frequencies in PPG 2025 and 4000. The dielectric data of Yano *et al.* are presented in Cole–Cole plots[11] 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 relaxation[5] and dynamic light scattering (photon correlation[1] and Brillouin scattering[3]) 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 BST[1] 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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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 decay[1]. 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 PEG[12]. In the latter study, a value of 3.85 kcal mol^{-1} is reported for the energy barrier of conformational transitions[12]. 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 paper[13] contrary to their present argumentation. Accordingly, in

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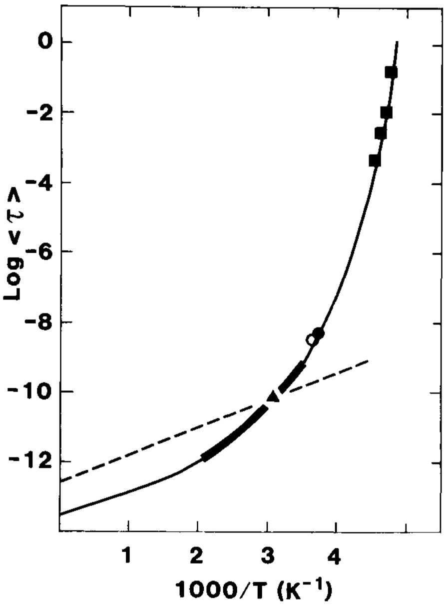

Figure 1 Arrhenius plot of the structural relaxation time for PPG. (▲) Brillouin scattering results[1]; (●, ○) nuclear magnetic resonance results (refs. 21 and 22, respectively); (■) PCS results[20]. The solid line is a VTF fit to the data (see ref. 1), the heavy solid line marks the temperature range of the Brillouin scattering experiments of reference 1 and the broken line is the Arrhenius relation proposed by NRW in the Comment to be valid in the temperature range of Brillouin scattering

the quoted reference, they attribute the activation energies reported from BS (4.4, 4.15 kcal mol^{-1}) and depolarized light scattering (5.9 and 4.54 kcal mol^{-1}) by Wang *et al.*[14–17] as well as that obtained from quasielastic neutron scattering (4.2 kcal mol^{-1})[18] to the corresponding activation barrier for conformational transitions in PPG. In all these reports, in which an Arrhenius temperature dependence has been assumed, the activation energies are considerably larger than the 3.5 kcal mol^{-1} NRW have proposed in their Comment. Thus, we find their suggestion rather surprising. Furthermore, a more recent high resolution quasi-elastic neutron scattering study of PPG[19], in about the same temperature range as the BS data (340–423 K), reveals an apparent activation energy of 5.9 kcal mol^{-1} which is also a much larger value than that proposed by NRW. The value of the apparent activation energy obtained from the latter technique is expected to be much more accurate than any of the other values mentioned above. If we try to apply any of the activation energies discussed above (4.15–5.9 kcal mol^{-1}), which are based on experimental results, it is still not possible to reproduce the hypersonic relaxation data using SRT. We therefore conclude, as we did in reference 1, that an exponential relaxation function in combination with an Arrhenius temperature dependence do not give an appropriate description of the BS results.

We will next discuss the general form of $\langle\tau\rangle$ vs. T for the structural relaxation process in PPG. It has been shown by Wang *et al.* from photon correlation spectroscopy (PCS) studies[20] of the same motion in PPG as probed by BS that $\langle\tau\rangle$ follows a Vogel–Tamman–Fulcher (VTF) equation in the wide time range of 1–10^6 s. The time range of PCS can be further expanded by including nuclear magnetic resonance[21,22] and BS results (*Figure 1* and also ref. 1). It is then found that the data are well described by one single VTF equation over the enormous $\langle\tau\rangle$ range of 11 decades and with essentially the same coefficients as those reported by Wang *et al.*[20] to fit the PCS results. In this context it is also interesting to note that Wang *et al.*[14] have obtained dielectric data on PPG for probe frequencies up to the GHz range and reported that 'it is remarkable that a VTF equation fits the loss-peak location of undiluted PPG over a range of frequency of nearly 12 orders of magnitude and a range of temperature of about 105 K. This is the severest experimental test of this relation presently available for a polymer', as directly cited from their own report. This is obviously in conflict with their suggestion in the Comment of an Arrhenius relation in the high frequency range. Thus, dielectric data also conform to a VTF equation. Therefore, based on dielectric, PCS, BS and nuclear magnetic resonance results, a VTF equation was chosen for the analysis in reference 1.

It is hard to consider the relaxation process NRW propose. It changes abruptly its nature at the BS timescale from a VTF temperature dependence, which fits all reported experimental results (including BS results) over 11 decades of frequency, to an Arrhenius temperature dependence of much lower apparent activation energy. In our opinion such a large discontinuous change of the apparent activation energy at the Brillouin point in *Figure 1* is unlikely since it implies an unexpected critical behaviour. The incorrectness of the proposed Arrhenius relation is further emphasized by its large deviation from the VTF relation at the low temperature limit of the Brillouin measurements where the VTF relation is well established by nuclear magnetic resonance results. (The temperature range of the BS measurements has been marked by a bold solid line in *Figure 1*.)

In the following the time decay of the relaxation function will be discussed. NRW claim in their comment that the dielectric data of reference 14 approaches a single exponential at higher temperatures. This statement is based on the temperature evolution of the form of the Cole–Cole arcs in Figure 6 of reference 14. We find it questionable to make such a conclusion from the rather crude arcs presented in the figure. However, much more precise information of the width of the dielectric loss peak can be obtained from Figure 5 of the same reference 14 by transforming the temperature scale to a time scale using their own reported VTF relation[14]. It is then found that the width of the dielectric loss peak is about 2 decades and *independent of frequency* within the observed range of frequencies from 0.1 kHz to 2.5 GHz. A width of 2 decades is also consistent with that reported by Johari[23], however, then restricted to a smaller temperature range. A width of 2 decades implies a non-exponential relaxation function and corresponds to a KWW relaxation function with $\beta = 0.52$. Furthermore, a constant β (≈ 0.4) has been reported for the structural relaxation in the wide time range of 1–10^{-6} s from light scattering (PCS) studies[20] of PPG by one of the authors of the Comment. We also found the same β value (≈ 0.4), now obtained in the short time (10^{-11} s) of BS[1] and recently confirmed in a series of investigations of various PPG systems[24–28]. Note that the two light scattering techniques (PCS and BS) reveal not only the same time decay ($\beta \approx 0.4$) for the relaxation process but also the same VTF temperature dependence (discussed above). More interesting is to note that there is no tendency of any narrowing of the relaxation function with increasing temperature/frequency neither from dielectric nor from light scattering observations of the structural relaxation in PPG. These observations, which are to a large extent based on data reported by one of the authors of the Comment (Wang)[14–17], are contradictory to the statements of the Comment by NRW. The width of the dielectric relaxation function is somewhat narrower than that for the light scattering data. The difference in width between dielectric and mechanical relaxation data has been observed in many other systems previously[6], and is therefore expected.

Further argument for the observation that BS data do not necessarily conform to a single exponential in polymers, as NRW claims, is that careful measurements of the structural relaxation in alkanes using light scattering studies of the Mountain peak[29] again demonstrate the failure of a single exponential relaxation function.

It should also be noted that in the cases of simple glassforming liquids for which a single exponential relaxation function has been established by BS, then crossover from non-exponential to exponential decay is clearly observable in the 'masterplot' of the hypersonic longitudinal modulus vs. log $(\omega\tau)$[8]. It is found that the absorption loss peak is strongly asymmetric. A broad wing is observed on the long time (low temperature) side of the loss maximum which depart considerably from the curve corresponding to exponential decay while a close fit to single relaxation time behaviour is found on the short time (high temperature) side of the loss peak[8]. Such an asymmetric behaviour is clearly not observed in the present case[1]. We also want to point out that the present findings of PPG are supported by a series of BS studies of PPG–salt complexes recently performed in this laboratory[25–28].

In conclusion, we have shown that the hypersonic relaxation data of PPG cannot be fitted to a single exponential and an Arrhenius law, rather it is found that a single VTF equation and a KWW relaxation function with a constant β value of 0.40 describe the structural relaxation process observed by light scattering over the enormous time range of 11 orders of magnitude. The result is remarkable in the sense that it demonstrates a distinction of the relaxation behaviour of polymers as compared with other glassforming liquids. The distinction seems reasonable since for cooperative motions of the relaxing units, which must always exist in polymers even at high temperatures/frequencies, a non-exponential relaxation is expected. The result also shows the importance of using more refined models in analysing light scattering data than those commonly applied. In view of the above, we think it is desirable to reanalyse impartially previously reported BS relaxation data of polymers.

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