Study of Internal Modes of a "Living Polymer" by Transient Electric Birefringence

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We use a pulsed electric field to study transient electric birefringence in "living polymers." The decay of birefringence is nonexponential and depends on the pulse width of the electric field. The relaxation is modeled in terms of the collective modes of the individual polymers with Zimm dynamics. Using this model, we find that the living polymer behaves as a flexible chain even at very low concentrations. Two distinct growth regimes are found for the polymer contour length $\bar{L}$ as a function of surfactant concentration ϕ. In the very dilute regime $\bar{L}$ increases as $\sqrt{\phi}$, and levels off at higher concentrations.

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The dynamic response of complex fluids when subjected to external perturbations, such as electric and magnetic fields and hydrodynamic flows, is extremely complicated, yet there are some unifying features [1,2]. For example, these systems often have a broad distribution of relaxation times and show nonexponential relaxation. It is believed that the broad distribution of time scales is responsible for a wide variety of interesting phenomena in complex fluids, ranging from plastic flow in polymer glasses [3] to turbulent-drag reduction in dilute polymer solutions [4]. An understanding of the physical origins of the anomalous relaxation is of great practical and fundamental interest.

A "living polymer" is a paradigm for studying dynamics in a linear self-assembling system. These polymerlike aggregates arise when a system of small spherical micelles at low concentrations undergo uniaxial growth to form wormlike structures [5,6]. A unique feature of a living polymer is that the molecular weight distribution satisfies thermal equilibrium, in marked contrast with ordinary polymer solutions for which the molecular weight is fixed. Previous experiments have shown that the extra degrees of freedom in living polymers lead to an unparalleled richness in the dynamics, such as shear induced gelation and hydrodynamic instability [7].

In this Letter, we present a transient electric birefringence (TEB) measurement of a polymerlike micelle, N,N dimethylhexadecylamine + sodium salicylate in water. The relaxation is found to be nonexponential and depends on the duration of the applied field, becoming independent of the pulse width only in the long pulse limit. The pulse-width dependence can be used as a temporal filter to study excitations on different time scales [8]. We show that the TEB experiment can be understood in terms of the internal collective modes of the individual polymers. In particular, we construct a model in terms of these modes using the Zimm model of polymer dynamics [9]. Applying this model, we study the living polymers as a function of surfactant concentration ϕ. In contrast to previous experiments, we find that the living polymer is flexible, rather than rodlike, even at concentrations slightly above the critical micellar concentration ϕ_c (CMC). For very dilute concentrations, $0.003\% < \phi < 0.03\%$, the average length $\bar{L}$ is proportional to $\sqrt{\phi}$ as predicted theoretically [10,11]. However, for intermediate concentrations, $0.03\% < \phi < 0.1\%$, but less than the overlap concentration ϕ^*, $\bar{L}$ increases at a slower rate.

Aqueous solutions were prepared by dissolving the surfactant monomers N,N dimethylhexadecylamine with sodium salicylate at 1:1 molar ratio. The added aromatic salt closely binds to the micellar surface, so that the electrostatic interaction between different segments of the micelles is negligible. The different concentrations were prepared by diluting a master solution using double distilled and deionized water. We determined the CMC, $\phi_c \simeq 0.002\%$, using a surface tension measurement.

In the TEB experiment, we applied rectangular electric pulses in the micellar solution and measured the decay of the birefringence signal after the termination of the electric field. A horizontal electric field **E** was applied using two platinum electrodes. A weakly focused HeNe laser beam was passed through a polarizer, the sample cell (with thickness $L=2$ cm), a quarter-wave plate, and an analyzer. The optical axes of the polarizer and the quarter-wave plate were set at 45° with respect to **E**, and the analyzer was set at $90° - \alpha$ ($\alpha = 0.4°$) with respect to the polarizer. The transmitted light intensity at the detector is

$$I(t) = I_0 \sin^2[\pi \Delta n(t) L/\lambda + \alpha] , \tag{1}$$

where I_0 is the input intensity, t is the time, $\lambda = 0.633$ μm is the wavelength, and the birefringence Δn is the difference in the indices of refraction parallel and perpendicular to **E**. For $\pi \Delta n(t) L/\lambda \ll \alpha \ll 1$, $I(t)$ is proportional to $\Delta n(t)$. To obtain a good signal-to-noise ratio, a train of pulses at a duty cycle of $< 0.5\%$ was applied and the transmitted light intensity was averaged using a digital oscilloscope.

In this experiment we measured the normalized transmitted light intensity, $R(t)=I(t)/I(0)$. For simplicity, we only analyze the free decay of the birefringence. For all pulse widths of the applied field, the TEB signal is nonexponential and, at long times, can be approximately fitted with a stretched exponential form $R(t)=\exp[-(t/\tau)^{\beta}]$. However, both parameters τ and β depend strongly on the pulse width T, with β decreasing and τ increasing for longer pulses. Figure 1 shows the pulse-width dependence of $R(t)$ for a sample with $\phi \sim 0.05\%$ and $E=50$ kV/cm. The decay of the birefringence gradually approaches a limiting form as T increases from 30 to 300 μs. For $T>300$ μs, the pulse-width dependence is unobservable. Similar trends were also observed for other concentrations and electric-field amplitudes. The dependence on T implies that the relaxation depends on the way the system is perturbed and, as will be discussed, is due to a broad distribution of relaxation times. To ascertain that the pulse-width dependence is not caused by nonlinear effects, we measured the relaxation at a fixed T while varying the strength of the electric field for the same sample. The amplitude of the birefringence scales as E^2 and the normalized transmission intensities collapse onto a single curve as shown in the inset of Fig. 1. Therefore, the measurements are in the Kerr regime and the optical anisotropy is due to induced dipoles.

We can understand the experimental data using a simple model. Assuming the interchain interactions are negligible, we consider a single polymer chain of N monomers and persistence length ξ. The birefringence signal due to a square pulse of duration T is

$$\Delta n(t,N)=\int_{-T}^{0} dt'\,\mu(t-t',N)E^2\,, \tag{2}$$

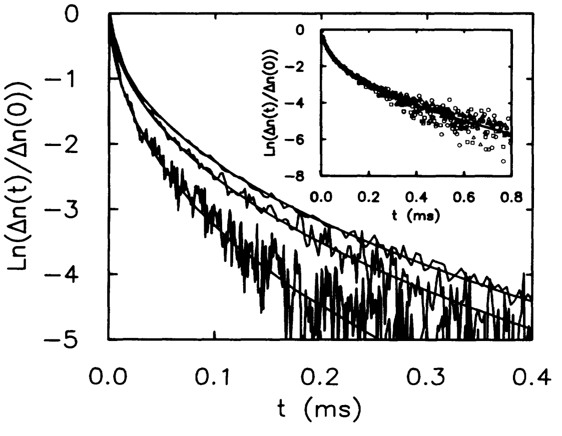

FIG. 1. TEB as a function of pulse width T. From bottom to top, T is 30, 60, and 300 μs. The solid lines are calculated using Eq. (8). The inset is TEB as a function of the amplitude of applied field, E. In increasing order, E is 2 (○), 4 (□), and 7 (△) kV/cm.

where $\mu(t,N)$ is the linear-response function. The normalized relaxation will be independent of the pulse width only if μ is a single exponential. If this is not the case, there will be a nontrivial T dependence. Dynamical linear-response theory relates μ to the equilibrium correlation between the observed quantity, Δn, and the coupling to the applied field [12]. For induced dipoles, the coupling is also proportional to Δn, so that

$$\mu(t-t',N)\propto -\frac{\partial}{\partial t}\langle \Delta n(t)\Delta n(t')\rangle\,, \tag{3}$$

where the brackets give the zero-field expectation value.

The solution scatters light very weakly, indicating that the indices of refraction of the micelles and solvent are well matched. Since the form birefringence is proportional to the mismatch, it can be neglected relative to the intrinsic birefringence. We can write the intrinsic birefringence in terms of the Fourier transform along the polymer chain, $\mathbf{R}_q=\sum_{n=1}^{N}\mathbf{R}(n)\cos(2\pi qn)$, where $\mathbf{R}(n)$ is the position of the nth monomer, $q=p/N$, and p is an integer. The Fourier transforms are the collective modes of the polymer chain. Each mode relaxes exponentially but, due to the different length scales associated with each mode, there is a large variation in the relaxation times. The intrinsic birefringence is

$$\Delta n \propto \frac{1}{N}\sum_q q^2(Z_qZ_{-q}-X_qX_{-q})\,, \tag{4}$$

where Z_q and X_q are the $\hat{\mathbf{z}}$ and $\hat{\mathbf{x}}$ components of $\mathbf{R}_q$ with $\hat{\mathbf{z}}$ being the direction of the applied field. Combining Eqs. (3) and (4) we find

$$\mu(t-t',N)\propto \sum_q \frac{q^4\langle Z_qZ_{-q}\rangle^2}{N^2\tau_q}\exp\left[-\frac{2(t-t')}{\tau_q}\right], \tag{5}$$

where $\langle Z_qZ_{-q}\rangle$ is the equal-time expectation value and τ_q is the relaxation time of the qth mode.

We factor $\langle Z_qZ_{-q}\rangle^2$ into scaling and nonscaling parts,

$$\langle Z_qZ_{-q}\rangle^2=Nq^{-(4\nu+2)}F(q)\,, \tag{6}$$

where ν is the Flory exponent and $F(q)$ is a cutoff function which smoothly decreases the amplitude of modes with length scale shorter than ξ. We choose $F(q)$ to be a Gaussian, $F(q)=\exp[-2(\xi q/b)^2]$, where the "monomer" size b is taken to be the diameter of the polymer strand and ξ/b is the number of monomers in a persistence length. Other forms of $F(q)$ with the same qualitative features give similar results. Since hydrodynamic effects determine the long-time-scale dynamics, we use τ_q obtained from Zimm model of polymer dynamics. In the scaling regime, $\tau_q \propto q^{-3\nu}$. Using ξ as a reference, we take $\tau_q=(\eta_s\xi^3/k_BT)(\xi q/b)^{-3\nu}$, where η_s is the solvent viscosity. As will be shown, our simple model is sufficient to qualitatively explain the present experiment. Precise quantitative results will require a more accurate modeling of the short-length-scale dynamics.

Using these results, the observed birefringence due to a chain of length N is [Eq. (2)]

$$\Delta n(t,N) \sim E_0^2 \sum_q \left(\frac{1}{q}\right)^{4\nu-2} (1-e^{-T/\tau_q})(1-e^{-t/\tau_q}) F(q) . \tag{7}$$

Each term in the sum corresponds to a different collective mode, so that the TEB is a probe of these microscopic degrees of freedom. The collective modes have a broad distribution of relaxation times which lead naturally to nonexponential decay and pulse-width-dependent relaxation. Note that a distribution of polymer sizes is not necessary for nonexponential behavior; the birefringence of even a single polymer relaxes nonexponentially.

For living polymers with a distribution of contour lengths, the birefringence must be weighed accordingly. If electrostatic interactions are negligible, the micellar size distribution is $P(L)=(1/L)\exp(-L/\bar{L})$, where $\bar{L}$ is the average contour length [10]. In the low concentration limit $\bar{L}=b\sqrt{\phi}\exp[E/2k_BT]$, where E is the scission energy associated with creating two end caps [10]. Using this distribution function the full expression for the birefringence is

$$\Delta n(t) = \frac{1}{\bar{N}} \sum_{N=1}^{\infty} \Delta n(t,N) \exp(-N/\bar{N}) , \tag{8}$$

where in our discrete model $\bar{N}$ is the average number of monomers per polymer chain. The measured relaxation is $R(t)=\Delta n(t)/\Delta n(0)$.

This model captures all the features we observed experimentally. The transmitted intensity is proportional to E^2 as is required in the Kerr regime. The pulse-width dependence is given by the factor $1-\exp(-T/\tau_q)$. This factor behaves as a high-pass filter which selects a particular range of collective modes of the polymers. For a short pulse, only the high-q modes ($\tau_q < T$) are excited and the relaxation is fast. On the other hand, for a very long pulse all modes are excited, the relaxation is slow, and is independent of T. This pulse-width-dependent relaxation is a general feature of systems with many degrees of freedom and will be useful as a spectroscopic tool to investigate interesting dynamics in complex systems [8].

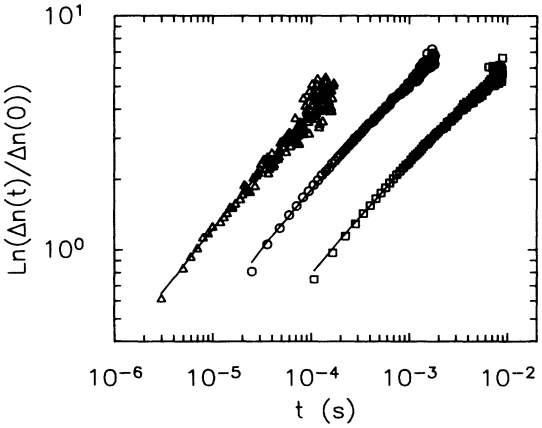

FIG. 2. $\log_{10}\{-\ln[\Delta n(t)/\Delta n(0)]\}$ vs $\log_{10}(t)$. The concentrations ϕ are 0.003% (triangles), 0.05% (circles), and 0.1% (squares). The solid lines are the fits using the model. At large times the TEB can be fitted approximately with a stretched exponential with $\beta=0.5$, 0.45, and 0.4 for $\phi=0.003\%$, 0.05%, and 0.1%, respectively.

We fit our experimental data using Eq. (8). There are only two fitting parameters, ξ/b and $\bar{N}$. As shown by the solid lines in Fig. 1, the model mimics remarkably well the experiment for different pulse widths and electric fields. For this particular sample, the fitting procedure gives $\xi/b \approx 5$ and $\bar{N} \approx 30$. The diameter of the polymer strand, b, was measured to be 5 nm by scanning electron microscopy, and therefore $\xi \approx 25$ nm. We note that the data cannot be fitted without the polymer size distribution.

We next analyze $R(t)$ in the large T limit as a function of surfactant concentration ϕ. Figure 2 shows $R(t)$ for $\phi=0.003\%$, 0.05%, and 0.1%. The data can be adequately fitted with the model except at very short times. The short-time discrepancy is expected because the large-q fluctuations are only partially accounted for in the model. At long times, our experimental data can also be fitted approximately with a stretched exponential. The stretch exponent β decreases from 0.5 to 0.4 as ϕ increases. However, in our model the stretched exponential is not the asymptotic decay but is merely a good approximation within the experimental time windows.

Figure 3 shows the average contour length $\bar{L}(=b\bar{N})$ vs $(\phi-\phi_c)^{1/2}$. We found that $\bar{L}$ increases from ~50 nm at small ϕ to ~300 nm at the largest ϕ in the experiment. The persistence length ξ increases slowly from $3b$ to $5b$ as a function of ϕ. Two growth regimes were identified. For $0.003\% < \phi < 0.03\%$ our data are consistent with the theoretical prediction of $\bar{L} \sim \sqrt{\phi}$. On the other hand, for

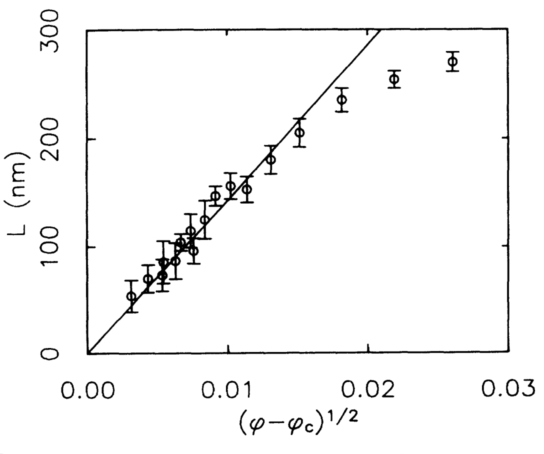

FIG. 3. Average contour length as a function of ϕ. At small ϕ, $\bar{L}$ increases as $\sqrt{\phi}$, and at the higher ϕ, $\bar{L}$ increases at a slower rate. The solid line is the fit for small ϕ.

$\phi > 0.03\%$, $\bar{L}$ increases at a slower rate. This result has not been previously observed and is not accounted for in the current theory [10,11]. From the slope of Fig. 3 we derive the scission energy to be $E \approx 15k_BT$. The large scission energy suggests a strong preference for uniaxial growth, and is consistent with our observation of a very small CMC. The scission energy measured in our TEB experiment is comparable to a well-known living polymer solution, SDS in NaCl, where Missel *et al.* found $E \simeq 10k_BT$ [5].

It is interesting that good agreement is obtained with the model even at low surfactant concentrations. For the smallest ϕ, $\bar{L}$ is $\sim 3\xi$, indicating that the polymer is still flexible. The observed ϕ dependence of $R(t)$ is entirely different from that seen in a recent birefringence experiment by Bellini *et al.* for a different living polymer [13]. They fit their data by a stretched exponential, but their effective exponent β is an increasing function of ϕ rather than a decreasing function of ϕ as observed here. Nevertheless, the exponents are about the same at large ϕ in both experiments. This suggests that at these concentrations their micelles also behave like flexible polymers. At low concentrations, Bellini *et al.* interpreted their result to indicate a rodlike phase. We conclude that, since our observed ξ/b is small and the ϕ dependence of $R(t)$ is quite different from that of Bellini *et al.*, any rodlike phase of our micelle is restricted to an extremely narrow concentration regime near CMC. A possible reason for the difference is that our living polymer has an extremely small persistence length and a large scission energy which gives rise to the interesting polymeric behavior even at low concentrations.

We also measured the hydrodynamic radius R_H of the living polymers using quasielastic light scattering (QELS). Since $R_H \ll \lambda$, QELS measures the polymer diffusion rather than the internal modes of the polymer. For small ϕ, R_H can be obtained from the diffusion constant using the Stokes-Einstein relation. However, the living polymer scatters light very weakly, so that R_H can only be measured for $\phi > 0.05\%$. We found that the average R_H is consistent with the radius of gyration, R_g, obtained from our model.

In summary, we performed a transient electric birefringence experiment on a living polymer solution. We showed that both the nonexponential relaxation and the pulse-width dependence can be understood in terms of a model based on the collective modes of the polymers. We found that the average contour length increases as $\sqrt{\phi}$ at low concentrations while leveling off at higher concentrations. The deviation from $\sqrt{\phi}$ dependence for $\bar{L}$ is not well understood and should be explored further. We also found that the micelles are flexible even very close to the critical micellar concentration. This is in marked contrast with previous studies where a rodlike phase is found prior to the polymeric phase. We note a preprint by Hong *et al.* [14] which applied similar ideas to a TEB experiment for DNA.

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