Local Vitrification Model for Melt Dynamics

Boaz Ilan and Roger F. Loring*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853

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1. Introduction

The richness and complexity of the dynamics of dense polymer fluids arises from the wide range of time scales that characterize relaxation in these systems. According to the principle of time−temperature superposition, disparate relaxation times in wide portions of this spectrum can vary with temperature in the same way.[1,3] This principle permits the finite range of time scales accessible in a relaxation experiment to be extended through variation of the temperature. This procedure has been demonstrated to be valid for dielectric and mechanical relaxation measurements on diverse polymeric systems over wide ranges of temperatures and time scales.[1] Time−temperature superposition is a property of the most basic model of polymer physics, the Rouse model.[2] In this model, the same friction coefficient governs the relaxation of each normal mode, independent of the mode wavelength. The ratio of relaxation times of two distinct normal modes is therefore independent of temperature.

Despite the wide utility of time−temperature superposition, an accumulation of evidence suggests that, at sufficiently low temperatures, the principle does not apply. Both dielectric and mechanical relaxation measurements have shown that as the glass transition temperature (T_g) is approached from above, relaxation times for short length scale dynamics increase more rapidly than those reflecting motions on longer length scales.[4−11]

Adachi and Hirano[10] have recently reported dielectric relaxation studies of *cis*-polyisoprene at temperatures approaching T_g. These dielectric loss spectra display two peaks: a low-frequency peak at ω_n reflecting the relaxation of the end-to-end vector (normal mode), and a high-frequency peak at ω_s arising from relaxation of the segmental dipoles.[3,10,12] For $T > T_g + 30$ K, time−temperature superposition holds for the portion of the spectrum that includes both peaks. At $T < T_g + 30$ K, time−temperature superposition holds for the segmental and normal mode peaks individually, but not for the full spectrum. This breakdown of time−temperature superposition is best quantified in Figure 7 of ref 10, which shows the temperature dependence of ω_s/ω_n. This quantity is roughly constant for $T > T_g + 30$ K, but drops sharply as T_g is approached. Adachi and Hirano[10] interpret this result with a “local vitrification” picture of dynamical hetereogeneity.[13−16] At a particular low temperature, certain regions of the polymer are relatively immobile, while other portions relax more rapidly. As T decreases, the fraction of the chain that is locally vitrified increases.

Nicolai and Floudas have measured dielectric and viscoelastic relaxation of poly(oxypropylene) melts.[11] Both measurements demonstrate that in this system, as in polyisoprene, segmental relaxation times increase more strongly than normal mode relaxation times as T_g is approached. The temperature dependence of the ratio of shift factors for segmental and normal mode spectra is similar to that observed by Adachi and Hirano.[10] Nicolai and Floudas ascribe this phenomenon to dynamical heterogeneity.[13−16]

In this Note, we analyze the breakdown of time−temperature superposition within a dynamical mean-field model that is consistent with the spirit of a local vitrification picture. This is the dynamically disordered Rouse (DDR) model, which is described in detail in ref 17. The DDR model generalizes the Rouse model[2] by assigning to each bead a mobility that fluctuates in time between zero and a finite value. In addition to the Rouse parameters, w, the segmental relaxation rate, b, the root-mean-squared separation of neighboring beads, and N, the chain length, the DDR model introduces c, the equilibrium fraction of mobile beads, and γ, the rate at which bead mobilities fluctuate.[17] We have eliminated γ from this list of adjustable parameters, by calculating it self-consistently through an ansatz that associates γ with the shortest wavelength relaxation rate of the chain.[17] The resulting expression for γ vanishes below a threshold value of c, $c^* \equiv 3 - 2^{3/2} \approx 0.1716$. Reducing the value of c simultaneously decreases the fraction of mobile beads and decreases the rate at which mobile and immobile beads change mobilities. Temperature does not enter explicitly in this stochastic theory in a significant way, so c should be regarded[17] as varying monotonically with temperature, with c^* playing the role of a Vogel−Fulcher temperature.[13] We will treat the variation of c in the DDR model as equivalent to varying T in the laboratory. The DDR model gives results that are in qualitative agreement[17] with bond fluctuation Monte Carlo simulations of glassy dynamics in melts by Okun et al.[18] It must be emphasized that the DDR model is not a first principles, mechanistic explanation of the glass transition but instead a theory of the effects on polymer dynamics of the approach to the glass transition from the high-temperature side.[17] The existence of the parameter c^* does not imply that this theory is based on the notion of an underlying thermodynamic phase transition.[13]

2. Results and Discussion

In the DDR model, the Laplace transforms of the autocorrelation functions of the qth Rouse mode and of the polymer’s end-to-end vector are given by

$$\hat{C}_{qq}(s) = \frac{1}{s + 4w\psi(s)\sin^2\frac{q\pi}{2N}}; \quad q = 1, ..., N-1 \quad (1)$$

$$\hat{C}_{\mathrm{ete}}(s) = \frac{2}{N(N-1)}\sum_{q=1,3,5,...}^{N-1}\cot^2\left(\frac{q\pi}{2N}\right)\hat{C}_{qq}(s) \quad (2)$$

The Laplace frequency is denoted s. Each autocorrelation function is normalized by its value at zero time. In eq 1, $\psi(s)$, the effective medium function, is given by

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* To whom correspondence should be addressed. E-mail: rfl2@cornell.edu.

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$$\psi(s) = \Big[(1-c)^2 w + (1+c)(s+\gamma) - (1-c)\sqrt{(s+\gamma)^2 + 2w(s+\gamma)(1+c) + w^2(1-c)^2}\Big] \Big/ 2(s+\gamma) \quad (3)$$

$$\gamma = 4w\left(\frac{c-c^*}{1-c^*}\right) \quad (4)$$

The effective medium function is a dimensionless bead mobility, whose frequency dependence reflects the dynamics of the polymer's environment. For $c = 1$, $\psi = 1$, and the expressions in eqs 1 and 2 become exactly correct for the Rouse model. To calculate the dielectric loss spectrum, we employ the linear-response relation between the dielectric function, $\epsilon(\omega)$, and the Laplace transform of the dipole autocorrelation function, $\hat{C}(s)$:[12]

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\Delta\epsilon} = 1 - i\omega\hat{C}(i\omega) \quad (5)$$

We calculate the segmental and normal mode portions of the dielectric loss spectrum by substituting the expressions in eqs 1 and 2, respectively, for $\hat{C}$ into eq 5, and taking the imaginary part of the resulting expression, ϵ''. The relaxation strength $\Delta\epsilon$ is not calculated. The validity of time−temperature superposition for relaxation on long length scales is assessed in Figure 1, which shows ϵ_n'', the dielectric loss spectrum associated with normal-mode dynamics for $c = 1$ (solid curve) and $c = 0.1717$ (dashed curve). The chain length is $N = 40$. The frequency axis for each plot has been scaled by ω_n, the frequency at which each attains its maximum. For any value of c and $N \gg 1$, ω_n scales with chain length as N^{-2}, as in the Rouse model. The $c = 1$ result is identical to a calculation from the Rouse model. At $c = 0.1717$, the system is slightly above the threshold, c^*. Although the values of ω_n differ by more than 3 orders of magnitude, the spectra are seen to have the same shape, except at the highest frequencies. The same finding was demonstrated in the time domain in Figure 1 of ref 17, where it was shown that the early time decay of $C_{ete}(t)$ is well-fit by a stretched exponential with exponent 0.67, while the decay at later times more closely approximates an exponential.

A similar test is performed for the relaxation of a short-wavelength Rouse mode in Figure 2, which shows ϵ_s'', the contribution to dielectric relaxation from segmental dynamics. This quantity is defined by eq 5 with the dipole autocorrelation function represented by $\hat{C}_{qq}$ with $q = N - 1$, and so reflects relaxation of the shortest-wavelength Rouse mode. The coarse-grained Rouse picture need not represent dynamics at the truly segmental length scale, but we will use "segmental" to describe the smallest length scale in our model. In Figure 2, $N = 40$. For any value of c and $N \gg 1$, the segmental loss spectrum is independent of N. For $c > 0.3$, the spectrum shows a single peak. For $c^* < c < 0.3$, the spectrum is composed of two peaks: a high-frequency peak, whose peak frequency depends weakly on c, and a low-frequency peak, whose peak frequency vanishes proportional to $c - c^*$. The high-frequency peak reflects dynamics on time scales short compared to the relaxation of immobile beads, γ^{-1}. This peak arises from motions of beads with nonzero mobilities, whose dynamics are constrained by the beads with zero mobility. The low frequency peak represents terminal relaxation including the dynamics of initially immobile beads. We anticipate that in a more general version of the DDR model that included a distribution of mobilities and relaxation rates, the appearance of a second distinct peak in ϵ_s'' would be replaced by a broadening of the spectrum.

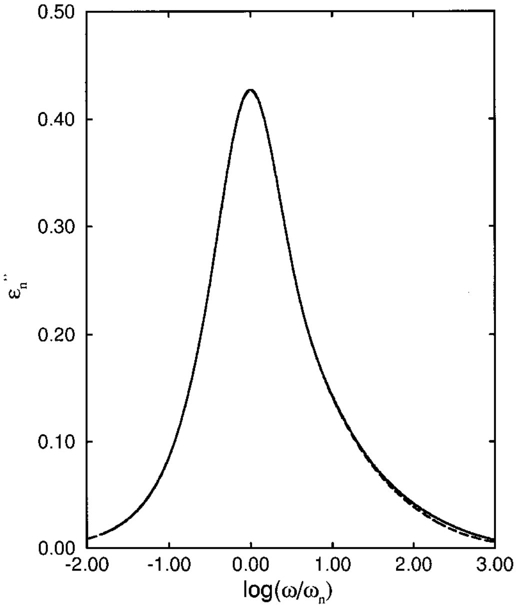

Figure 1. Dielectric loss spectra reflecting normal mode relaxation are shown for $c = 1$ (solid line) and $c = 0.1717$ (dashed line). The frequency for each spectrum is scaled by the peak frequency, ω_n.

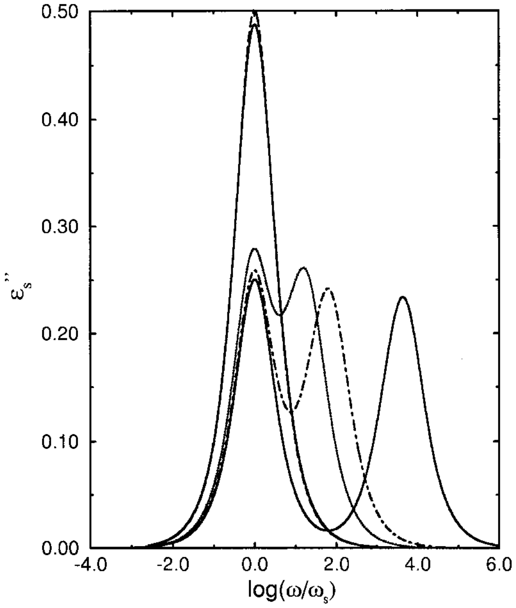

Figure 2. Dielectric loss spectra reflecting segmental relaxation are shown for $c = 1$ (dashed line), $c = 0.8$ (solid line, 1 peak), $c = 0.2$ (dotted line), $c = 0.18$ (dot−dashed line), and $c = 0.1717$ (solid line, 2 peaks). For $c > 0.3$, the spectrum displays one peak, while for $c^* < c < 0.3$, the spectrum is bimodal. The frequency for each spectrum is scaled by ω_s, the peak frequency for $c > 0.3$, or the frequency of the lowest frequency peak for $c < 0.3$.

For each plot in Figure 2, the frequency is scaled by ω_s, defined to be the frequency of the single peak for $c > 0.3$ and the frequency of the lower frequency peak for $c^* < c < 0.3$. Spectra are shown for $c = 1$ (dashed line), $c = 0.8$ (solid line, 1 peak), $c = 0.2$ (dotted line), $c = 0.18$ (dot−dashed line), and $c = 0.1717$ (solid line, 2 peaks). At high temperature ($c \approx 1$), ϵ_s'' preserves its shape for varying c. The plots for $c = 1$ and $c = 0.8$ are

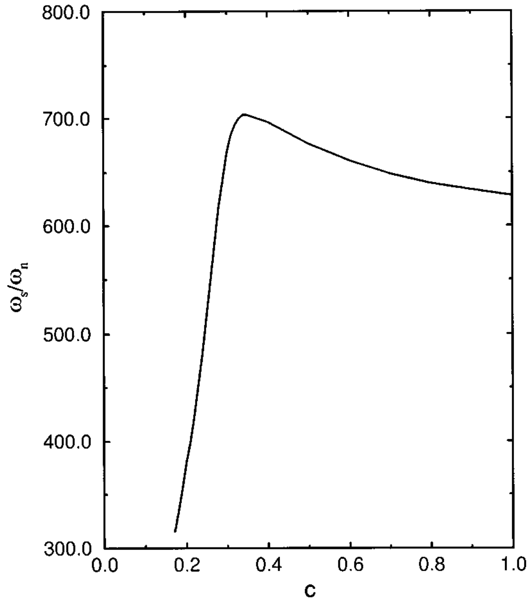

Figure 3. Ratio of peak frequencies of dielectric loss spectra for segmental and normal mode relaxation, ω_s/ω_n, is plotted vs c.

distinguishable only near the peak. Time–temperature superposition breaks down gradually as c is decreased from unity, and then fails qualitatively near $c \approx 0.3$, with the appearance of a second peak. For $c \approx c^*$, the low-frequency side of the low-frequency peak in the spectrum has a shape that is approximately invariant to changes in c. As c is decreased from unity, ϵ_n'' loses the time–temperature superposition property at $c = c^*$, while this property breaks down for ϵ_s'' well above c^*. The DDR model predicts that ϵ_s'' loses its time–temperature superposition property at higher temperature than does ϵ_n''. This phenomenon was not observed by Adachi and Hirano[10] for *cis*-polyisoprene, nor by Nicolai and Floudas[11] for poly(oxypropylene). However, two-dimensional NMR studies of *cis*-polyisoprene by Schaefer and Spiess[19] and by Chung, Kornfield, and Smith[20] have shown that the spectrum of correlation times associated with segmental relaxation broadens as $T \rightarrow T_g$. The spectra in Figures 1 and 2 reflect the differing effects of dynamical disorder on Rouse modes of long wavelength (Figure 1) and short wavelength (Figure 2). The effects of dynamical disorder on Rouse modes of intermediate wavelength are discussed in ref 17. The dependence of relaxation behavior in a supercooled melt on Rouse mode wavelength has also been treated by Rehkopf et al.[21]

The ratio of the peak frequencies of segmental and normal mode relaxation, ω_s/ω_n, is plotted vs c in Figure 3 for $N = 40$. As c is decreased from unity, this ratio initially increases. This dependence can be interpreted as follows. Let Λ denote the mean contour length between temporarily immobile beads. If Λ is much larger than the Rouse mode wavelength, $2\pi/q$, then the relaxation of the qth mode is relatively unaffected by the presence of immobile beads. If Λ is comparable to or smaller than the Rouse mode wavelength, the mode relaxation will be significantly affected by immobile beads. The normal mode relaxation is dominated by contributions from the longest wavelength Rouse modes. Therefore, as c is decreased from unity, the slowing of the normal mode relaxation exceeds that for segmental relaxation. As c decreases further, Λ becomes sufficiently small for the immobile beads to affect segmental relaxation. As $c \rightarrow c^*$, both ω_n and ω_s vanish proportional to $c - c^*$. This "critical" dependence on the fraction of mobile beads cancels out of the ratio, leaving behind a "noncritical" c dependence that produces the drop in the ratio as $c \rightarrow c^*$. By "critical" we mean vanishing or diverging as $c \rightarrow c^*$. The ratio ω_s/ω_n approaches a finite limit, approximately 0.20 N^2, as $c \rightarrow c^*$. This decrease in ω_s/ω_n is qualitatively consistent with the T dependence of this quantity as $T \rightarrow T_g$, described by Adachi and Hirano[10] and by Nicolai and Floudas.[11]

The DDR model is characterized by significant simplifications. The bead mobility is either zero or a finite value, with each bead making transitions between these states at the same rate. The probability that a given bead occupies either state is uncorrelated with the states of its neighbors. A more realistic model would incorporate a distribution of mobilities and of relaxation rates of mobility states, as well as the existence of spatial correlations. Nevertheless, the DDR model in its present form represents a tractable, mean-field approach that describes the effects of spatial dynamical heterogeneity[13–16] on melt relaxation.

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