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Laser Light Beating Spectroscopic Studies of Dynamics in Bulk Polymers: Poly(propylene glycol)

C. H. Wang*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

G. Fytas, D. Lilge, and Th. Dorfmüller

University of Bielefeld, Faculty of Chemistry, 4800 Bielefeld 1, West Germany.
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ABSTRACT: A comprehensive homodyne beating spectroscopic study of poly(propylene glycol) (PPG) with molecular weights 425, 1025, 2025, and 4000 has been carried out from −45 to −65 °C. The homodyne time correlation functions for both VV and VH scattering configurations have been obtained over the time scale from 1 to 10^{-6} s. The time correlation functions show a wide distribution of relaxation times, and this has been related to the glass transition phenomena in this polymer. The average relaxation times derived for both isotropic and anisotropic scattering spectra are found to have the same values over the temperature range studied. This suggests that segmental reorientation is strongly coupled to the segmental center-of-mass translational motion. The mean relaxation times for all polymers are also found to depend only on temperature and not on the shear viscosity associated with the difference in the molecular weight. The shear viscosities for all four polymers have been measured from −30 to −40 °C. Over the molecular weight range (425–4000), the viscosity is found to be proportional to the molecular weight. The total scattering intensity and the relaxation strength are also measured for each polymer at several temperatures. The dynamic and static data obtained for PPG at various molecular weights serve to illustrate the importance of the effects of local segmental motion on the glass–rubber transition of bulk PPG.

Introduction

Dynamic light scattering is a useful technique for the study of relaxation processes in polymer liquids. In previous work, in which a Fabry-Perot interferometer was used for spectral analysis, it has been shown that Rayleigh–Brillouin scattering and depolarized Rayleigh scattering can be used to study the effects of segmental motion[1-5] and orientational fluctuations[6-8] in pure polymers and polymer solutions in the time scale of 10^{-8}–10^{-12} s. At a longer time scale (e.g., below 10^{-6} s), the light scattering spectrum can be analyzed by using the photon correlation spectroscopic technique.[9-13] Thus, dynamic light scattering complements well the techniques of dielectric relaxation, nuclear magnetic relaxation, and neutron scattering for the study of the dynamics of relaxation processes of polymers in the liquid state.

Continuing the effort in the investigation of the segmental motion of bulk polymers, we have carried out a comprehensive homodyne photon correlation spectroscopic study of undiluted liquid poly(propylene glycol) (PPG) as a function of molecular weight and temperature. The objective of this work is to obtain information about the characteristics of the relaxational processes of bulk polymers and the effects of segmental motion on the glass–rubber transition. We have measured the shape of the homodyne correlation functions for the polarized (VV) and depolarized (VH) spectra over the time scale of 10^{-6} to 1 s and deduced from them the distribution of relaxation times as well as the mean relaxation time as a function of temperature. The total scattering intensity and the relaxation strength are measured as a function of temperature and molecular weight. These dynamic and static data should provide useful insight into the physical process associated with the glass–rubber transition of PPG.

Baur and Stockmayer were first to investigate, using the dielectric relaxation technique, the temperature and molecular weight dependence of the principal loss peak of PPG.[14] They found that the principal (β) dielectric loss peak occurs at essentially the same frequency at a given temperature for all molecular weights. The dielectric relaxation work was subsequently extended by Yano et al. to cover a wider frequency range (covering 12 decades) as a function of temperature.[15] By comparing the dielectric relaxation data with the Brillouin scattering results,[15] Yano et al. showed that at high temperature (and hence high frequency) the frequency of the dielectric loss maximum lies lower than the frequency at which hypersonic attenuation occurs. They have, thus, suggested that in PPG a more rapid process than that causing the dielectric relaxation is probed by Brillouin scattering. However, Patterson et al.[16] have interpolated their hypersonic attenuation data and reported a secondary maximum at a temperature higher than the primary maximum in PPG at about 50 °C, first observed by Huang and Wang.[1] Consequently, they have made the identification of the Brillouin attenuation maxima to the primary (α) and secondary (β) dielectric loss peaks. The double-maximum structure in the hypersonic attenuation data of PPG 4000 is, however, not confirmed by our recent careful Brillouin scattering measurement.[17]

The idea of identifying the Brillouin attenuation maximum with either primary or secondary relaxation peaks[18,19] in dielectric relaxation has recently been criticized. On the basis of their careful study of the Rayleigh–Brillouin spectra of poly(phenylmethylsiloxane) and poly[(dimethylphenyl)methylsiloxane], Fytas et al.[5] have pointed out that the structural relaxation which occurs in Brillouin scattering is, in general, faster than the α- or the β-mode motion, as Brillouin scattering is associated with the translational motion of local segments, which may not affect dielectric relaxation. This observation is in agreement with the conclusion of Yano et al.[15]

The types of motion in PPG which are probed in dielectric relaxation and in light scattering have previously been discussed by Jones and Wang.[7] However, near but above the glass transition temperature, the isothermal part of the density fluctuation gradually freezes out, and only very local segmental motion can make a contribution to the density fluctuation. In such a temperature region, conformation transitions occurring on a local scale may become the main mechanism for both light scattering and dielectric relaxation. For those specific conformational

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changes which also lead to the translational motion of the polymer segment, isotropic light scattering will reflect the dynamic process of the conformational change through the translational motion of the segment. If such a conformational change also results in the reorientation of the dipole moment of the segment, then the β peak in dielectric relaxation and isotropic light scattering (which monitors the density fluctuation) will probe the same conformational transition process. In PPG, reorientation of the component of the dipole moment which bisects the C–O–C bond angle is the mechanism for the principal (β) loss peak. through the gauche migration or the gauche production mechanism,[20] the reorientation of the dipole moment by flipping the C–O–C unit about the chain backbone will also result in a translation of the center of mass of the scattering segment. Thus, in this system, both the dielectric loss and the light scattering measurements may yield a similar relaxation time value near T_g.

Accurate dielectric relaxation data of PPG (T_g = –75 °C) at low temperature (–40 to –75 °C) are available.[14,15] Since the dynamic fluctuation of PPG in this temperature range is too slow for the Fabry-Perot interferometer, we have carried out the photon correlation spectroscopic study of PPG in the same temperature range in order to compare the dielectric data with light scattering.

In a series of papers dealing with the Rayleigh–Brillouin scattering and depolarized scattering of PPG by Wang and co-workers,[1-4,7,15,21] it has been shown that in the time scale of the interferometric range (10^{-8}–10^{-12} s) localized segmental motions of the polymer backbone are responsible for the modulation of isotropic and anisotropic components of the polarizability density. The modulation arising from these motions gives rise to the hypersonic velocity dispersion and the line widths for the Rayleigh–Brillouin as well as the depolarized Rayleigh scattering spectra. Moreover, the segmental motion also gives rise to an additional structural relaxation (Mountain) component centered at the laser frequency.[21] This structural component displays a strong temperature dependence and narrows dramatically as the temperature is decreased. It merges into the central Rayleigh peak at temperatures below –40 °C.[21] In order to follow up the dynamics of this structural relaxation mode below –40 °C, we have carried out the photon correlation measurement of this structural component.

Experimental Section

Photon correlation spectra of PPG 425, 1025, 2025, and 4000 were taken at temperatures between –45 and –65 °C at a 90° scattering angle with the apparatus described previously.[22] PPG 2025 was studied at three scattering angles (θ = 45, 90, and 135°) at –61 °C, corresponding to a change of a factor of 5.83 in q^2, q being the magnitude of the scattering vector. The excitation light source was an argon ion laser (Spectra-Physics 165) operating at 5145 Å with about 400-mW power. Polarized (VV) spectra were obtained by making the polarization of the incident beam perpendicular to the scattering plane. The depolarized (HV) scattering intensity of PPG is small; the depolarized spectra were obtained with the incident polarization made parallel to the scattering plane, no analyzer was inserted in the scattered beam, and, in this case, both HV and HH intensities were collected. Glan-Thompson analyzers with an extinction ratio better than 10^{-5} were used for polarization selections.

The single-clipped photon count autocorrelation function was measured with a 96-channel Malvern correlator. The incident light was focused with a lens (f.l. = 30 cm) on the sample. The scattered light was passed through two 300-μm pinholes, with one placed next to the sample cell and the other in front of the photomultiplier tube (Bendix Type 7500-5201, S-20 response). The distance between the two pinholes was adjusted to give about one coherence area at the photocathode of the photomultiplier tube. Before the photon count was processed, the scattered light was passed through a band-pass filter (~100 Å) centered at 5145 Å to remove Raman scattered light.

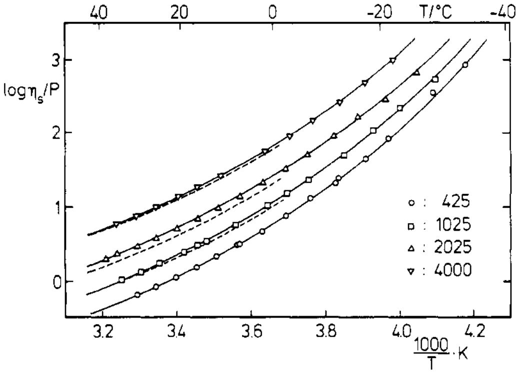

Figure 1. Logarithm of shear viscosity plotted vs. temperature for four PPG polymers. The data presented as dashed lines are from ref 14. The discrepancy for PPG 2025 is especially significant. η_s is in poise.

Table I
Parameters Associated with the Least-Squares Fit of the Shear Viscosities to the Antoine-WLF Equation for PPG

MW	$\ln \eta_0$	B/K	T_0/K
425	-7.82 ± 0.15	955 ± 39	174 ± 1.8
1025	-7.31 ± 0.14	994 ± 64	172 ± 3
2025	-6.25 ± 0.26	971 ± 54	171 ± 2.8
4000	-4.99 ± 0.09	898 ± 18	176 ± 1

The angular-dependent measurements were first performed with a 0.18% by weight solution of polystyrene (Pressure Chemical Co., MW = 233 000, M_w/M_n = 1.06) in CCl_4 at room temperature to calibrate the proper intensity response and also to certify the q^{-2} dependence for the translational relaxation time of polystyrene due to concentration fluctuations.

PPG samples with molecular weights 425, 1025, and 2025 were purchased from Merck, West Germany. The 4000 molecular weight sample was obtained from the H. C. Ørsted Institute, University of Copenhagen. The samples were filtered through 0.22-μm Millipore filters directly into dust-free scattering cells. High-quality rectangular optical cells were used in the 90° scattering experiments, and a cylindrical cell was employed in the angular-dependent measurements.

A Lauda temperature bath controlled the sample cell temperature to ±0.05 K by circulating CH_3OH around a copper holder containing the scattering cell. Because of the large change in the relaxation time with temperature, great care was taken to ensure the stability of the sample temperature the data were recorded.

The viscosity of each sample studied was measured from –30 to –40 °C with a Höppler (falling ball) viscometer. The data for PPG 1025 and 4000 above 0 °C are in good agreement with those cited by Baur and Stockmayer.[14] Our measured data below 0 °C improve the extrapolation of the viscosities over the temperature range of our light scattering experiments. The viscosity data for PPG at several molecular weights are given in Figure 1 as a function of temperature, together with the data given in Baur and Stockmayer's paper[14] for comparison. The viscosity data are fit to the Antoine–WLF-type equation of the form

$$\ln \eta_s = \ln \eta_0 + B/(T - T_0) \tag{1}$$

where η_0, B, and T_0 are parameters whose physical meanings are given in the discussion section. For η_s in poise and T in Kelvin, the constants for the four polymers are shown in Table I.

Data Analysis

The measured single-clipped photoelectron-count autocorrelation function is

$$G_k^{(2)}(t) = \langle n_k(t) n(0) \rangle \tag{2}$$

where n_k is the clipped photoelectron count, which is equal to 1 if the number of counts observed within the increment sample

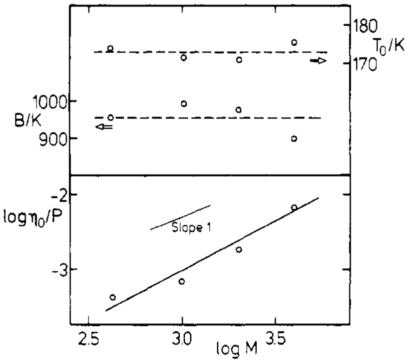

Figure 2. ln η_0, B, and T_0 fitted to the Antoine-WLF equation for shear viscosities of four PPG polymers plotted as a function of molecular weight.

time exceeds the clipping level k and equal to 0 otherwise. For a detector with a finite effective photocathode, the normalized time correlation function of the scattered field $g^{(1)}(t)$ as a function of delay time t is related to the single-clipped homodyne autocorrelation function as (assuming a Gaussian process)[23]

$$G_k^{(2)}(t) = A\left(1 + \frac{1+k}{1+\langle n\rangle} f(\Omega,\tau)|g^{(1)}(t)|^2\right) \tag{3}$$

where $\langle n\rangle$ is the average number of photon counts per sample time and $f(\Omega,\tau)$ is a spatial coherence factor which depends on the number of coherence areas observed in the sample volume and increment sample time τ. We have determined this factor to calibrate our system by measuring the total scattered intensites of pure CCl_4 and a solution of polystyrene in CCl_4 at room temperature. The background factor A can be computed or measured at large delay times. In the case that the computed background does not agree with the measured value at large delay times, either the system is not operating properly or the sample contains dust.

However, due to the nature of homodyne beating spectroscopy, physical processes with fluctuations having time scales τ_f shorter than (or the order of) the shortest increment sample time τ_s (=50 ns) contribute only to the background and not to the correlation function. Therefore, the part of density fluctuations which give rise to hypersonic waves as monitored by Brillouin scattering or the thermal diffusion process etc. will appear as a background in the photon correlation spectrum. Furthermore, fluctuations in electronics and laser power due to long accumulation time or failure to monitor real relaxation processes with very long relaxation times also affect the background and the value of $\langle n\rangle$. Thus, in practice the measured correlation function is given by

$$G_{\text{obsd}}^{(2)}(t) = A(1 + a + b|g^{(1)}(t)|^2) \tag{4}$$

where b is treated as a parameter. In the present work, we have found that b is less than 25% of the calculated value of $[(1 + k)/(1 + \langle n\rangle)]f(\Omega,\tau)$. The background factor A as computed theoretically agrees with the measured value to within 0.15%. The factor a is a small number which is introduced to account for the nonzero background which may result from real processes with longer relaxation times compared with the one being measured. In order to cover a wide dynamic range, we obtained overlapping data from runs using at least three increment sample times differing by a factor of 3 for each run for each temperature and matched them to give the composite correlation functions. To accomplish this, we sometimes needed to adjust the value of a to provide a good match, but for PPG the adjusted a value never exceeded 0.001, thus indicating that the composite correlation function has effectively included all long relaxation processes. The representative correlation functions $|g^{(1)}(t)|^2$ for PPG 1025 at four temperatures extracted according to this procedure are plotted as a function of log t, as shown in Figure 3. In this figure, the correlation functions are normalized to a value α_r^2. We now describe the meaning of this quantity.

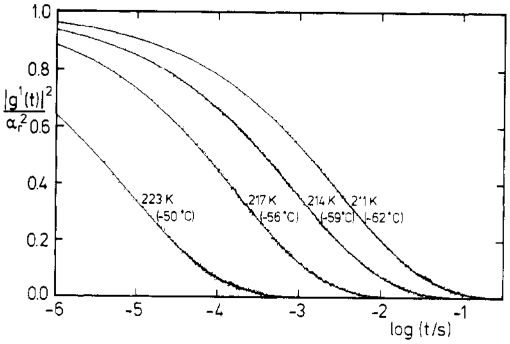

Figure 3. Normalized correlation functions of PPG 1025 plotted vs. log t for four temperatures fitted to the Williams-Watts equation. The correlation functions are normalized to unity at t = 0. The dots are experimental points and the lines are calculated according to the William-Watts equation.

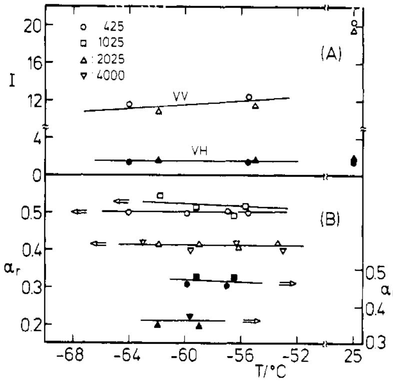

Figure 4. Total integrated scattering intensities (A) and relaxation strength (B) obtained for VV (empty symbols) and VH (solid symbols) scattering configurations plotted as a function of temperature.

Results and Discussion

A. Intensity and Relaxation Strength. If I_{iso} is defined as the total scattered intensity due to fluctuations in the average (or the trace of) polarizability tensor, the I_{iso} is proportional to the mean-square density fluctuation and can be computed from the experimentally observable I_{VV} and I_{HV} components by[24]

$$I_{\text{iso}} = I_{VV} - \tfrac{4}{3}I_{HV} \tag{5}$$

where I_{HV} can be related to the fluctuations in optical anisotropy. For PPG the depolarization ratio $\rho = I_{VH}/I_{VV}$ is small, equal to 0.13 at -55 °C for PPG 2025; it decreases slightly with increasing temperature but is not sensitive to molecular weight. Thus, the intensity of I_{VV} is due mainly to I_{iso}. In Figure 4A the total intensities for the VV and VH components are given for the PPG polymers as a function of temperature. The total I_{VH} intensity is found to be nearly independent of temperature and the I_{VV} intensity increases linearly with increasing temperature, consistent with that is expected for the density fluctuation for $T > T_g$.

However, the full I_{iso} and I_{VH} intensity fluctuations are not observed in homodyne beating spectroscopy. Fluctuations faster than the shortest sample time are excluded in the homodyne beating experiment. If we separate $g^{(1)}(t)$ into two components, one probed by homodyne spectroscopy and the other a fast component which contributes only to the background, we can write for $t > \tau_s$ (τ_s being the shortest time monitored in the light beating experiment)

$$\begin{aligned}|g^{(1)}(t)|^2 &= |\alpha_r e^{-(t/\tau_0)^\beta} + (1 - \alpha_r)g'(t)|^2 \\ &\simeq \alpha_r^2 e^{-2(t/\tau_0)^\beta}\end{aligned} \tag{6}$$

where α_r^2 is the homodyne intensity and α_r is the relaxation

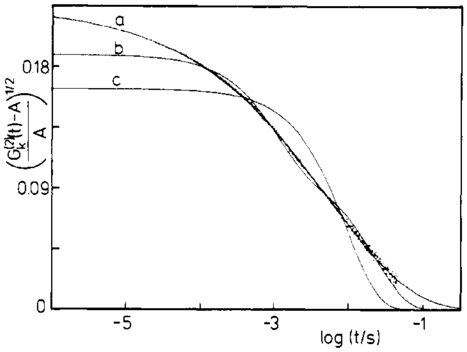

Figure 5. Comparison of the observed correlation function (a) with the bimodal distribution of relaxation times (b) and best single-exponential (c) fits.

strength. The last line in eq 6 follows because $g'(t)$ is assumed to be too fast for the correlator. The quantity α_r can be determined from eq 4 according to

$$\alpha_r = \left(\frac{G_{\text{obsd}}(0) - A}{bA}\right)^{1/2} \tag{7}$$

where $G_{\text{obsd}}(0)$ is the value of $G_{\text{obsd}}(t)$ at $t = 0$. The values for α_r obtained for VV and VH spectra for four PPG polymers as a function of temperature are shown in Figure 4B. Two points should be noted: First, the values of both VV and VH are about 50% of the total $g^{(1)}(t)$ and second, there is about a 10% difference between the (425, 1025) and (2025, 4000) molecular weight samples, the second sample group having a lower α_r. The low α_r in the VV component is presumably due to the Brillouin components and the intensity from the Rayleigh wing passing through the interference filter. In VH scattering, the low α_r is probably due to the Rayleigh wing and some fast segmental mode, which are in fact observed by the Fabry-Perot interferometer.[7] Finally, it should be pointed out that the fast segmental mode as probed by the interferometer depends on the macroscopic shear viscosity[7] as well as temperature, in contrast to the relaxation modes, which depend only on the temperature, as studied in the present work. It is our intent to carry out in future work a detailed interferometric concentration-dependence study of PPG to elucidate the nature of the fast component.

B. Correlation Function and Correlation Times. Clearly the correlation functions at all temperatures cannot be represented by a single exponential. Shown in Figure 5 are the departures of the best single-exponential fit (c) and the bimodal distribution of relaxation time fit (b) from the observed correlation function (a) for PPG 1025 at 214 K. However, the observed correlation function for each temperature appears to be well fit with the single Williams-Watts expression

$$g^{(1)}(t) = \exp(-t/\tau_0)^{\beta} \tag{8}$$

where τ_0 is the primary relaxation time and β $(0 < \beta \leq 1)$ is a measure of the width of the distribution of relaxation times. The parameter β equals unity for a single exponential and decreases as the width of the distribution becomes broader. The mean relaxation time $\bar{\tau}$ is related to the parameter τ_0 by

$$\bar{\tau} = \int_0^{\infty} \mathrm{d}t \, \exp(-t/\tau_0)^{\beta} = \frac{\tau_0}{\beta}\Gamma(\beta^{-1}) \tag{9}$$

where $\Gamma(\beta^{-1})$ is the gamma function. The William-Watts fits to the observed correlation functions are shown in Figure 3.

Table II
Mean Relaxation Times and the Relaxation Time Distribution Parameters β Obtained for VV and VH Correlation Functions

MW	T/°C	$\bar{\tau}_{\text{VV}}$/s	β_{VV}	$\bar{\tau}_{\text{VH}}$/s	β_{VH}
425	−50.2	2.09×10^{-4}	0.38		
	−53.1	6.14×10^{-4}	0.37		
	−53.8	8.3×10^{-4}	0.38		
	−57.0	3.67×10^{-3}	0.40	4.5×10^{-3}	0.48
	−59.6	1.32×10^{-2}	0.41		
	−59.9			1.3×10^{-2}	0.58
	−64.1	1.26×10^{-1}	0.46		
1025	−46.1	3.9×10^{-5}	0.39		
	−50.5	1.64×10^{-4}	0.39		
	−55.5	1.88×10^{-3}	0.39		
	−59.3	1.69×10^{-2}	0.40	1.8×10^{-2}	0.52
	−61.8	6.7×10^{-2}	0.40		
2025	−53.4	5.25×10^{-4}	0.37		
	−56.2	1.96×10^{-3}	0.38		
	−59.0	8.4×10^{-3}	0.39	1.1×10^{-2}	0.52
	−61.9	4.0×10^{-2}	0.40	5.6×10^{-2}	0.51
4000	−52.9	4.17×10^{-4}	0.37		
	−56.3	2.56×10^{-3}	0.37		
	−59.6	1.15×10^{-2}	0.39		
	−63.0	1.48×10^{-1}	0.40	1.9×10^{-1}	0.50

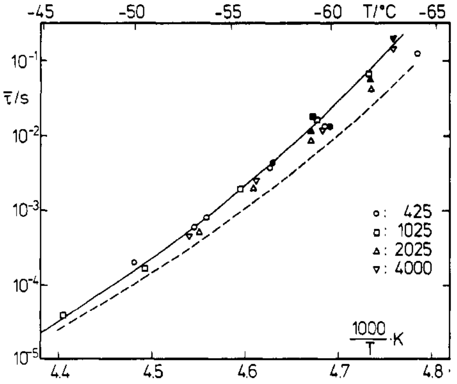

Figure 6. Mean relaxation times ($\bar{\tau}$) plotted vs. temperature for four PPG polymers. Empty symbols denote $\bar{\tau}$ calculated from the VV spectra and solid symbols denote $\bar{\tau}$ calculated from the VH spectra.

Shown in Table II are values of β and $\bar{\tau}$ calculated with eq 9 for PPG of various molecular weights as a function of temperature, for both VV and VH spectra. The values of $\bar{\tau}$ obtained in VV and VH scattering are plotted as a function of temperature for all four polymers in Figure 6. Since the depolarization ratio is small for PPG, the VV spectra are essentially due to the isotropic scattering component and the VH spectra reflect only the anisotropic component. One notes that both VV and VH scattering give nearly the same $\bar{\tau}$, consistent with results found for polystyrene,[11,12] 2,4-pentanediol,[25] and *o*-terphenyl.[26] The mean relaxation times at a given temperature are insensitive to molecular weight. The $\bar{\tau}$ value increases with decreasing temperature, as shown in the Arrhenius plot of Figure 6. Over the temperature range −45 to −65 °C, the temperature variation of $\bar{\tau}$ does not follow the Arrhenius equation with a constant activation energy. A fit of ln $\bar{\tau}$ values for PPG 1025 to the Antoine–WLF equation of the form

$$\ln \bar{\tau} = \ln \bar{\tau}_0 + B'(T - T_0') \tag{10}$$

gives values for $\bar{\tau}_0 = 7.29 \times 10^{-14}$ s, $B' = 1137$ K, and $T_0' = 170$ K. The B' and T_0' values are close to the corresponding values for viscosity (see Table I).

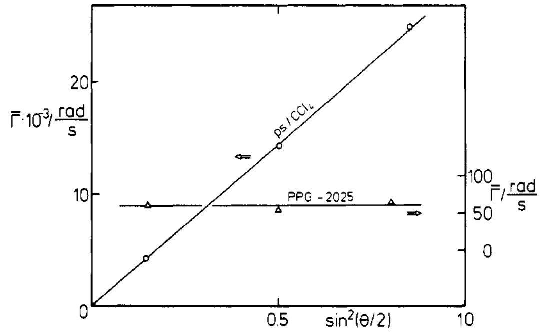

Figure 7. Mean relaxation rates ($\bar{\Gamma} = \bar{\tau}^{-1}$) obtained for PPG 2025 plotted vs. $\sin^2(\theta/2)$, to illustrate the independence of the scattering angle θ. Polystyrene–CCl_4 data are also included to show the calibration of the proper q^2 dependence.

In Figure 2, η_0, B, and T_0' obtained by fitting the measured viscosity data of PPG to eq 1 are plotted as a function of the molecular weight (M). One notes that while B and T_0 are independent of M, η_0 is proportional to M. The linear dependence on molecular weight for the shear viscosity of a bulk polymer liquid is expected because the flow of a long macromolecule requires a cooperative motion among all segments of the molecular chain. Thus, the viscosity of a polymer melt is expected to increase with molecular weight initially until M exceeds a value above which complex intermolecular interaction, such as chain entanglement, occurs. The linear variation of η_0 with M observed in the four PPG samples thus indicates the absence of a strong intermolecular interaction in this molecular weight range. The independence of M for parameters B and T_0 can be understood in terms of conformational properties. In fact, using a simple three-state rotational isomer model, Miller has related B to the barrier to rotation about the main-chain bonds by the expression $E_0 = RB$ (R being the gas constant) and T_0 to the conformational entropy.[27] In this picture, the viscosity of PPG is considered as due to the coordination of intrachain segments whose motions are associated with the rotational isomerization about the chain backbone. Thus according to this model, the rotational barrier E_0 about the chain backbone for PPG is equal to 1.90 kcal/mol for viscosity, which is about equal to the RB' value (2.2 kcal/mol) obtained from the fit of $\bar{\tau}$ data to eq 10. These values are consistent with those found in the corresponding polymers.[27] An Arrhenius fit for the $\bar{\tau}$ data would give an activation energy equal to 46.2 kcal/mol, which is consistent with the high activation energy value obtained for polystyrene[12] near T_g. But, as one sees clearly here, the Arrhenius fit does not bring forth the basic physical picture associated with the temperature variation of η_s and $\bar{\tau}$.

The fact that B' and T_0' are close to the corresponding values for viscosity suggests that local modes of molecular motion associated with the conformation transformation are the mechanisms which are responsible for the homodyne beating spectra of the PPG at temperatures near T_g. The reorientation or translational motion involving a whole molecular unit does not play a role, as clearly shown by the molecular weight independence of $\bar{\tau}$.

To rule out the possible contribution of collective propagating modes or the presence of the defect diffusion mechanism which is found to be present in bulk siloxane polymer liquids,[13] we have carried out an angular-dependent experiment for PPG 2025 at -61 °C. The results at three scattering angles are shown in Figure 7, together with the polystyrene–CCl_4 solution data serving as a calibration for the proper angular dependence. The absence of the scattering vector and of the molecular weight dependence shows clearly that the distribution of the relaxation times is neither associated with defect diffusion nor involves the collective modes. A mechanism such as the Rouse–Zimm modes observed in the dielectric relaxation loss in PPG 2025 and 4000 by Baur and Stockmayer[14] is apparently inactive in light scattering.

While in dilute polymer solution, concentration fluctuations which give rise to the homodyne spectrum are accounted for by a translational diffusion mechanism, and the relaxation time has a q^{-2} dependence. In the bulk or as the concentration is increased beyond the semidilute region, the diffusion of the center of mass of the polymer chain is drastically slowed down, and localized segmental motion leading to structural relaxation plays a dominant role in the scattering spectrum. Scattering from localized segmental motion in concentrated polymer solution or in the bulk has been shown to be independent of q.[28]

Recent theoretical and experimental work of de Gennes,[29,30] Doi and Edwards,[31] Klein,[32] and others[33,34] has led to the view that diffusion of polymer molecules in the bulk and in concentrated solution may occur by reptation. The theory deals with long polymer chains and requires that the conformational behavior of a polymer chain be represented by a large number of statistically independent subunits. For low molecular weight samples, such as the PPG used in the present study, this approximation is probably not valid. The prediction of the molecular weight dependence of the relaxation times associated with reptation and with tube reorganization by de Gennes[29,30] and by Doi and Edwards[31] is not realized in the present low molecular weight poly(propylene glycol) system, despite the fact that a recent PPG Kerr-effect relaxation study has indicated a $\tau \propto M^{-2}$ dependence for PPG 2025,[35] predicted by de Gennes[29,30] for a reptating chain. However, a similar analysis of the Kerr-effect data for PPG 4000 has yielded a $\tau \propto M^{-3.7}$ dependence.[35] This indicates that the Kerr data reported in ref 35 is probably reflected by other mechanisms, regardless of the fact that in principle the Kerr-effect relaxation is related to the reorientational motion of the polymer segments.

Depolarized light scattering in a liquid composed of small optically anisotropic molecules is due to reorientation of the molecules. The reorientation relaxation can be described by[36]

$$\tau_R = V\eta_s/k_BT + C \qquad (11)$$

where V is the hydrodynamic volume of the reorienting unit and k_B is the Boltzmann constant. C is a small intercept observed experimentally for some simple molecular liquids.

For a liquid consisting of macromolecules, the depolarized light spectrum cannot be interpreted in terms of overall molecular reorientation or reorientation of chain segments alone; the position of the segment center of mass, which also appears in the time correlation formula in the VH spectrum, cannot be neglected. While the depolarized scattering spectra of PPG 425 and solutions of PPG 425, 1025, and 2025 in cyclohexane at high temperature (>294 K) are shown to reflect the segmental motion of the polymer backbone, at a given η_s/T value the relaxation times for dilute solutions were found to be higher than those for concentrated solutions.[7] This suggests the inadequacy of eq 11, despite the fact that the segmental motion is known to play a significant role in this temperature range.

As shown in Table II, in the temperature range (-45 to -65 °C) investigated in the present work, the mean relaxation time $\bar{\tau}$ from anisotropic scattering is equal to the isotropic relaxation time. Thus, one can reasonably assume

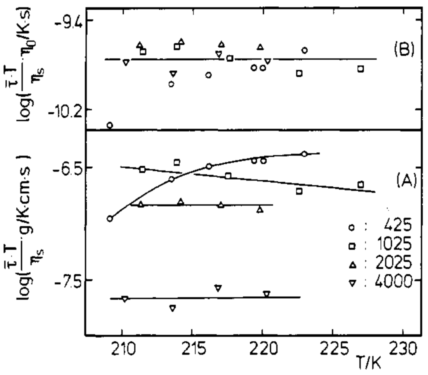

Figure 8. (A) $\bar{\tau}T/\eta_s$ and (B) $\bar{\tau}T\eta_0/\eta_s$ plotted vs. temperature for four PPG samples. A logarithmic scale is used for the vertical axis.

that both isotropic and anisotropic scattering spectra in the homodyne experiment arise from the same process. If one assumes that the anisotropic scattering spectrum is due to reorientation of segments, then a plot of the quantity $\bar{\tau}T/\eta_s$ (which according to eq 11 is proportional to the hydrodynamic volume of the reorienting unit) vs. T should be constant and the constant should increase with increasing molecular weight. Such a plot is presented in Figure 8A for all four PPG's, in disagreement with the expected result. thus, $\bar{\tau}$, as monitored in the VH scattering spectrum, does not reflect the simple polymer backbone reorientation mechanism indicated by eq 11.

However, considering the fact that $\bar{\tau}$ depends on temperature and is independent of molecular weight, it is likely that the relaxation time $\bar{\tau}$ is determined by an average local viscosity appropriate for the reorienting segmental unit rather than the macroscopic shear viscosity. Since η_0 is proportional to the molecular weight (Figure 2), it is reasonable to assume that the local viscosity is proportional to η_s/η_0 and, as such, the appropriate Stokes–Einstein plot for $\bar{\tau}$ should be given in terms of the average local viscosity (η_s/η_0). The $\bar{\tau}T/(\eta_s/\eta_0)$ vs. T plot, as shown in Figure 8B, indeed yields the expected molecular weight independent result, thus suggesting that reorientation of a submolecular unit is responsible for the anisotropic scattering spectrum. This result clearly shows the importance of carrying out a molecular weight dependent study in order to arrive at a correct picture regarding the relaxation mechanism.

The dielectric relaxation data presented in Figure 6 are calculated from $\tau_d = 1/(2\pi f_m)$, where f_m is the frequency in cycles per second at which the maximum loss occurs, as obtained for PPG 4000 reported by Yano et al.[15] At −65 °C, τ_d is shorter than $\bar{\tau}$ by a factor of 3.5 and at −45 °C, the ratio decreases to 1.5. While the difference in the two values is greater than the experimental uncertainty, it is not significantly large.

As mentioned previously, for PPG at low temperature one may expect $\tau_d \simeq \bar{\tau}$. However, it should be emphasized that the dielectric relaxation technique probes relaxation processes associated with dynamic variables of odd parity and light scattering monitors those of even parity. In general, the two techniques do not monitor the same relaxation function. However, even if is it assumed that both techniques monitor the same relaxation function, one can show that for the William–Watts function with $\beta = 0.4$, $\bar{\tau} = 0.66\tau_d$;[37] that is, the dielectric relaxation time τ_d is about a factor of 1.2 longer than the average light scattering relaxation time. While the difference between the two relaxation times is not large for PPG, the quantitative comparison between the two results clearly shows that these techniques are probing different aspects of, essentially, the same molecular motion.

In general, the α mode in the dielectric relaxation is due mainly to collective motions involving a number of polymer chains, and the β mode is sensitive to the local segmental motion of dipole moments in the chain. The mechanisms which give rise to the β peak are basically the side-group orientation or the backbone motion associated with the conformational flip which changes the dipole orientation. On the other hand, the structural relaxation which is probed in Rayleigh–Brillouin scattering is affected only by the translational motion of the segmental center of mass. However, in the case when there is strong coupling between the segmental reorientation and the segmental center-of-mass motion, as believed to occur in the present polymer system, both light scattering and dielectric relaxation will reflect the different types of molecular motion.

It should be mentioned that with the exception of the present study, to our knowledge other bulk polymers have not been investigated as a function of molecular weight in previous homodyne beating spectroscopic studies. For bulk PPG, light scattering appears to be insensitive to the collective or α-mode motion. It is not known whether this result applies only to PPG or whether it is a general characteristic of bulk polymers that the α-mode motion does not cause a sufficient change of polarizability density to make it active in light scattering, although the result of a recent light beating study of bulk polystyrene above T_g has been associated with the α-mode motion.[10] Further studies of this aspect are in order.

It is interesting to mention that Lindsey, Patterson, and Stevens[11] have compared their light scattering results on polystyrene with the dielectric data and have found that $\bar{\tau}$ is longer than $\bar{\tau}_d$. In that paper, they provided reasons to explain why the light scattering result differs from the dielectric relaxation, in a reversal of the position previously held by Patterson.[12,38] While most of their arguments are consistent with what has been given in the present paper, it is not at all clear, as has been pointed out by them, that the mechanical modulus will always relax slower than the dielectric compliance, as found in polystyrene.

The fact that for PPG at low temperature $\bar{\tau}_R$ obtained from anisotropic scattering is equal to $\bar{\tau}$ from isotropic scattering is an important observation which needs further elaboration. This result has been found in several systems near the glass transition temperature, for example, in polystyrene[12] and nonpolymeric glass-forming liquids such as 2,4-pentanediol[25] and o-terphenyl.[26] To understand this result, we assume that each monomer serves as a scattering unit; then in VH scattering it can be shown that $g^{(1)}(t)$ is a measure of the correlation function $C_{ani}(q,t)$ (excluding fast processes such as the shear wave phenomena), given by

$$C_{ani}(\mathbf{q},t) = \langle \sum_{m,n} \sum_{i,j} \alpha_{yz}^{(m,i)}[\Omega_{mi}(0)]\alpha_{yz}^{(n,j)}[\Omega_{nj}(t)]e^{i\mathbf{q}\cdot[\mathbf{r}_{mi}(0)-\mathbf{r}_{nj}(t)]}\rangle \quad (12)$$

where $\alpha_{yz}^{(n,j)}[\Omega_{nj}(t)]$ is the yz component of the polarizability of polymer segments j in chain n at time t in the laboratory-fixed coordinate system; $\Omega_{nj}(t)$ and $\mathbf{r}_{nj}(t)$ are, respectively, the orientation angles and the position of the center of mass of segment j of chain n at time t. The angle brackets denote the ensemble average. On the other hand, except for a small part of the scattering intensity coming from anisotropic scattering, the correlation function $g^{(1)}(t)$ in PPG entering the VV spectrum is proportional to $C_{iso}(\mathbf{q},t)$ (excluding fast processes, such as longitudinal hypersonic wave and thermal conductivity) given by

$$C_{iso}(\mathbf{q},t) = \langle \sum_{m,n} \sum_{i,j} e^{i\mathbf{q}\cdot[\mathbf{r}_{mi}(0)-\mathbf{r}_{nj}(t)]}\rangle \quad (13)$$

Only the position of the segment center of mass is present in the isotropic scattering expression. For bulk polymers, eq 12 and 13 are complicated by the effects due to interactions of segments on different chains, and this prevents a rigorous calculation. However, some observations can be made from these general expressions.

One first notes in eq 12 the segmental reorientation is, in general, coupled to the center-of-mass motion. Within the same chain, if segments are close to one another, then the center-of-mass motion is affected by the segment reorientation which takes place when the conformation changes of chemical units in a scattering segment occur. In a polymeric fluid, in addition to the intermolecular effects, the anisotropic component as monitored in VH scattering reflects two mechanisms: segment reorientation and segmental center-of-mass motion. In contrast, according to eq 13, the isotropic scattering component which is responsible for most of the VV scattering intensity in PPg occurs only through the segmental center-of-mass motion. It should be emphasized that eq 13 is simply equal to the density–density correlation function. In bulk polymers, the density fluctuation occurs mainly due to the segmental center-of-mass motion.[21] Therefore, the fact that $\bar{\tau}$ is the same for both VV and VH in PPG indicates that the center-of-mass motion plays a dominant role in affecting the scattering process near the glass transition.

In bulk polymers, the effect of internal rotation barriers and the effect of intermolecular interactions on the conformation transitions due to the temperature change are believed to be the features which manifest themselves in the glass transition and the high-temperature dielectric or mechanical relaxation peaks.[15,20] However, as was mentioned previously, the characteristics of amorphous polymer near the glass transition can be discussed in terms of transitions between rotational isomeric states with a temperature-dependent activation energy which determines the rate of transitions. If one assumes that the conformational state of PPG can be discussed in terms of the poly(ethylene glycol) chain, the rotational isomeric state model would have one trans and two gauche conformations, with one gauche higher and the other lower in rotation barrier than the trans.[39] Helfand has pointed out[20] that the gauche migration step $\mathrm{PgttQ} \rightleftharpoons \mathrm{P'ttgQ'}$ or the gauche production step $\mathrm{PtttQ} \rightleftharpoons \mathrm{Pg^+tg^-Q'}$ will result in a translation of Q relative to P, where P and Q are the rest of the segments attached to the one under consideration. Furthermore, he has shown that the translation as induced by these conformational transitions is not seriously inhibited by the energy barrier. If these mechanisms are indeed important in affecting both the VV and VH scattering spectra, it then suggests that the reorientation of the chemical units is strongly coupled to the center-of-mass translational motion of the polymer segments. In this case, both VV and VH scattering spectra will have the same relaxation time.

As mentioned above, the reorientation of the component of the dipole moment bisecting the C–O–C bond angles, which is responsible for the principal loss peak in PPG, will result in a translation of polymer segments through the gauche migration or the gauche production mechanism. Further, considering the fact that the dielectric relaxation τ_d is due to the result of reorienting the perpendicular dipole component, it is not difficult to conclude that in PPG the segmental reorientation and the segmental center-of-mass motion are strongly coupled.

In passing, it should be noted that reorientation of the methyl group also occurs when the C–O–C unit flips. While the methyl group reorientation will not affect significantly the dielectric relaxation, it is expected to contribute to light scattering. Thus we conclude that the scattering intensity in PPG is due to the reorientation of the $\mathrm{C(CH_3)}$–O–C unit which also results in the translation of the monomer unit.

Further, in isotropic scattering, a complete relaxation dynamical process of density fluctuations (excluding the fast processes not monitored in the homodyne beating experiment) is present, whereas in anisotropic scattering only a limited subset of the translational relaxation processes is coupled to segmental reorientation, as clearly shown in eq 12. As a result, one expects to observe a wider distribution of relaxation times in the VV scattering spectrum than in the VH scattering spectrum. This conclusion is entirely consistent with the experimental results (see Table II), in which one finds that the β parameter for the VV spectra is smaller than that for the VH spectra. We expect this to be a general result for all systems in which strong coupling between translational and reorientation occurs.

Summary and Conclusion

Continuing the effort in the investigation of the segmental motion of bulk polymers, we have carried out a homodyne light beating spectroscopic study of undiluted liquid poly(propylene glycol) as functions of molecular weight and temperature from −45 to −65 °C. The shear viscosity has also been measured from −40 to −30 °C for PPG 425, 1025, 2025, and 4000. We have measured the homodyne correlation functions over the time scale 10^{-6} to 1 s and have deduced from them the mean relaxation times and the relaxation time distribution parameters as a function of temperature for both VV and VH scattering spectra. We have found that over the temperature range studied the mean relaxation times for both VV and VH spectra are the same, but the VV spectra have a broader relaxation time distribution. The mean relaxation times for both VV and VH spectra depend only on temperature and not on the viscosity associated with different molecular weight samples, in contrast to the result obtained previously at high temperature by interferometry. The temperature dependence of the viscosity and the mean relaxation time cannot be fitted to an Arrhenius equation; but they can be fit to the Antoine–WLF type of equation.

We have discussed the difference in the types of motion which are probed by dielectric relaxation loss and by light scattering experiments. We have pointed out that while the α-mode motion in bulk polymers is active in dielectric relaxation experiments, its effect on light scattering spectra has not been clearly demonstrated. Further, over this temperature range, we have not observed the molecular weight dependent collective mode associated with the reptation of the polymer chain, in contrast to the results of the relaxation Kerr-effect study of the same polymer by Williams and co-workers. Comparing the present light scattering mean relaxation times for VV and VH with the principal dielectric relaxation time data of Yano et al., we have suggested that the segmental reorientation is strongly coupled to the segmental center-of-mass motion in PPG as the glass transition is approached from above. We have obtained the rotation barrier energy to be about 2 kcal/mol for all four PPG polymers, despite the fact that the apparent activation energy deduced from the Arrhenius equation fit is as high as 48 kcal/mol. The result of this work indicates that the effect of localized segmental motions on the glass–rubber transition is a very important mechanism which cannot be overlooked in the interpretation of the light scattering data of bulk polymers near the glass transition temperature.

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Light Spectroscopy Investigation of Dilute and Semidilute Poly(dimethylsiloxane) Solutions

J. P. Munch,[†] J. Herz,[‡] S. Boileau,[§] and S. Candau*,[†]

Laboratoire d'Acoustique Moléculaire (ERA au CNRS), Université Louis Pasteur, 67070 Strasbourg Cedex, France, Centre de Recherches sur les Macromolécules, CNRS, 67083 Strasbourg Cedex, France, and Laboratoire de Chimie Macromoléculaire, Associé au CNRS No. 24, Collège de France, 75231 Paris Cedex 05, France. Received January 29, 1981

ABSTRACT: The hydrodynamic radius and the hydrodynamic correlation length of dilute and semidilute poly(dimethylsiloxane) solutions have been measured by light spectroscopy as a function of temperature and for various solvents. The results show that the hydrodynamic behavior of these systems cannot be described by the reduced temperature parameter alone and demonstrate specific polymer–solvent interactions.

Introduction

Recently, a number of papers have been devoted to the study of dilute and semidilute solutions of flexible polymers by light scattering.[1-8] In these studies, new experimental results as well as collected data were used to test the recent theories based on scaling concepts.[9] More especially, the radius of gyration R_G and the hydrodynamic radius R_H of macromolecules in dilute solutions were investigated as a function of molecular weight M_w and of temperature T. The scaling arguments developed by de Gennes[9] predict that both R_G and R_H are proportional to N^ν in a good solvent and for large values of N, which is the equivalent number of links in the statistical chain, and the most accurate value of ν is 0.588 ± 0.001.[10] From the experimental studies on the molecular weight dependence of R_G for different systems, the results give values of ν which are rather close to the theoretical one.

On the other hand, measurements of the translational diffusion coefficient of macromolecules using either an interferometric method[11] or, more recently, the light spectroscopy technique[12,13] led to a N^{ν_H} variation of R_H, with $\nu_H < \nu$ $(0.54 < \nu_H < 0.58)$.

[†] Université Louis Pasteur.
[‡] Centre de Recherches sur les Macromolécules.
[§] Collège de France.

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