum of the sample with $M = 550$ Da includes only a single chain mode and thus can be approximated by

$$\chi''(\omega) = \chi''_{\mathrm{micro}}(\omega) + \chi''_{\mathrm{seg}}(\omega) + \chi''_{\mathrm{chain}}(\omega) = \frac{A_1\omega\tau_{\mathrm{m}}}{1+(\omega\tau_{\mathrm{m}})^2} + \frac{A_2\omega\tau_{\mathrm{seg}}}{1+(\omega\tau_{\mathrm{seg}})^2} + \frac{A_3\omega\tau'_1}{1+(\omega\tau'_1)^2} \quad (15)$$

The fit of eq 15 describes the spectrum well (Figure 2a), giving relaxation time ~2.9 ± 0.2 ps for the segmental mode and 27 ± 3 ps for the chain (Rouse) mode (Table 1).

Assumption that the smallest Rouse subchain in PDMS has molecular weight ~560 Da leads to noninteger number of Rouse modes in PDMS chains with $M = 1250$ Da. In a crude approximation we assume that these chains have two Rouse segments, and the chain relaxation spectrum includes two chain modes:

$$\chi''(\omega) = \chi''_{\mathrm{micro}}(\omega) + \chi''_{\mathrm{seg}}(\omega) + \chi''_{\mathrm{chain}}(\omega) = \frac{A_1\omega\tau_{\mathrm{m}}}{1+(\omega\tau_{\mathrm{m}})^2} + \frac{A_2\omega\tau_{\mathrm{seg}}}{1+(\omega\tau_{\mathrm{seg}})^2} + A_3\left[\frac{\omega\tau'_1}{1+(\omega\tau'_1)^2} + \frac{\omega(\tau'_1/4)}{1+\{\omega(\tau'_1/4)\}^2}\right] \quad (16)$$

These two modes have the same amplitude and their relaxation time follows the Rouse prediction: $\tau'_{\mathrm{P}} = \tau'_1/p^2$. Here τ'_1 is the longest relaxation time, and τ'_p is the relaxation time of the pth Rouse mode. The free fit of eq 16 describes the spectrum well (Figure 2b), giving relaxation time $\tau_\alpha \sim 3.9 \pm 0.2$ ps for the segmental mode and $\tau'_1 \sim 168 \pm 13$ ps for the longest chain (Rouse) mode (Table 1). Thus, the model gives a good description of the depolarized light scattering spectra, with the chain relaxation contribution described by a summation of Lorentzian functions having equal amplitude (The amplitude of a Rouse mode is defined as the maximum value of the susceptibility loss at $\omega\tau = 1$.)

Analysis of the results (Table 1) shows that the relaxation time of the microscopic process is in the range characteristic for the fast process. The segmental relaxation time shows the usual increase with increasing molecular weight (in PDMS for $M < 10^4$ Da[21]). The characteristic τ_α of the segmental relaxation agrees well with earlier data, $\tau \approx 3.2$ ps ($\nu_\alpha \approx 50$ GHz at 400 K), obtained by quasi-elastic neutron scattering measurements on PDMS with $M = 6462$ Da.[9,20]

The most interesting quantitative test of the model is analysis of the Rouse relaxation time extracted from the fit of the DLS spectra. Specifically, the relaxation time of the Rouse mode, associated with molecular weight = 550 Da, is estimated as $\tau'_1 \sim 27 \pm 3$ ps, while for the chain with $M = 1250$ Da $\tau'_1 \sim 168 \pm 13$ ps. Taking into account the fact that the relaxation time estimated from DLS is half that of the corresponding mechanical measurements, we predict that the mechanical Rouse time is $\tau_1 \sim 54 \pm 6$ ps for PDMS chain with $M = 550$ and $\tau_1 \sim 336 \pm 26$ ps for PDMS chain with $M = 1250$. We note that, although the spectral dependence of the DLS estimated in ref 10 is basically in agreement with our model, the relation of the relaxation time in ref 10 to that of the Rouse model is not given clearly. Moreover, molecular weight scaling of the Rouse time with that from DLS gives $\tau_1(1250)/\tau_1(550) = 6.2$. However, according to the Rouse model, $\tau_1 \sim M^2$, the ratio of τ_1 between these two molecular weight should be $(1250/550)^2 \sim 5.2$. This difference is discussed in the following section.

IV.3. Comparison with Viscoelastic Measurements. To verify the Rouse relaxation time extracted from DLS spectra, viscosity measurements were carried out on the same PDMS samples from which relaxation times are deduced. At high temperature, the zero-shear-rate viscosity exhibits an Arrhenius temperature dependence. For PDMS with $M = 550$ Da

$$\log \eta_0\ (\mathrm{Pa\ s}) = -4.85(\pm 0.06) + 706(\pm 16)/T \quad (17)$$

which gives $\log \eta_0(\mathrm{Pa\ s}) = -3.09 \pm 0.04$ at 400 K. For $M = 1250$ Da

$$\log \eta_0\ (\mathrm{Pa\ s}) = -4.59(\pm 0.01) + 773(\pm 4)/T \quad (18)$$

yielding for 400 K $\log \eta_0$ (Pa s) $= -2.66 \pm 0.01$.

The zero-shear viscosity is related to the longest Rouse relaxation time as[1,22]

$$\tau_1 = \frac{6}{\pi^2}\frac{M}{\rho RT}\eta_0 \quad (19)$$

in which ρ is the mass density. For $M = 550$ Da, $\rho(400\ \mathrm{K}) = 0.794$ g/mL,[23] and eq 19 gives $\tau_1 = 103 \pm 9$ ps. For $M = 1250$ Da, $\rho(400\ \mathrm{K}) = 0.832$ g/mL,[23] and we obtain $\tau_1 = 604 \pm 11$ ps.

For unentangled polymers, the Rouse model predicts the relaxation time to vary as M^2. Thus, the ratio of relaxation times for chains with $M = 1250$ and $M = 550$ is expected to be ~5.2. The viscoelastic measurements reveal stronger variation: $\tau_1(1250)/\tau_1(550) \sim 5.9$, consistent with estimates from DLS. This stronger variation may be ascribed to the change of the segmental relaxation time (i.e., T_g) with molecular weight (Table 1), which in turn changes the effective friction coefficient of the melt.

Analysis of the DLS spectra in the framework of the proposed model provides an estimate of the relaxation time for the longest Rouse modes in the two PDMS samples. These are compared in Table 1 to the τ_1 determined from the viscosities. We note that the two methods give results that differ by a factor of 2. The most obvious source of error is polydispersity in the samples. According to the manufacturer, $M_w/M_n = 1.5-2$. The viscosity is governed primarily by the weight-average, M_w, so that the differences in Table 1 are well within the uncertainty arising from the molecular weight distributions. The other source of error is the ambiguity in fitting eqs 15 and 16 to the DLS spectra in Figure 2 (which extends just over 2 decades). Moreover, the experimental limitation of the light scattering (reliable data have been obtained only at $\omega/2\pi > 0.8-1$ GHz) does not allow estimation of the longest chain modes. We can conclude that the disagreement between τ_1 estimated from DLS and that from the viscosity is well within the accuracy of the experiments.

V. Conclusion

In this paper, a theoretical model for the contribution of chain relaxation modes to the DLS spectrum is developed. We apply it to the determination of the frequency dependence of the light scattering susceptibility spectrum and predict a close similarity to that of the shear loss modulus, i.e., $\chi''(\omega) \sim \omega^{0.5}$. However, the chain relaxation times from light scattering are predicted to be a one-half the magnitude of the mechanical Rouse relaxation times. Using our model, we are able to describe the experimental DLS spectra of unentangled PDMS melts. Relaxation times extracted from the fit of the DLS spectra were compared to Rouse relaxation times obtained from the viscosity of the same samples. The agreement was satisfactory, given the experimental uncertainties.

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