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Photon Correlation Spectroscopy of Poly(vinyl acetate)

In recent reports, Wang and Fischer[1] have presented a theoretical derivation which leads to the conclusion that the photon correlation function of light isotropically scattered by bulk amorphous polymers near the glass transition temperature is equivalent to a measurement of the time-dependent longitudinal compliance. This conclusion was bolstered by an experimental study[2] of light scattered by poly(vinyl acetate) (PVac) in which the relaxation spectrum evaluated from the photon correlation data was found to be closely similar to that which characterized the bulk compliance of PVAc by McKinney and Belcher.[3]

In the discussion of their PVAc light scattering data, Fytas et al. note[2] that their data are not in agreement with an earlier study in our laboratory.[4] They assign the discrepancy to the analytical problems which derive from the splicing procedures used to generate correlation functions in our study. By contrast, their experiment utilized a logarithmic correlator, thus avoiding the need to splice data sets. While this experimental difference may influence the comparison of their data with ours, we write this paper to point out that the difference between the two studies is, in fact, for the most part due to the difference in glass transition temperatures of the two samples. The sample used in our study[4] was of molecular weight $M_w = 4.4 \times 10^6$ and $T_g = 32 \pm 2$ °C; for the sample of Fytas et al.[2], $M_w = 15\,000$ and $T_g = 17$ °C. It is not therefore surprising that at comparable temperatures, the average relaxation times $\langle\tau\rangle$ measured by Fytas et al.[2] are several orders of magnitude larger than ours.

To illustrate this, we have plotted in Figure 1 relaxation time data in the form log $\langle\tau\rangle$ vs. $(T - T_g)$, the temperature distance from T_g. Clearly, our $\langle\tau\rangle$ values are reasonably consistent with those of Fytas et al.[2] for $(T - T_g) \sim 15$ °C. However, Figure 1 indicates that, for our data which extend into a temperature regime closer to T_g, the apparent activation energy is significantly smaller than would be calculated from the WLF equation which fits the data of Fytas et al.[2] A further difference between the two sets of data is that, as stated by Fytas et al.[2], the exponent β, estimated from fractional exponential fits to experimental correlation functions, i.e., $\phi = \exp(-t/\tau)^\beta$, is found to be somewhat larger in our work (0.45 vs. 0.35).

These differences may indeed be the result of the errors attendant to analysis of spliced correlation functions as

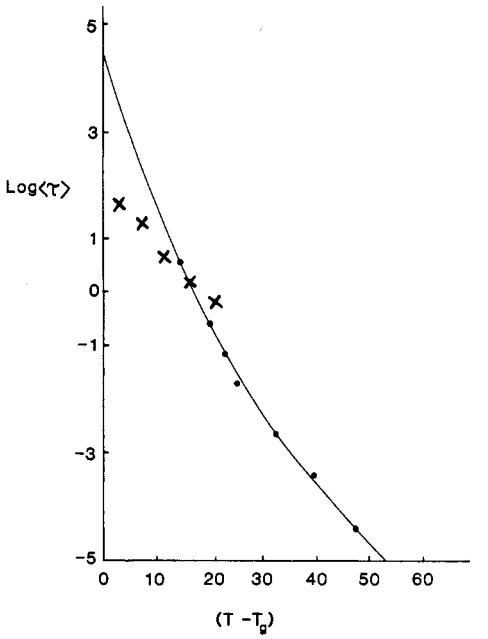

Figure 1. Logarithm of the average relaxation time derived from photon correlation analysis of light isotropically scattered by poly(vinyl acetate) in the bulk state near T_g, plotted vs. the temperature distance $(T - T_g)$: (●) data of Fytas et al.;[2] (×) data of Tribone et al.;[4] the solid line is a WLF fit to the data of Fytas et al.

stated by Fytas et al.[2] However, it is worth noting that at least two studies[5,6] have observed that the apparent activation energy of viscoelastic properties just above or below T_g may be smaller than that predicted by extrapolation based on the WLF equation applicable for $T \gg T_g$. Also, for a low-T_g polymer, it is possible that the width of the relaxation spectrum may be increased because of the molecular weight distribution and the associated spread in T_g. This could be a contributing factor in the smaller β-parameter observed by Fytas et al.[2] Definitive comparison between different experimental data sets under circumstances where T_g is molecular weight dependent requires identical or at least closely similar samples.

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Solid-Phase Block Copolymer Synthesis by the Iniferter Technique

In 1982 we proposed the concept of an iniferter (*ini*tiator–trans*fer* agent–*ter*minator) for design of polymer

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