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Relaxation Time Distributions of Entangled Polymer Solutions from Dynamic Light Scattering and Dynamic Mechanical Measurements

Recent Laplace inversion analyses of dynamic light-scattering (DLS) data on semidilute solutions of high molecular weight polystyrene (PS) at the Θ temperature established the existence of a distribution of slower relaxation times, which was independent of the wave vector ($\mathbf{q}$) of the incident light, in addition to the fast $\mathbf{q}^2$-dependent relaxation time which describes the cooperative diffusion of the polymer chains.[1–4] Although the contribution of the slower relaxational modes to the correlation function persists at temperatures well above the Θ temperature and is even detectable in thermodynamically good solvents, their relative amplitude is only considerable (dominant) at temperatures in the vicinity of Θ.

A theory of Brochard and de Gennes[5,6] with a modification in ref 7, is partially successful in explaining the experimental observations. Accordingly, the response of the system to spontaneous concentration fluctuations starts by diffusion of solvent molecules until an equilibrium is reached between the osmotic force and the elastic force arising from the transient network formed by topological entanglements of the polymer chains. As the entanglements are not fixed as in a permanent network, the system can continue to relax in a second stage through disentanglement of the chains.

As we have recently shown,[1] this theory successfully describes the variation of the cooperative diffusion coefficient with polymer concentration. However, contrary to the experimental findings,[1–4] the theory predicts the existence of only one $\mathbf{q}$-independent slow relaxation mode. The latter follows from the assumption that the disentanglement of the chains forming the transient network is a unique process characterized by a single relaxation time. Mechanical measurements[8] show that this is an oversimplification for most polymer systems. A comparison of the values for the slowest relaxation time from DLS measurements and dynamical shear moduli determinations on the same systems strongly suggests that these two techniques are probing closely related processes. It is therefore ventured that the distribution of relaxation times deduced from analyses of DLS data is the result of a more complex disentanglement process and moreover that this should also be reflected in similarly treated dynamic mechanical data. There have been reported very few oscillatory shear measurements on semidilute solutions. To examine the plausibility of this explanation, DLS measurements and oscillatory shear viscosity measurements have been performed on the same solutions of high molecular weight PS in the solvent dioctyl phthalate (DOP) at the Θ temperature (22 °C).[9] This solvent is convenient for rheological measurements with an open-cell geometry because of its very low vapor pressure. The Θ system is suited to present purposes since in good solvents the cooperative diffusion almost completely dominates the correlation function. The present communication is a preliminary report sketching the main findings. A paper dealing with the influence of concentration, molecular weight, and the influence of temperature on the light-scattering and dynamic mechanical distributions will follow and will include a more detailed description of the analysis methods, as well as a comparison with alternative distribution models, such as the Williams–Watts function.

The elastic storage and loss shear moduli, G' and G'', were measured on a Rheometrics RFS 8500 instrument, employing a cone and plate geometry (diameter 50 mm, 0.02 angle rad). The frequency range was 0.01–100 rad/s, and 10 points were taken per decade. The strain amplitude was between 0.05 and 0.50, and it was ensured that all measurements were made in the linear viscoelastic region. The stress relaxation shear modulus, $G(t)$, was calculated from G' and G'' by use of the approximative expression of Ninomiya and Ferry (see eq 4.48 of ref 11)

$$G(t) = G'(\omega) - 0.40G''(0.4\omega) + 0.01G''(10\omega) \qquad (1)$$

which uses G' at the frequency $1/t$ and G'' at two other frequencies. (It is not possible to accurately evaluate $G(t)$ directly by Fourier inversion since this would necessitate knowledge of G' and G'' over a much wider range of frequencies than could be measured. It is not possible to extend the frequency range in the present case by employing time–temperature superposition since it would involve changes in the thermodynamic properties of the system.)

For the DLS measurements the autocorrelator was a multi-τ model from ALV, Langen, FRG, employing 23 simultaneous sampling times and thus allowing monitoring of widely spaced decays in the same experiment. Approximately 8 decades in relaxation time could be covered. The measurements were made in the homodyne mode using a wavelength of 633 nm.

A Laplace inversion routine called REPES[10] has been used to analyze both the measured DLS correlation function, $g^2(t)$, and the square of the time-dependent shear modulus, $G(t)$. The algorithm differs from the often-used program CONTIN[12] in that it directly minimizes the sum of squared differences between the measured and calculated $g^2(t)$ function using nonlinear programming and an a priori chosen parameter P, "probability to reject" (we use $P = 0.5$). The decay time distributions were found to be closely similar to those obtained using the comparable Laplace inversion routines MAXENT[13] and CONTIN.

The basis for the proposed comparison is not immediately obvious since $g(t)$ is related to the longitudinal elastic modulus (M) and not the shear modulus.[14] The observed close similarity shown below between the dynamic mechanical and dynamic light-scattering decay time distributions suggests that the bulk elastic modulus may have the same frequency dependence as the shear modulus, since the longitudinal modulus is a linear combination of these two moduli. This may be understood by the fact that the frequency dependence of the two moduli derives from the same process of chain disentanglement. Candau et al.[15] have shown that the variation in M (obtained from static light-scattering measurements on polystyrene gels swollen in benzene) closely follows variations in the static shear modulus.

Although a comparison of the relaxation time distributions from DLS and dynamic mechanical measurements has not previously been made for semidilute solutions, the approach is not in itself new. Such a comparison has been made for polymer melts. Wang et al.[16] established a relationship between the longitudinal compliance and the time correlation function of the density fluctuations as measured by DLS. Good agreement between the latter and the dynamic mechanical data was obtained.[16,17] Retardation spectra, calculated using the Laplace inversion routine CONTIN, from the light-scattering and dynamic mechanical data showed a close resemblance.[18,19]

However, melts and semidilute solutions are different: whereas in the case of melts it is argued that the response of the system to density fluctuations is related to the longitudinal compliance,[16] in semidilute solutions and gels the response of the system to concentration fluctuations is related to the longitudinal elastic modulus.[11,21] Furthermore, in semidilute solutions the cooperative diffusion complicates the results from the light-scattering experiment.

In this paper we report some preliminary results of parallel viscoelastic and dynamic light-scattering measurements on semidilute solutions of polystyrene (narrow molecular weight distribution samples from Toya Soda Ltd., Tokyo) in DOP. Since the time range in which $G(t)$ could be determined was limited to the 4 decades between 0.01 and 100 s, only part of $g(t)$ can be compared with $G(t)$. The autocorrelation functions were measured at a high scattering angle (140°) so that the cooperative diffusion mode was shifted as far as possible to the fast end of the time spectrum and a larger portion of $g(t)$ could be utilized for the comparison. We have demonstrated earlier[1] that the cooperative diffusion component can be subtracted from the time correlation function and that the decay times and amplitudes of the slower, $\mathbf{q}$-independent components are uninfluenced by this procedure. This validates the present qualitative comparison between the slower part of $g(t)$ and $G(t)$ from the dynamic mechanical measurements, which appear to reflect closely related processes. A more quantitative appraisal will be given subsequently.

Figure 1 compares relaxation time distributions obtained from the Laplace inversion of $G(t)$ and $g(t)$ for a sample of $M_w = 3 \times 10^6$ and at a concentration of 5.75% ($6.1C^*$). $G(t)$ has been estimated from the measured $G'(\omega)$ and $G''(\omega)$ using eq 4.48 of ref 11. A first Laplace inversion analysis of $G(t)$ gave a large contribution from a relaxation with a characteristic decay time at the fast edge of the relaxation time spectrum and which lay at the frequency limit at which G' and G'' could be measured. For this reason the first two measurement points were not included in the analysis. The weighted residuals to the fit are given in Figure 2. They are random and thus show that the fit is good in both cases. The maximum deviation for the fit is 0.4×10^{-4} (light scattering) and 1.9×10^{-4} (dynamic mechanical).

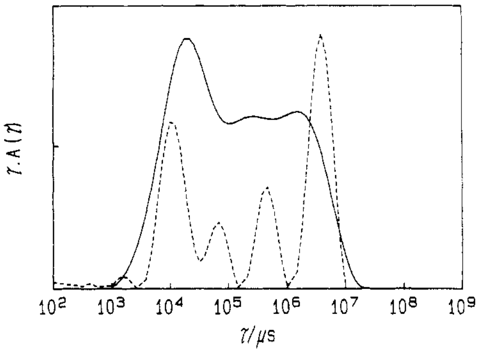

Figure 1. Decay time distributions from Laplace inversion of dynamic light-scattering data (dotted line) and dynamical mechanical oscillatory measurements (full line). The product $\tau\ A(\tau)$, where $A(\tau)$ is the distribution of relaxation times for the light-scattering data (cf. refs 1–3) (respectively, $\tau\ H(\tau)$ for the oscillatory data), has been plotted on the ordinate (arbitrary units) to give an equal area representation. These data are for polystyrene ($M_w = 3 \times 10^6$) in dioctyl phthalate at concentration 5.75% ($6.1C^*$).[23] The measurements were made at 22 °C (Θ conditions).

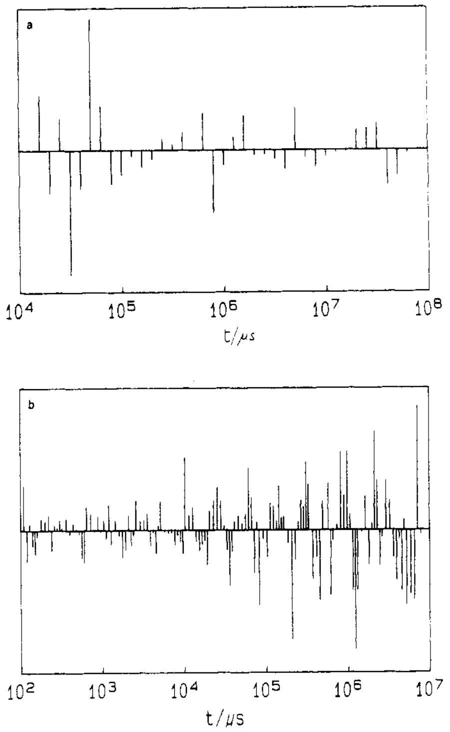

Figure 2. Residuals to the fit (arbitrary units) corresponding to the data in Figure 1: (a) mechanical oscillatory measurements, (b) dynamic light scattering.

It is clear from the comparison of the relaxation time distributions that the range of relaxation times is the same for the light-scattering and mechanical measurements. The dynamic mechanical distributions are considerably more smoothed, however, than those from DLS, an aspect that will be dealt with in more detail in a forthcoming paper. The correspondence in time range strongly suggests (but, of course, does not prove) that the same processes are probed with these two experimental techniques. Comparison of the relative amplitudes at corresponding times shows that there are also pronounced differences in the distributions. These data may be compared with those for the melts where a broad unimodal distribution is characteristic. The latter covers a range in a region of retardation times corresponding to that of

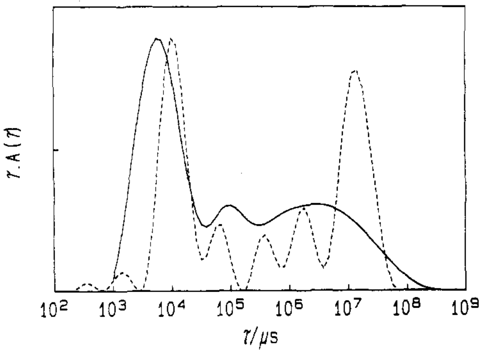

Figure 3. Analogous data to those in Figure 1 but for polystyrene ($M_w = 8 \times 10^6$) in DOP at 3.87% (6.7C^*) and 22 °C.

the local segmental motion, although the dispersion in the latter was not interpreted to mean that it corresponds to a distribution of relaxation times.[20]

The relaxation spectrum ($H(\tau)$) may also be obtained from G' and G'' using approximate relationships, for example, those given in ref 11 (e.g., eqs 4.12 and 4.26). While they reproduce the range of the relaxations correctly, these expressions give very highly smoothed distributions in comparison with Laplace inversion and give highly nonrandom residuals to the fit.

A different sample ($M_w = 8 \times 10^6$) shows the same qualitative features (see Figure 3). The range of relaxation times for both the light-scattering and viscoelastic data is extended to longer time by about a decade in comparison with the data for the lower molecular weight sample. Again, there is a contrast with the melt since bulk viscoelastic properties depend only on local motions of the polymer chains and are largely independent of molecular weight.

Although the concentration is lower (3.87%; 6.7C^*), this slowing down is anticipated since the time required for a complete disentanglement of the chains depends strongly on the sample M_w.[19] We find that the relative amplitudes of the relaxation modes contributing to the distribution are different with the two techniques. With both molecular weights there is a larger contribution of the slowest mode in the light-scattering time distribution. In the absence of a model, there is as yet no explanation for this difference.

We conclude with the following:

1. The slower modes obtained from dynamic light-scattering experiments on semidilute solutions of high molecular weight polymers in a Θ solvent are closely related to the processes probed by dynamic mechanical measurement.
2. Dynamic processes leading to disentanglement of polymer chains are rather complex as is demonstrated by a broad relaxation spectrum.
3. There are large differences in the relative contributions of the corresponding components in the distributions obtained from light-scattering and oscillatory experiments which require further investigation.

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(23) $C^* = 3M/4\pi R_g^3 N_A$, where R_g is the radius of gyration.

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