polymer papers

Brillouin scattering studies of structural relaxations in poly(propylene glycol)

L. Börjesson, J. R. Stevens* and L. M. Torell
Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden
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Structural relaxation processes in poly(propylene glycol) (PPG), molecular weight 10 000, have been examined at the high frequencies of Brillouin scattering. By combining the high-frequency results with reported photon correlation data, the relaxation time τ is established over a wide timescale of 1–10^{-11} s. Over the whole range, the relaxation times can be described by a single equation, $\tau = \tau_0 \exp[B/(T - T_0)]$, where $\tau_0 = 3.5 \times 10^{-14}$ s, $T_0 = 170$ K and $B = 1169$ K. At high temperatures ($1/T \rightarrow 0$), τ extrapolates to the characteristic bending and stretching times of the polymer chain (10^{-14} s). At the other extreme, the value of T_0, the so-called 'ideal glass' transition temperature, is in accordance with viscosity, photon correlation and dielectric relaxation results. Single relaxation time theory does not fit the experimental results; the width is characterized by $\beta = 0.4$ in a Williams–Watts distribution of relaxation times. The observed behaviour is explained in terms of restricted local intrachain motions.

(Keywords: Brillouin scattering; poly(propylene glycol); structural relaxation; Williams–Watts distribution; distribution of relaxation times; hypersonic properties)

INTRODUCTION

We present results from a Brillouin scattering study of poly(propylene glycol) (PPG) of a higher molecular weight (10 000) than the PPG systems previously investigated by light scattering techniques. By using the high-frequency short-time data of Brillouin scattering in PPG 10 000 together with reported longer-time data from photon correlation measurements of PPG 425–4000[1], the processes responsible for light scattering can be followed over a very wide timescale extending from the photon correlation time range 1–10^{-6} s to Brillouin times at 10^{-11} s. Relaxation processes of the polymer chain can thereby be identified, analysed and compared over a broad temperature range, which is the aim of the present study.

It has been shown at lower temperatures that the relaxation phenomenon observed in PPG by depolarized light scattering (photon correlation)[1] is also present as one of the processes probed by dielectric relaxation loss measurements[2–4]. In dielectric investigations of PPG, two relaxation ranges above the glass transition temperature, T_g, are observed[2–5]: a high-temperature small-magnitude relaxation (α') which is dependent on molecular weight and a lower-temperature process (α) which is insensitive to molecular weight and of considerably larger strength. It is suggested[2,5] that the weaker process, α', is related to the cumulative dipole moment along the polymer chain and is dependent on motions of whole chains, whereas the stronger one, α, is due to the local orientations of the individual dipole moments of the C–O–C bond and is dependent on local hindered segmental reorientations within the chain. It is the latter intrachain process (α) which, when 'frozen in' over all possible times, leads to the glass transition.

In light scattering measurements, the structural relaxation observed in PPG has been identified by Wang *et al.*[1,6] to be related to the translational motion of local segments of the polymer backbone. These local motions lead to a relaxation behaviour which is independent of long or short chain lengths. This is the conclusion of Wang *et al.*[6] from light scattering results for PPG molecular weights in the range 425–4000. At low temperatures the relaxation times obtained[1] are in agreement with the relaxation times of the α process reported from the dielectric relaxation studies[2,3]. Therefore it is suggested[1] that in PPG, as the glass transition is approached, the segmental centre of mass motion observed by light scattering is strongly coupled to the segmental reorientations studied by dielectric relaxation measurements. However, when the temperature (and the probe frequency) is increased the relaxation time curves determined by the two techniques diverge[1–4,6]. In the hypersonic region (gigahertz frequencies) Patterson *et al.*[7] reported the existence of two relaxation processes from Brillouin scattering spectra of PPG 4000. The lower-temperature relaxation is greater in strength and occurs in the same temperature range as the process observed by Wang *et al.*[6] (and confirmed by us[8]) from Brillouin scattering in a series of PPG of different molecular weights. Patterson *et al.*[7] conclude that this relaxation is the secondary (β) process, in disagreement with Wang *et al.*[6] who attributed it to the primary (α) process. The second high-temperature relaxation of weaker strength observed by Patterson *et al.*[7] is identified by these authors as the primary (α) process. Wang *et al.*[6] do not observe this high-temperature relaxation.

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* On leave from the Department of Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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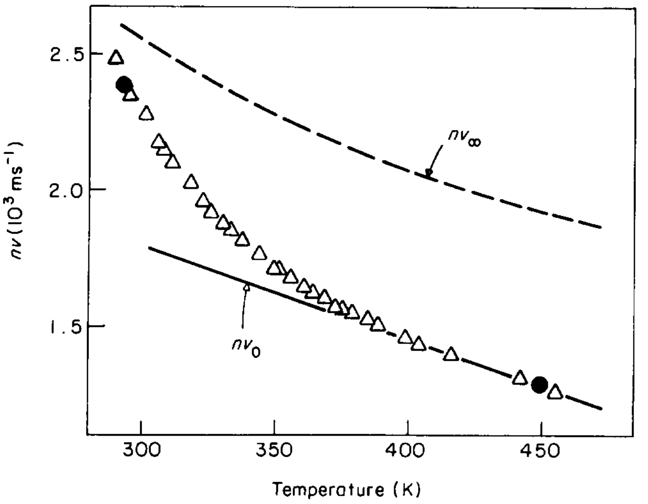

Figure 1 Temperature dependence of the hypersonic velocity for PPG 10000. Present results are shown as open triangles. The two end values shown as closed circles represent the corresponding velocity range from the study of PPG 4000 by Patterson *et al.*[7]. The full line for nv_0 is extrapolated from the high-temperature results. The broken curve for nv_∞ is obtained from the fitting procedure for $\beta=0.4$ using the low-temperature value as a fiducial point.

The two relaxation ranges of Patterson's study of PPG 4000 were manifested by two absorption peaks of different magnitude and partly overlapping[7]. In the present work a polymer of higher molecular weight, PPG 10000, has been used for a detailed high-frequency investigation. A higher molecular weight was chosen since, if the second (high-temperature) process of Patterson's report has a molecular weight dependence, then the corresponding peak will be observed at higher temperatures[4,5] and the overlapping will diminish. Also, to increase the accuracy of the Brillouin width, we have taken advantage of a higher-contrast (triple-passed) Fabry–Perot interferometer.

In Brillouin scattering investigations any observed relaxation phenomenon is structural in character and in the short-time region ($\sim 10^{-11}$ s). Through this technique the acoustical properties of the scattering medium are probed at high frequencies (~ 10 GHz). For an isotropic medium the frequency shift of the Brillouin lines, f_B, is related to the velocity of sound, v, through the relation:

$$v = f_B \lambda_0 / 2n \sin(\theta/2) \tag{1}$$

where λ_0 is the wavelength of the incident light, n the refractive index of the medium and θ the scattering angle. In a frequency/temperature region where relaxation effects occur, the acoustic wave will be attenuated. This will lead to velocity dispersion and absorption, which for a single relaxation time process are expressed by:

$$\frac{v^2 - v_0^2}{v_\infty^2 - v_0^2} = \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \tag{2}$$

$$\alpha = \frac{v_\infty^2 - v_0^2}{2v^3}\,\frac{\omega^2\tau}{1+\omega^2\tau^2} \tag{3}$$

where v_0 and v_∞ are low- and high-frequency limits of the velocity, respectively, and α is the absorption coefficient related to the broadening of the Brillouin line Γ_B according to:

$$\Gamma_B = \alpha v / 2\pi \tag{4}$$

The single relaxation time τ is a function of temperature, which is usually taken to be Arrhenius in the low-viscosity region.

EXPERIMENTAL

The Brillouin scattering set-up includes a single-mode laser, a triple-passed piezoelectrically scanned Fabry–Perot interferometer and photon counting equipment. The 488 nm 'blue' line of an Ar^+ laser was used. A Burleigh DAS 10 stabilization system optimized the finesse of the scanning Fabry–Perot interferometer. All the spectra were recorded using a free spectral range of 16.00 GHz and 90° scattering geometry. The weight-average molecular weight, M_w, of the PPG was 10000 and the number-average molecular weight, M_n, was 5600. The molecular weight was determined by the Department of Polymer Technology, Chalmers University of Technology. Dust-free PPG 10000 samples were obtained by pressure filtration through a 1 μm Millipore filter into the light scattering cell in a dry N_2 atmosphere. The sample was degassed and sealed, and then placed in a thermostat. The cell was cylindrical in shape (diameter 7 mm) and with an optical window fused to the bottom. The experimental system and the thermostat have been described previously[9]. It should be noted that reference made to PPG 425–4000 refers to samples with M_n in the range of 425 to 4000 but with $M_w/M_n \approx 1$.

RESULTS AND DISCUSSION

Velocity dispersion and acoustic attenuation

Brillouin spectra of PPG 10000 in the liquid state were recorded from room temperature to ~ 450 K. From the measured Brillouin frequency shift f_B and half-width Γ_B, the velocity v and absorption coefficient α were obtained. Since the refractive index n is not known, values for nv and α/n were calculated using equation (1) and (4) and the corresponding data are shown in *Figures 1* and *2*.

The frequency shifts of the Brillouin components decreased rapidly with temperature from ~ 7 GHz to ~ 3.5 GHz over a temperature range of about 150 K. The

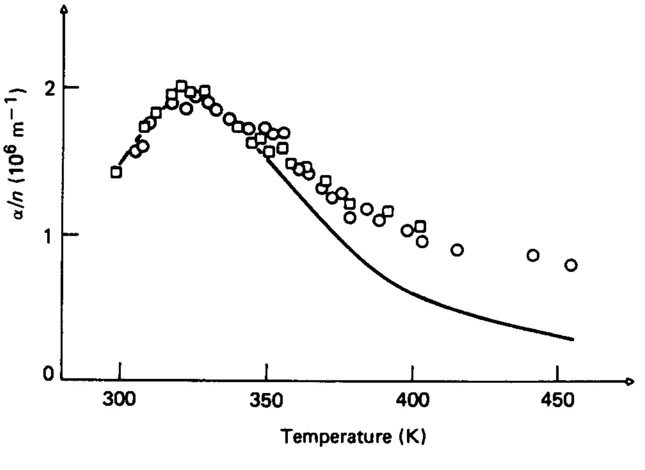

Figure 2 Temperature dependence of the attenuation in PPG 10000. Open circles (temperature up) and open squares (temperature down) are experimental data and the full curve represents a single relaxation time fit based on equation (3) with an Arrhenius temperature dependence for τ ($=8.74\times10^{-15}\exp(E/kT)$; $E=5.2$ kcal mol^{-1})

results for the corresponding hypersonic velocity in PPG 10 000 *versus* temperature (see *Figure 1*) show a nonlinear behaviour, a dispersion curve, in accordance with previous findings by Wang *et al.*[6] from studies of PPG of lower M_n and confirmed by us[8]. Wang *et al.* measured the hypersonic velocity over a range of molecular weights, PPG 425–4000, and found no dependence on M_n. However, for the relaxed systems our measurements[8] show a slight dependence of the hypersonic velocity on M_n for low M_n (400–4000); the velocity is increasing with decreasing M_n due to a decrease in the flexibility of the polymer backbone with decreasing M_n as determined from the D-LAM (disordered longitudinal acoustic mode) Raman complex mode[10]. The effect is small and only observable at higher temperatures and it is discussed in detail in ref. 8. Since the velocity difference in the temperature range over which relaxation occurs is negligibly small, the effect is of little interest in the present study. In the report of Patterson *et al.*[7] the hypersonic velocity data for PPG 4000 are in agreement with those of Wang *et al.* and with present results for PPG 10 000. (See *Figure 1*, where the limits of the velocity range obtained by Patterson *et al.* are presented as well.)

The approximate independence of velocity with molecular weight is supported by recent preliminary results from our laboratory from studies of high molecular weight poly(propylene oxide) (HMPPO), $M_w > 10^5$, which give velocity values in accordance with those of the present low molecular weight study. The similarity in the velocity data reflects the apparent lack of dependence of the glass transition temperature T_g on molecular weight[4] in the range 400 to $>10^5$. It is, however, to be noted that the viscosity properties change markedly in the series of different PPG[1,11]. At room temperature HMPPO is an elastomer, whereas at the other extreme, PPG 400 is a low-viscosity liquid. All the low molecular weight PPG (400–10 000) are liquids with increasing viscosity at room temperature from low-viscosity PPG 400 to rather viscous PPG 10 000. Despite the macroscopic change from an elastomer to a liquid by decreasing the degree of polymerization, a typical mechanical property such as the longitudinal sound velocity is hardly affected. The velocity seems to be determined by the local ordering within the chain, which is independent of M_n, rather than by the behaviour of entire macromolecules. This is therefore also true for the velocity-related elastic properties, such as longitudinal modulus, compressibility, etc. In polymers, these values therefore reflect the local structure rather than the macroscopic behaviour.

The dispersion of the velocity indicates relaxation effects which are confirmed by the absorption measurements. The increasing and later decreasing width of the Brillouin lines with increasing temperature corresponds to an absorption with a maximum value obtained at a temperature $T \approx 325$ K. Only one absorption peak is observed (see *Figure 2*) in accordance with the findings of Wang *et al.* for PPG 425–4000[6] and it is located in the same temperature range. This is in contrast with the results of Patterson *et al.*[7] of two absorption peaks reported for PPG 4000. The lower-temperature peak in the report of Patterson *et al.*, i.e. the large-amplitude process at 323 K, corresponds very well with our findings. However, the high-temperature peak of relatively small magnitude is reported at 373 K where no indication of an extra peak was present in our spectra for PPG 10 000. If the high-temperature process reported by Patterson *et al.*[7] for PPG 4000 is dependent on the molecular weight of the polymer chain, then it is expected to occur at a higher temperature in our case of PPG 10 000 and it should be clearly resolved[4,5]. As can be seen in *Figure 2* no such absorption is present.

Relaxation characteristics

In the photon correlation study at longer times and lower temperatures, a broad distribution of relaxation times was observed for PPG 425–4000[1]. We have previously noted that, for ionic glass-forming liquids, the broad distribution of relaxation times found at lower probe frequencies/temperatures sharpens up to become a single relaxation time in the hypersonic region[12–14]. To discuss the high-temperature behaviour observed at the shorter times of Brillouin scattering, single relaxation time expressions, equations (2) and (3), have been used as a starting point for our analysis. Therefore expressions for nv_∞ and nv_0 as a function of temperature were required. The first, nv_∞, was obtained by combining the low-temperature velocity result at 263 K of Patterson *et al.*[7] with present nv_∞, determined at the temperature of the peak absorption (325 K) by using the peak condition ($\omega\tau \approx 1$) and equation (2). A linear temperature dependence for $(nv_\infty)^{-2}$ was assumed[9,13].

The temperature dependence of the low-frequency velocity v_0 is obtained from the linear region of the velocity dispersion at high temperatures (see *Figure 1*) and is

$$nv_0 = 2839 - 3.464T(\mathrm{K}) \qquad \mathrm{m\,s^{-1}} \tag{5}$$

which corresponds to the velocity of a relaxed system independent of whether a single relaxation time or a distribution of relaxation times is appropriate. The resulting calculated absorption curve is obtained by combining equations (2) and (3) and is shown in *Figure 2* as a full curve. The good agreement close to the peak is a consequence of the fitting procedure since the parameter nv_∞ was chosen from the peak condition assuming $\omega\tau = 1$. It is more significant that departures from the theoretical curve begin 20 K from the peak value and thereafter increase with temperature. Single relaxation time theory cannot explain the short-time behaviour of the polymer in contrast to earlier findings from light scattering in ionic liquids[12–14]. The results are also contrary to the conclusions of Lin and Wang[15] in their light scattering study of PPG. In this study the Brillouin spectra were fitted to their theory using three adjustable parameters and assuming single relaxation time behaviour.

Relaxation time distribution

It has generally been observed[16] that photon correlation spectra can be fitted with a fractional power exponential or William–Watts (WW) relaxation function $\phi(t)$:

$$\phi(t) = \exp(-t/\tau)^\beta \tag{6}$$

where τ is the relaxation time representing the 1/e point and $0 < \beta \leqslant 1$. The value of β is a measure of the width of the distribution of relaxation times, being 1 for a single relaxation time. The average relaxation time is given by

$$\langle\tau\rangle = (\tau/\beta)\Gamma(1/\beta) \tag{7}$$

where $\Gamma(x)$ is the gamma function.

The photon correlation results of Wang *et al.*[1] were no exception. These authors found that $\langle\tau\rangle$ at a given temperature was independent of M_n and that β was in the range 0.37–0.41 and essentially independent of M_n and temperature. Johari[2] in dielectric relaxation measurements also found that β for the α relaxation in PPG 4000 was independent of temperature.

For the Brillouin scattering study reported here, the relaxation characteristics can be investigated from a master plot of the reduced real and imaginary parts, N' and N'', of the complex longitudinal modulus M^*. At a particular temperature $T>T_g$:

$$M^*(\mathrm{i}\omega)=M'(\omega)-\mathrm{i}M''(\omega) \tag{8}$$

The reduced parts N' and N'' are determined from experimental data at a particular temperature according to the following definitions:

$$N'(\omega)=\frac{M'(\omega)-M_0(\omega)}{M_\infty(\omega)-M_0(\omega)}=\frac{v^2(\omega)-v_0^2(\omega)}{v_\infty^2(\omega)-v_0^2(\omega)} \tag{9}$$

$$N''(\omega)=\frac{M''(\omega)}{M_\infty(\omega)-M_0(\omega)}=\frac{2\alpha(\omega)v^3(\omega)}{\omega[v_\infty^2(\omega)-v_0^2(\omega)]} \tag{10}$$

Recall that we actually measured nv and α/n as functions of temperature and that we assumed a linear temperature functional relationship for nv_0 from our data (equation (5)). Only one value of nv_∞ is known, that at 263 K (ref. 7). We used this value as our fiducial point and allowed values of nv_∞ at other temperatures to be adjustable.

Analytically, N' and N'' can be expressed as:

$$N'(\omega')=\omega'\int_0^\infty \mathrm{d}t'\sin(\omega't')\phi(t') \tag{11}$$

$$N''(\omega')=\omega'\int_0^\infty \mathrm{d}t'\cos(\omega't')\phi(t') \tag{12}$$

where

$$\phi(t')=\int_0^\infty \mathrm{d}\tau\, g(\tau)\exp(-t') \tag{13}$$

and $t'=t/\tau$, $\omega'=\omega\tau$ and $g(\tau)$ gives the distribution of relaxation times.

Unfortunately we do not know $g(\tau)$ so we assume a WW distribution of relaxation times and use equation (6) in equations (11) and (12) instead of equation (13).

From equations (9) and (10) we can calculate a set of values of N' and N'' for the temperatures at which measurements were taken. Equations (11) and (12) with equation (6) can be numerically integrated using a range of values of β and assuming that β is independent of temperature. This gives us values of N' and N'' at various values of ln ω' for a range of values of β. To compare these two sets of data (N' and N'' vs. T (experimental) with N' and N'' vs. ln ω' (analytical)) and to determine the WW relaxation parameters $\langle\tau\rangle$ and β, we require a relationship between ln ω' and temperature. Fortunately, there is an empirical relationship that has been used successfully to fit the experimental data for most (if not all) glass-forming systems at temperatures above the glass transition. This relationship has the form:

$$\ln\langle\tau\rangle=\ln\langle\tau_0\rangle+B/(T-T_0) \tag{14}$$

where $\langle\tau_0\rangle$, B and T_0 are adjustable parameters and where T_0 is often identified with the 'ideal glass' transition.

As our initial values for comparing the two sets of data referred to above we used the values of $\langle\tau_0\rangle$, B and T_0 as published by Wang *et al*[1] for PPG 425–4000, i.e. $\langle\tau_0\rangle=7.29\times10^{-14}$ s, $B=1137$ K and $T_0=170$ K. Equation (7) was used to relate $\langle\tau\rangle$, β and τ. By an iterative procedure we found the best values of $\langle\tau_0\rangle$, B, T_0, β and nv_∞ as functions of temperature (with the one known point at 263 K). We obtained $\beta=0.4$, $\langle\tau_0\rangle=3.46\times10^{-14}$, $B=1169$ K and $T_0=170$ K, very close to the results obtained by Wang *et al.*[1]. A plot of nv_∞ for $\beta=0.4$ is shown in *Figure 1* (broken curve). *Figures 3a* and *3b* are plots of N' and N'' *versus* $\log_{10}\omega\tau$ showing the fit with equations (11) and (12) plus the empirical equation (6) (broken lines) and also, for comparison, calculations for a single relaxation time (full curves).

It is interesting to notice that the broad distribution of times obtained in the present high-frequency study of PPG 10000 is in contrast with the general relaxation characteristics found for glass-forming *ionic* liquids[12–14]. In these ionic liquids a broad distribution of relaxation times seems to be the normal case at lower temperatures,

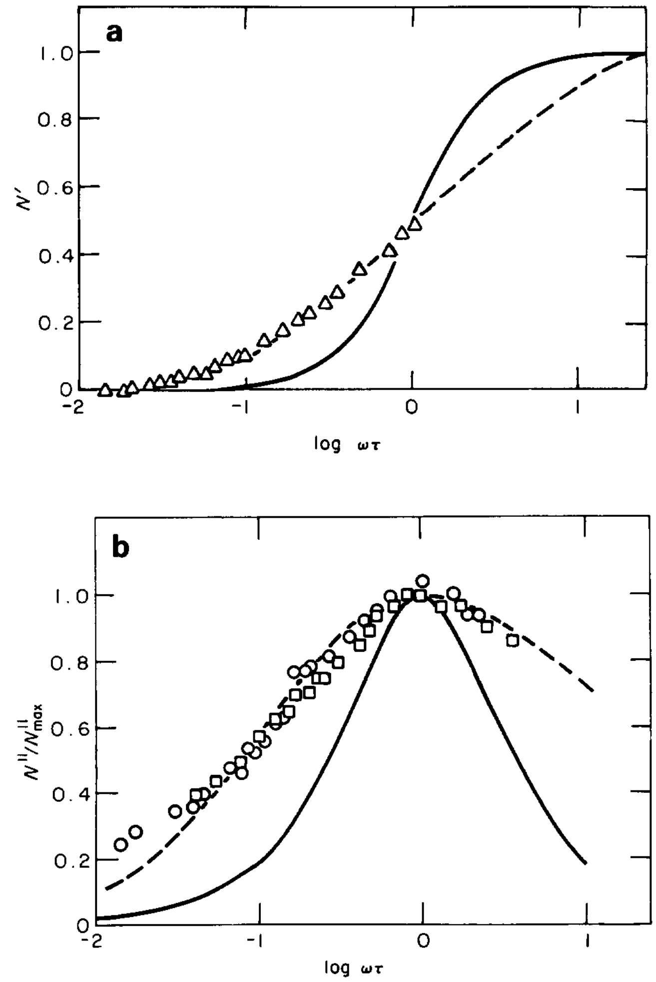

Figure 3 (a) Normalized real N' *versus* $\log_{10}\omega\tau$ for PPG 10000. Open triangles are experimental points with results for increasing and decreasing temperature strongly overlapping. The broken curve is obtained using equation (11) with equation (6) and $\beta=0.4$. The full curve is for a single relaxation time. (b) Normalized imaginary N'' *versus* $\log_{10}\omega\tau$ for PPG 10000. Open circles are experimental points for increasing temperature and open squares are for decreasing temperature. The broken curve is obtained using equation (12) with equation (6) and $\beta=0.4$. The full curve is for a single relaxation time

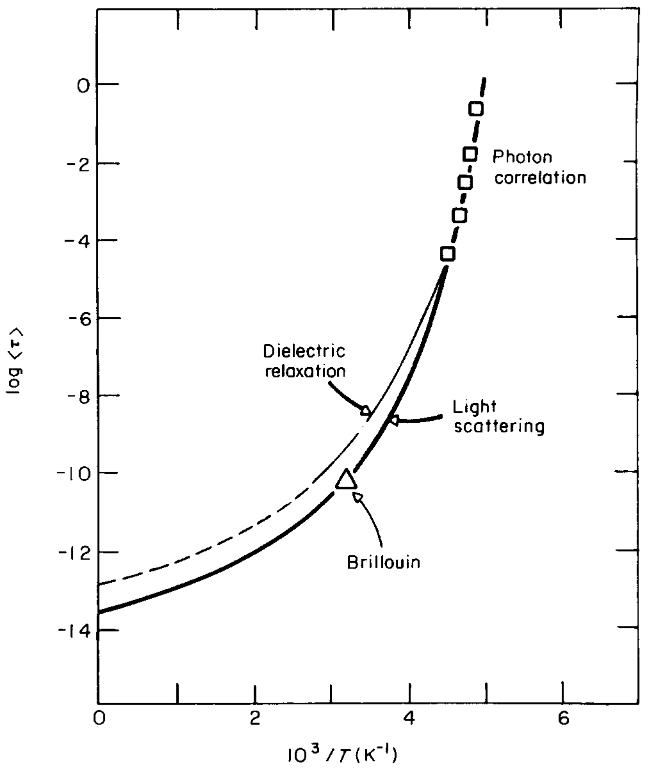

Figure 4 $\text{Log}_{10}\langle\tau\rangle$ *versus* temperature in PPG. The full curve marked 'light scattering' is based on photon correlation results[1] (□) and present Brillouin data (△), see equation (14). Dielectric relaxation results[3] are also shown for comparison

but with a temperature-dependent width, which narrows markedly to become a single exponential in the high-temperature/short-time region of Brillouin scattering. The structural relaxation time curve in these ionic glass formers follows closely that of the macroscopic viscosity, where a macroscopic behaviour including many relaxation processes can be probed at long times. Many of the processes are frozen out with increasing probe frequency, with a narrowing time distribution as a result. In PPG on the other hand, it is the *local* motions (microscopic viscosity) that contribute to the relaxations observed from the light scattering spectra. These motions are characterized by a broad distribution of relaxation times[1]· They are mobile enough even to follow the propagation of the present high-frequency (gigahertz) waves and consequently the relaxation time distribution stays constant. Motions of whole chains (macroscopic viscosity), however, do not influence the light scattering spectra, which therefore are relatively insensitive to molecular weight, to viscosity and to macroscopic behaviour as discussed in the subsection on 'Velocity dispersion'. At very high frequencies, there could conceivably be a narrowing of the distribution of relaxation times in PPG but there is no evidence for this at Brillouin frequencies.

General form of τ *vs.* T

From the results presented in the previous subsection, we have $\log_{10}\langle\tau_0\rangle = -13.5$ whereas Wang *et al.*[1] reported $\log_{10}\langle\tau_0\rangle = -13.1$. These values of $\langle\tau_0\rangle$ are to be compared with the shortest possible time process typical for polymers. For example, we draw attention to the D-LAM (disordered longitudinal acoustic mode) at 239 cm^{-1} ($\log_{10}\langle\tau_0\rangle = -13.7$) obtained from Raman scattering in PPG 2000 and attributed to bending or torsional motion of the polymer backbone or the C–C stretching or C–O–C stretching with vibration frequencies of typically 1000 cm^{-1} ($\log_{10}\langle\tau_0\rangle = -14.3$)[15]. We have previously found that the relaxation time in the limit $1/T \rightarrow 0$ is tending towards the inverse of the infra-red or Raman vibration frequency in glass-forming materials[12–14]. This is again demonstrated by present results obtained for polymers.

The average relaxation time curve (equation (14)) for PPG is presented in *Figure 4*, where results from photon correlation (PPG 425–4000[1]) are included together with the present results for PPG 10000. An outstanding feature of the relaxation time is demonstrated in *Figure 4*, where it can be seen that one single equation can describe the temperature dependence of the average relaxation time over a very broad time range, from the longest times of photon correlation (≈ 1 s) to the limiting times observed in Raman investigations ($\approx 10^{-14}$ s).

The high-temperature limit has already been discussed above. In the following the low-temperature limit will be examined. Here it is useful to discuss the empirical behaviour represented by equation (14) which was previously reported from dielectric relaxation measurements performed on PPG over a frequency range of nearly 12 orders in magnitude[3]. These results of Yano *et al.*[3] are also shown in *Figure 4*. At higher temperatures a longer relaxation time process is probed by the dielectric measurements than by the light scattering technique[3,6], which results in the longer-time prefactor ($\log_{10}\langle\tau_0\rangle = 12.8$) of equation (14). However, near the glass transition temperature the light scattering and dielectric curves overlap and similar values for the so-called 'ideal glass' transition temperature, T_0, are found. Dielectric relaxation studies give values of T_0 in the range 167–176 K[2,3] compared to the present light scattering result of 170 K. An equation of similar form to equation (14) also governs the temperature dependence of the shear viscosity, another structural property of PPG[1]. Here the prefactor is dependent on the molecular weight of PPG but T_0 (168–180 K) is relatively independent of M[1,11] as is the case for dielectric and light scattering results. Similar values of T_0 from these various experimental techniques reflect the dependence of this parameter on the conformational properties of the intrachain segmental motions[1,10,11].

From the above it follows that equation (14) is not only applicable for the present investigated structural relaxation over a wide timescale and broad temperature range, but also explains the temperature dependence of a variety of physical properties of PPG. The latter are all in different ways attributable to intrachain motions. The freezing out of these local motions determines the glass transition temperature. We therefore conclude, as did Wang *et al.*[1], that all of these local motions are closely related, especially near the glass transition temperature.

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