Mode Selection in the Dynamics of Sheared Polymer Solutions

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(Received 31 October 1991)

We report transient light scattering measurements upon the cessation of shear for a semidilute polymer solution under theta conditions. The polymer solution demonstrates two modes of relaxation for concentration fluctuations in equilibrium. The transient measurements show that the mechanism that couples the concentration fluctuations to the shear flow, and thereby enhances concentration fluctuations, selectively enhances only the slower of the two equilibrium modes. This selective enhancement generates a long-wavelength peak in the shear-enhanced structure.

PACS numbers: 82.70.Kj, 66.90.+r, 82.70.Dd

The coupling of elastic stress and diffusion in semidilute polymer solutions can have dramatic consequences. Near theta conditions, experiments in a wide variety of systems have shown that macroscopic shear flow strongly enhances concentration fluctuations and may, for sufficiently strong shear, induce phase separation [1,2]. The nonequilibrium structure of these systems has been measured by light scattering [3-6] and found to agree with the basic symmetries of recent theoretical models [7-9]. However, the measurements reveal a very-long-wavelength peak in the structure that is not accounted for within the theory. Milner has suggested that the models fail in this regard because they neglect the dynamics of the sheared polymer solution [10]. In this paper, we explore the nonequilibrium dynamics of the shear-enhanced concentration fluctuations by measuring the transient response of the light scattering upon the cessation of shear. While dynamic light scattering [11] shows that there are two modes of relaxation for equilibrium concentration fluctuations, our transient scattering measurements reveal that the shear flow selectively enhances only one of these modes. This selective enhancement generates the peak observed in the steady-state structure.

We perform our transient light scattering measurements using a transparent Couette cell described elsewhere [5]. Using this cell, we generate a steady shear rate $\dot{\gamma}$ and measure the relative scattering intensity, $I(\mathbf{q},\dot{\gamma})/I(\mathbf{q},0)$, for scattering wave vectors $\mathbf{q}$ which lie in the plane defined by the velocity v (x direction) and the velocity gradient ∇v (y direction). The direction of $\mathbf{q}$ is described by β, the angle $\mathbf{q}$ makes with the x axis. The design of the cell allows us to measure accurately the relative scattering intensity for $5\ \mu\mathrm{m}^{-1} < q < 28\ \mu\mathrm{m}^{-1}$ and for any β. Below $q = 5\ \mu\mathrm{m}^{-1}$, scattering from the cell walls makes an accurate determination of $I(\mathbf{q},\dot{\gamma})/I(\mathbf{q},0)$ impossible. Fortunately, this does not seriously inhibit our transient measurements, where we are concerned with the time evolution of the scattering and not the magnitude of the effect.

Our sample is a semidilute solution of polystyrene (PS) with a volume fraction $\phi = 0.04$ dissolved in dioctylphthalate (DOP). The PS has a molecular weight of $M_w = 1.86\times10^6$ and a polydispersity of $M_w/M_n = 1.06$. This gives a radius of gyration of $R_g \sim 250$ Å and an overlap concentration of $\phi^* \sim 0.008$. Thus, the solution is well into the semidilute regime. The critical point for this system is at $T_c = 10.2\,^\circ\mathrm{C}$ and $\phi_c = 0.02$; the theta temperature is $T_\theta = 22\,^\circ\mathrm{C}$ [12]. The bulk correlation length, determined from equilibrium static light scattering measurements, is given by $\xi_c = \xi_0(T/T_c - 1)^{-1/2}$, where $\xi_0 = 24$ Å. At 15.3 °C, where most transient measurements were performed, $\xi_c = 180$ Å. The long-wavelength, low-q collective diffusion coefficient is $D_c = 0.020 \pm 0.004\ \mu\mathrm{m}^2/\mathrm{s}$, which we measure with quasielastic light scattering (QELS). Measurements of the dynamic viscosity, $\eta(\omega)$, define a characteristic stress relaxation time, τ_R, such that for $\omega\tau_R \ll 1$, $\eta = \eta_0$ is a constant, and for $\omega\tau_R \gg 1$, $\eta \sim \omega^{-2/3}$. At 15.3 °C, $\tau_R = 0.57$ s, where τ_R is defined as the point where $\eta/\eta_0 = 0.7$ (3 dB).

The transient response measurement cycle entails setting an initial shear rate $\dot{\gamma}_i$ and allowing the system to reach steady state. The shear rate is then abruptly changed to the final shear rate $\dot{\gamma}_f$. The scattering intensity $I(\mathbf{q},t)$ is measured for 10 s prior to and 50 s after the change in $\dot{\gamma}$. The measurement cycle is repeated and the signal averaged until a reasonable signal-to-noise ratio is obtained. At small q, the number of cycles often exceeds 2000. We have established by independent means that the shear rate changes in less than 0.1 s while the measured relaxation times always exceed 0.5 s; this insures that we are measuring a true step response. The data presented in this paper were taken at $T = 15.3\,^\circ\mathrm{C}$; we also performed measurements at 11 and 25 °C that show similar behavior.

The transient response in this system is much more complicated at high shear ($\dot{\gamma}\tau_R > 1$) than it is at low shear ($\dot{\gamma}\tau_R < 1$). At high shear rates, elastic effects become important and the transient response of the polymer solution is both anisotropic and nonlinear. In this paper, we concentrate on the more tractable low shear behavior. At low shear rates, the transient response of this polymer solution is *linear*. We denote the normalized step

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response of the scattered intensity going from an initial state $\dot{\gamma}_i$ to a final state $\dot{\gamma}_f$ as

$$\Phi(\mathbf{q},\dot{\gamma}_i,\dot{\gamma}_f,t)=\left|\frac{I(\mathbf{q},\dot{\gamma},t)-I(\mathbf{q},\dot{\gamma}_f)}{I(\mathbf{q},\dot{\gamma}_i)-I(\mathbf{q},\dot{\gamma}_f)}\right| \tag{1}$$

so that $\Phi(\mathbf{q},\dot{\gamma}_i,\dot{\gamma}_f,t<0)=1$ and $\Phi(\mathbf{q},\dot{\gamma}_i,\dot{\gamma}_f,t\rightarrow+\infty)=0$. If the initial and final shear rates are low ($\dot{\gamma}\tau_R<1$), then we find that Φ is independent of $\dot{\gamma}_i$ and $\dot{\gamma}_f$, i.e., the response is linear. In particular, we see the same response for the initiation and cessation of shear. In addition, at low shear rates, Φ is only a function of q. That is, Φ is independent of β even though $I(\mathbf{q},\dot{\gamma})$ is a strong function of both q and β [5].

In Fig. 1(a), we plot the transient scattering Φ upon the cessation of shear for a range of q along $\beta=0°$ at an initial shear rate of $\dot{\gamma}_i=0.6\ \mathrm{s}^{-1}$ ($\dot{\gamma}_i\tau_R=0.34$). As a reference, the initial steady-state scattering at $\dot{\gamma}_i=0.6\ \mathrm{s}^{-1}$ is similar to the data presented for $\dot{\gamma}=0.4\ \mathrm{s}^{-1}$ in Fig. 2(a) of Ref. [5]. The curves are exponential fits, $\exp(-\Gamma t)$, to the data. Within the error, there is no systematic deviation from the fits. In Fig. 1(b), we plot the relaxation rate Γ [obtained from the fits of the data in Fig. 1(a)] vs q^2. We also show the values of Γ obtained from transient data obtained for $\beta=45°$; these measurements have been omitted from Fig. 1(a) for the sake of clarity. At small q, the relaxation rate is roughly quadratic in q; at large q, the relaxation rate saturates at $\Gamma\simeq1.7\ \mathrm{s}^{-1}$. If the relaxation mechanism were simply diffusive,

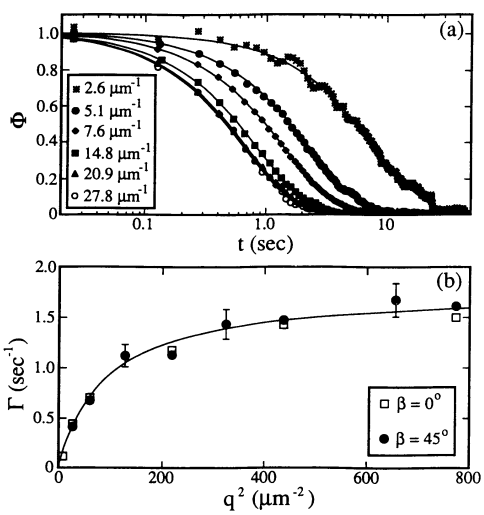

FIG. 1. (a) The normalized transient scattering response to the cessation of shear for $\dot{\gamma}_i=0.6\ \mathrm{s}^{-1}$ ($\dot{\gamma}_i\tau_R=0.34$). The data were taken for a range of q along $\beta=0°$. The curves are fits to the data with $\exp(-\Gamma t)$. (b) The relaxation rate Γ obtained from exponential fits to the data for a starting shear rate of $\dot{\gamma}_i=0.6\ \mathrm{s}^{-1}$ plotted vs q^2. The squares are for data acquired along $\beta=0°$ as is shown in (a); the solid circles correspond to data acquired along $\beta=45°$, which has been omitted from (a) for the sake of clarity. The curve is a best fit to the data using Eq. (2).

we would expect the data to fall along a straight line ($\Gamma\propto q^2$). The saturation of Γ suggests a crossover to a different relaxation mechanism at high q. The curve in Fig. 1(b) is a best fit to the data using the empirical form

$$\Gamma_m=[1/D_m q^2+\tau_m]^{-1}, \tag{2}$$

where D_m and τ_m are the measured diffusion coefficient and rate-limiting time, respectively. The values obtained from the fit are $D_m=0.017\pm0.003\ \mu\mathrm{m}^2/\mathrm{s}$ and $\tau_m=0.57\pm0.07$ s. These values are in good agreement with the independent measurements of the collective diffusion coefficient at small q, $D_c=0.020\pm0.004\ \mu\mathrm{m}^2/\mathrm{s}$, and the stress relaxation time, $\tau_R=0.57$ s. It should be noted, however, that the 3-dB definition of the stress relaxation time is somewhat arbitrary. While these enhanced fluctuations appear to be relaxing in a simple diffusive manner at low q, the data suggest that the relaxation of local stress is the limiting factor at high q. The crossover between these two regimes occurs at the wave vector $q_g\equiv(D_c\tau_R)^{-1/2}=9.4\pm2.0\ \mu\mathrm{m}^{-1}$ obtained by equating the diffusive relaxation rate $D_c q^2$ and the stress relaxation rate τ_R^{-1}. This is the same length scale introduced by Brochard and de Gennes (BD) to explain the crossover between diffusive and gel-like dynamics in equilibrium semidilute theta solutions [13].

To describe the dynamics of semidilute polymer solutions, BD [13–15] use a two-fluid model in which the dynamics of concentration and stress fluctuations are coupled. This leads to an equation of motion for the equilibrium polymer displacement, $u(q,\omega)$, of the form

$$(i\omega\phi_0/\mu)u=[K+M(\omega)]q^2u, \tag{3}$$

where ω is the frequency, ϕ_0 is the mean concentration, and μ is the mobility. The osmotic bulk modulus K is related to the osmotic pressure Π via $K=\phi\,\partial\Pi/\partial\phi$. The longitudinal gel modulus $M(\omega)$ is characterized by a simple Debye response $M(\omega)=M_g[i\omega\tau_R/(1+i\omega\tau_R)]$, where M_g is the elastic modulus of the transient gel. The dispersion in $M(\omega)$ leads to different diffusion coefficients in the low- and high-frequency limits. For $\omega\tau_R\ll1$, one obtains the familiar long-wavelength collective diffusion coefficient $D_c\equiv\mu K/\phi_0$. For $\omega\tau_R\gg1$, the diffusion coefficient is modified by the elastic response of the transient gel to be $D_c\equiv\mu(K+M_g)/\phi_0$. The ratio of these two diffusion coefficients, $\rho\equiv D_g/D_c=1+M_g/K$, is a measure of the relative strength of the elastic term. The two eigenmodes of Eq. (3) obey the dispersion relations

$$\Gamma_{f,s}=\frac{1}{2\tau_R}(1+\rho x^2)\left[1\pm\left(1-\frac{4x^2}{(1+\rho x^2)^2}\right)^{1/2}\right], \tag{4}$$

where $\Gamma_f(+)$ is the fast mode, $\Gamma_s(-)$ is the slow mode, and $x\equiv q/q_g$ is the normalized wave vector. The approximate forms

$$\Gamma_f\simeq\frac{1}{\tau_R}+D_g q^2,\quad \Gamma_s\simeq\left[\frac{1}{D_c q^2}+\rho\tau_R\right]^{-1} \tag{5}$$

are valid asymptotically but break down near q_g when $\rho-1\lesssim 1$. Both modes contribute to the relaxation of concentration fluctuations probed by equilibrium light scattering. The relative scattering intensity of the two modes is given by

$$\frac{A_f}{A_s}=\frac{\Gamma_s}{\Gamma_f}\left[\frac{\Gamma_f\tau_R-1}{1-\Gamma_s\tau_R}\right] \tag{6}$$

such that $A_f/A_s\rightarrow 0$ as $q\rightarrow 0$ and $A_f/A_s\rightarrow(\rho-1)^{-1}$ as $q\rightarrow\infty$. Thus, the intensity of the slow mode is 1 for $q\lesssim q_g$ and asymptotically approaches a value of $(\rho-1)^{-1}$ for $q\gg q_g$. In a good solvent, the osmotic modulus is typically much larger than the elastic modulus, i.e., $M_g/K\ll 1$. Under such conditions, the stress fluctuations effectively uncouple from the concentration fluctuations, and this result reduces to a single diffusive mode of the form $\Gamma=D_c q^2$. However, as theta conditions are approached, the polymer begins to collapse upon itself to the point where M_g and K are of comparable magnitude, and the stress mode mixes into the dynamics of the concentration fluctuations.

Adam and Delsanti (AD) performed QELS measurements on a range of polystyrene-cyclohexane solutions under theta solvent conditions and found fairly good agreement with the BD theory [11]. Likewise, we have performed QELS measurements on our PS+DOP system for a range of temperatures near T_θ. Our measurements at 15.3 °C show behavior similar to that observed by AD. At low q ($<q_g$), we observe a single diffusive mode with a diffusion coefficient $D_c=0.020\pm 0.004$ $\mu m^2/s$. At high q ($>q_g$), the correlation function is nonexponential and can be conveniently approximated by two exponential modes. The fast mode at high q also behaves in a diffusive manner and has a diffusion coefficient $D_g=0.023\pm 0.003$ $\mu m^2/s$. The slow mode at high q is essentially independent of q with a relaxation rate of $\Gamma_s=1.4\pm 0.4$ s^{-1}. The relative intensity of the two high-q modes is $A_f/A_s=2.5\pm 0.7$ for $q\gg q_g$. This gives $\rho=1.4\pm 0.4$, which is consistent with $D_g/D_c=1.2\pm 0.3$, as expected from Eq. (6).

In Fig. 2, we plot Γ vs q^2 for the QELS measurements and the transient-shear measurements. The transient-shear data represent an average of the two sets of data shown in Fig. 1(b). The curves are the BD prediction, Eq. (4), for the two modes using $D_c=0.020$ $\mu m^2/s$ and $\tau_R=0.57$ s, obtained from our QELS and viscosity measurements, and $\rho=1.4$, obtained from the relative intensity of the two modes at high q. The BD theory provides a good description of the data. Furthermore, the relaxation rates obtained for the shear-transient data are in general agreement with the slow mode in the QELS measurements. The most striking result, however, is that we observe *only* the slow mode in the shear-transient data, even though both the slow and fast modes are clearly visible in our QELS measurements. If the fast mode were present in our transient measurements, it would be easily distinguishable in time from the slow mode for $q>2q_g$ and would lead to observable deviations from a single exponential fit. Even if the fast mode were beyond our bandwidth, we would expect a sharp drop in the transient immediately after the shear flow was turned off. However, we see no evidence of the fast mode. Thus, we conclude that the mechanism that couples the concentration fluctuations to the shear flow, and thereby enhances concentration fluctuations, selects only the slow mode.

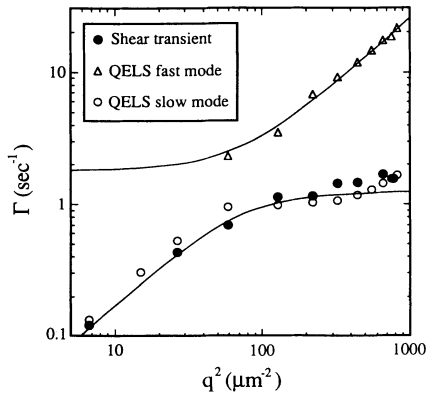

FIG. 2. A log-log plot of Γ vs q^2 for the shear-transient measurements shown in Fig. 1 and for QELS measurements at 15.3 °C on the same system. The shear-transient data are an average of the two sets shown in Fig. 1. For $q^2\lesssim 50$ μm^{-2}, the QELS data are consistent with the existence of only the slow mode. The two modes do not separate clearly in time until $q^2\gtrsim 200$ μm^{-2}. The curves are the BD prediction, Eq. (4), for the two modes assuming $D_c=0.020$ $\mu m^2/s$, $\tau_R=0.57$ s, and $\rho=1.4$.

A theory of the shear-enhanced scattering developed by Helfand and Fredrickson [7] (HF) and elaborated on by others [8,9,16] proposes that the thermally generated equilibrium concentration fluctuations are enhanced by a coupling between the polymer concentration and the shear flow through the concentration-dependent viscosity and normal stress coefficients. Recent light scattering experiments [3–5] confirm that the theory correctly predicts the basic symmetries of the shear-induced structure factor $S(\mathbf{q},\dot\gamma)$. However, there is a large peak at $q\simeq q_g\simeq 10$ μm^{-1} in $S(\mathbf{q},\dot\gamma)$ that cannot be accounted for within the HF theory [5]. Instead, the HF theory predicts that the enhancement in the structure factor should grow approximately as q^2 out to $q\sim 1/\xi_c\sim 100$ μm^{-1}. Milner [10] has proposed that the HF theory fails in this respect because it assumes that the stresses in the fluid respond instantaneously to the local concentration fluctuations. Instead, there is a characteristic response time τ_R necessary to induce the relative flow mechanism between the polymer and solvent. Thus, the HF assumption is valid in the limit of small q where the natural lifetime of fluctuations is long compared to τ_R, and fails at high q where the natural lifetime of fluctuations becomes shorter than τ_R.

Our measurements suggest that Milner's hypothesis only partially explains the peak observed in $S(\mathbf{q},\dot{\gamma})$. The major point of departure from Milner's suggestion is that the relaxation rate of the slow mode never becomes fast compared to τ_R, and yet there is still a peak. However, Milner's suggestion can explain why only the slow mode is selected by the HF mechanism. The relevant parameter in the enhancement of a fluctuation at a given q is the ratio of the stress relaxation time to the fluctuation lifetime, $\Gamma\tau_R$. If $\Gamma\tau_R < 1$, then the growth mechanism acts in the adiabatic limit and the HF result is recovered. However, if $\Gamma\tau_R > 1$, then the fluctuation does not live long enough for the mechanism to respond and the enhancement is suppressed relative to the HF result. As Fig. 2 reveals, the slow mode obeys $\Gamma\tau_R < 1$ for all q, while the fast mode always obeys $\Gamma\tau_R > 1$. Thus, only the slow mode is significantly enhanced by the shear. As a result, we observe only the slow mode in our transient measurements.

We suggest that the peak in the shear-enhanced structure results from a confluence of factors. The HF model predicts that the enhancement of fluctuations should increase as $\sim q^2$. This result will be modified in two ways. First, the amplitude of concentration fluctuations in the slow mode is a strong function of q [see Eq. (6)]. Thus, the scattering amplitude resulting from the shear flow will peak near the point where the product of q^2 and the amplitude of thermally generated fluctuations in the slow mode is greatest. Since this amplitude drops precipitously for $q > q_g$, the peak should occur near q_g. Second, for large q, the lifetime of fluctuations in the slow mode becomes comparable to τ_R, which further reduces the effectiveness of the enhancement mechanism in accordance with the Milner argument. This second factor may affect the shape of the peak, but it should not alter its position.

These measurements show that the mechanism that couples the concentration fluctuations to the shear flow, and thereby enhances concentration fluctuations, selects only the slowest mode in a semidilute theta solution. Thus, our transient measurements relax with a single exponential for all q even though the equilibrium QELS measurements relax nonexponentially. Within this context, the BD model provides a useful description of the salient features of the equilibrium dynamics and is consistent with the transient scattering data. Furthermore, the peak observed in the steady-state structure is a result of the selective enhancement that we observe in our transient measurements. This selective enhancement can be accounted for by assuming that the mechanism has a finite characteristic response time τ_R. Clearly, a full theoretical treatment of this phenomenon must include both the bimodal nature of the equilibrium dynamics and the finite response time of the enhancement mechanism.

We have benefited from discussions with S. Milner, G. Fredrickson, A. Onuki, T. Lubensky, P. Pincus, D. Pearson, G. Ver Strate, K. Wissbrun, and W. Graessley. We thank R. Gartner and D. Lohse for assisting with the rheology measurements. We also thank J. Huang and J. Sung for the use of their QELS apparatus.

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