

letters

Comments on 'Brillouin scattering studies of structural relaxations in poly(propylene glycol)*'

It is known that for the dynamics of structural relaxation at low temperature or at long times, as can be probed using photon correlation spectroscopy, the relaxation function displays a Kohlrausch-Williams-Watts (KWW), $\phi(t) = \exp[-(t/\tau)^\beta]$ function¹. However, for short time dynamics as probed by Brillouin scattering, the relaxation function will change from the KWW type to a single exponential² and the average relaxation time $\langle\tau\rangle$ from the Vogel-Fulcher-Tamann-Hesse (VFTH) equation, $\ln\langle\tau\rangle = \ln\langle\tau_0\rangle + B/(T - T_0)$, to an Arrhenius temperature dependence. The KWW and VFTH forms, used to describe the photon correlation data, are only appropriate at low temperatures or at long times.

In a recent paper, Börjesson, Stevens and Torrell (BST) have reported a Brillouin scattering study of poly(propylene glycol) (PPG) of molecular weight 10 000 (ref. 3). Their experimental results on hypersonic velocity dispersion and absorption are in agreement with the earlier Brillouin scattering data of Wang and coworkers⁴⁻⁶. However, in the data analysis, BST¹ have assumed that the VFTH equation will continue to describe the high temperature Brillouin scattering data. They have also further assumed that the empirical KWW function could be used as the relaxation function to compute a normalized complex longitudinal modulus at the Brillouin frequency in the GHz frequency range.

Thus, BST have suggested that, over a wide time scale of $1-10^{-11}$ s, the structural relaxation in PPG should be described by the KWW function with an almost constant $\beta=0.40$ and $\langle\tau\rangle$ should have VFTH temperature dependence. These conclusions are not in agreement with those reached by Wang and coworkers, who have found in PPG and in a closely related polymeric liquid polyethylene glycol (PEG)⁷, as well as by others in several different polymers^{8,9}, that for the structural relaxation at the short times or at high temperature as probed by Brillouin scattering, the relaxation function can be adequately described by a single exponential given by $\phi(t) = \exp(-t/\tau)$, and the relaxation time τ has an Arrhenius temperature dependence given by $\tau = \tau_\infty \exp(E_a/RT)$, where the activation energy E_a is very close to the energy barrier of the conformational transition^{2,10}.

The conclusion by BST about the inadequacy of the simple Brillouin data analysis method is based upon only one single choice of $E_a = 5.2$ kcal mol⁻¹ and $\tau_\infty = 8.74 \times 10^{-15}$ s, used in the expression $\tau = \tau_\infty \exp(E_a/RT)$. To show that other choices of the parameters can bring a better agreement, we have employed the same procedure as that used by BST and found that by lowering E_a , while adjusting τ_∞ such that

the condition ($\omega\tau \approx 1$) at the temperature of the peak absorption (325 K) continues to be satisfied, there is an increasing improvement in the agreement between the calculation and experimental data. The comparison between the calculation and the experimental data for the temperature dependence of the attenuation is shown in Figure 1a, and of the normalized longitudinal modulus N'' in Figure 1b. The agreement with experimental data for $E_a = 3.5$ kcal mol⁻¹ is comparable in quality to that attained by BST using a KWW with $\beta = 0.40$ and a VFTH equation. The activation energy E_a is lower than that associated with shear flow¹, but it is consistent with the energy barrier for the conformational transition in PPG.

The conclusion by BST is also at odds with the dielectric relaxation data of Yano *et al.*⁵ at GHz

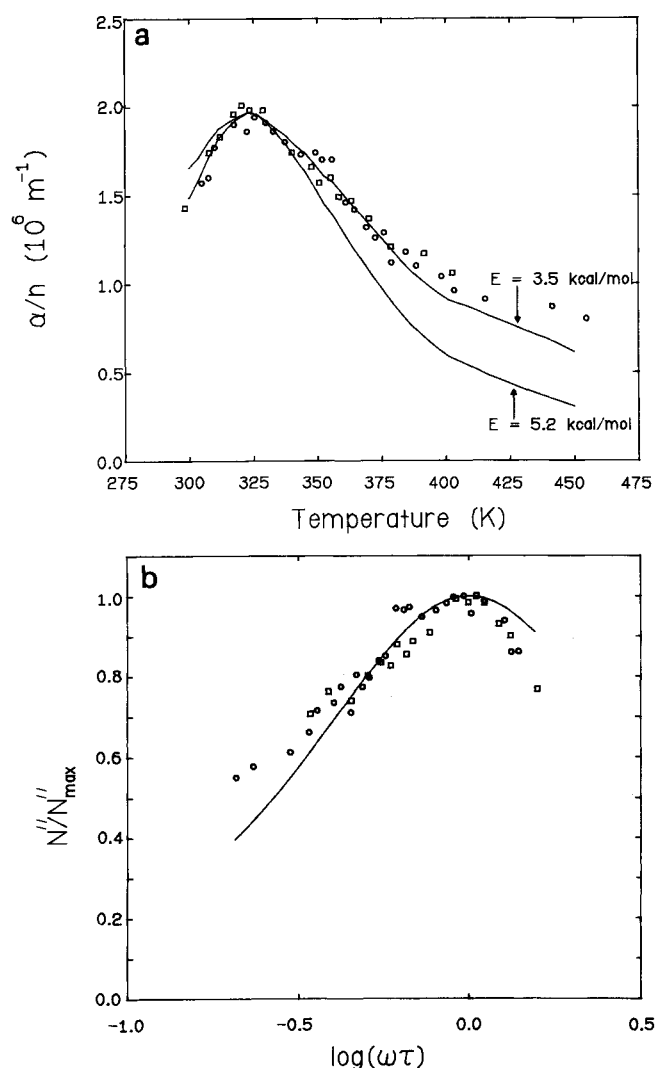


Figure 1 (a) Comparison between experimental data of reference 3 for the temperature dependence of the attenuation and calculations based on that procedure with a single exponential relaxation function (—). Agreement between calculation and experiment is acceptable using a lower activation energy, $E_a = 3.5$ kcal mol⁻¹, than the chosen $E_a = 5.2$ kcal mol⁻¹. (b) Comparison between experimental data of reference 3 for the normalized longitudinal modulus and a calculation based on that procedure with a single exponential relaxation function (—) with an activation energy $E_a = 3.5$ kcal mol⁻¹

* See reference 3

frequencies in PPG 2025 and 4000. The dielectric data of Yano *et al.* are presented in Cole–Cole plots¹¹ and the characteristic skew asymmetric arcs are evident (see Figure 5 of ref. 5) in the lower temperature region. However, as the temperature is increased to between 20°C and 88°C the Cole–Cole arc becomes more symmetric, with a tendency to become a semicircle at the highest temperature studied. This trend is especially clear in the 0.3–8 GHz range, indicating that the relaxation function approaches approximately the single exponential form as the frequency (or temperature) is increased. The dielectric data when analysed by the now popular KWW function also shows an increase of the KWW fractional exponent β towards unity in the relaxation time region between 5×10^{-10} s and 3.5×10^{-11} s.

Both dielectric relaxation⁵ and dynamic light scattering (photon correlation¹ and Brillouin scattering³) techniques monitor the structural relaxation of PPG. There are subtle differences as well as similarities in the characteristics of the structural relaxation obtained by these two techniques. The dielectric technique measures the electric compliance while the light scattering measures the longitudinal compliance.

In conclusion, the analysis of the Brillouin scattering data by BST¹ is not in agreement with dielectric relaxation data taken over the same frequency range. It is also shown that by using the same type of analysis as that used by BST, the Brillouin data can be satisfactorily fitted by assuming a single exponential relaxation function and an Arrhenius temperature dependence of the average relaxation time.

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K.L. Ngai, R. W. Rendell
Naval Research Laboratory,
Washington, DC 20375-5000, USA

and C. H. Wang
Department of Chemistry,
University of Utah,
Salt Lake City, Utah 84112, USA

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Reply to comments

The critique drawn by Ngai, Rendell and Wang (NRW) to our paper on Brillouin scattering (BS) in poly(propylene glycol) (PPG)¹ rests on the argument that an Arrhenius law in combination with a single exponential relaxation function is the only appropriate description of the temperature dependence and time decay of the structural relaxation process in the time/temperature region of BS. Moreover, they argue for a much lower activation energy than we found in our initial analysis assuming an Arrhenius law. In the following, we will show that these arguments are inadequate based on our own findings and other reported results to which two of the authors of the Comment (Wang and Ngai) have contributed considerably.

First we note that the statement by NRW 'for short time dynamics as probed by Brillouin scattering, the relaxation function will change from the KWW type to a single exponential and the average relaxation time from the Vogel–Fulcher–Tamman–Hesse equation to an Arrhenius temperature dependence' has in no way been proved. In all the references quoted by NRW throughout the Comment to support this statement an Arrhenius law and a single relaxation time have only been *assumed* and not proved to be valid. However, in the case of some simple non-polymeric glassforming liquids it has been shown that the relaxation function approaches a pure exponential in the time/temperature range of BS^{2–10}. Also, for the latter systems an Arrhenius temperature dependence for the average relaxation time ($\langle\tau\rangle$), as

NRW suggests, seems to be at least approximately valid^{3–6,9–11}.

In our first attempt to analyse the BS data of PPG (in the temperature range 290–450 K) we therefore assumed an Arrhenius law and exponential time decay¹. In reference 1 we showed that such an approach results in the reasonable value of the activation energy of 5.2 kcal mol⁻¹, however, an acceptable fit was limited to a too small temperature range. We therefore concluded that the initial assumptions (Arrhenius law and a single relaxation time) must be invalid.

NRW note that by assuming a lower activation energy to 3.5 kcal mol⁻¹ our hypersonic absorption data approach towards a single relaxation time (SRT) behaviour. (Note in Figure 1a of the Comment that the solid line, which is based on an activation energy of 3.5 kcal mol⁻¹, does not give a good fit in the high temperature range, thus indicating that the activation energy has to be even lower to actually fit the data to SRT behaviour.) This is not surprising since lowering the activation energy in the analysis will always decrease the apparent width of the relaxation function. NRW support their choice of a lower activation energy by fluorescence results reported from studies of excimers incorporated in the polymer chain of the related, but simpler, polymer PEG¹². In the latter study, a value of 3.85 kcal mol⁻¹ is reported for the energy barrier of conformational transitions¹². However, the energy barrier in case of PPG is expected to be higher because of the methyl group decoration. It is then interesting to note that this has also been suggested by Ngai and Wang in a recent paper¹³ contrary to their present argumentation. Accordingly, in