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Relaxation Anomalies in Linear Polymer Melts

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1. General Aims

The standard reptation picture[1] for monodisperse melts of flexible, entangled polymers predicts a relaxation structure with a long time behavior which is essentially exponential. For instance, the stress memory function is

$$M(t) \equiv \frac{\langle \sigma(0)\,\sigma(t)\rangle}{\langle \sigma^2\rangle} \rightarrow (\text{cont})\exp(-t/T_{\text{rep}}) \quad (t \gg T_{\text{rep}}) \quad (1)$$

In eq 1, σ is a shear stress component, the average signs correspond to thermal averages over fluctuations, and T_{rep} is a reptation time, with the structure

$$T_{\text{rep}} = \tau_0 N^3/N_{\text{e}} \quad (2)$$

where τ_0 is a microscopic jump time, N is the degree of polymerization, and N_{e} is the distance between entanglements. Equation 2 holds for entangled melts ($N \gg N_{\text{e}}$). In the opposite (nonentangled) limit, we also have an exponential decay as in eq 1 at long times t, but the characteristic time is a Rouse time:

$$T_{\text{Rouse}} = \tau_0 N^2 \quad (N \ll N_{\text{e}}) \quad (3)$$

Our aim, in the present note, is to consider the effects of polydispersity on the rheological behavior. We concentrate on pure linear chains: the effects of branching are very different and have, to some extent, been considered in the literature.[2]

Experiments have been carried out for bidisperse linear chains,[3] some theoretical ideas have been presented,[4] and some simulations of polydisperse melts (unentangled) are available.[5] In the present note, we emphasize another aspect: if the distribution of molecular weights (or polymerization indices N) falls out exponentially at large N, the memory function should show a *stretched exponential* form:

$$M(t) = \exp[-(t/\tau)^{\beta}] \quad (0 \leqslant \beta < 1) \quad (t \gg \tau) \quad (4)$$

Stretched exponentials often show up in relaxations of polymers near a glass transition point.[6] But the spectrum of relaxation times involved is due to local segmental motions. What we discuss here is completely different, related to large-scale chain motions far above T_{g} and present only for polydisperse systems. The exponent β is sensitive to the presence or absence of entanglements. But it should be temperature independent.

In section 2, we construct the basic formulas required to handle a broad distribution of relaxation times. In section 3, we apply these ideas to both Rouse dynamics and reptation dynamics.

All our ideas may already be familiar to some rheologists, but our search failed to find them in the current literature.

2. Justification for Stretched Exponentials

It is always permissible to analyze a memory function $M(t)$ in terms of a distribution over relaxation rates f:

$$M(t) = \int_0^{\infty} \mathrm{d}f\, W(f) \mathrm{e}^{-ft} \quad (5)$$

We shall be interested here in distributions $W(f)$ which fall out sharply at small f, with the form

$$W(f) = A(f)\exp\left[-\left(\frac{f_0}{f}\right)^{x}\right] \quad (6)$$

where $A(f)$ is an uninteresting power law, while the dominant term is the exponential, with a certain characteristic exponent x (>0).

Integrating eq 5 with eq 6, we find an exponential factor:

$$\exp[-S(f, t)] \equiv \exp\left[-ft - \left(\frac{f_0}{f}\right)^{x}\right] \quad (7)$$

We look for the minimum of S, with respect to f: this is $f = f^*(t)$, defined by

$$t = x\,\frac{f_0^{\,x}}{(f^*)^{x+1}} \quad (8)$$

The value of the S function at the minimum is

$$S^* = (1 + x^{-1}) f^* t = (\text{const})(f_0 t)^{\beta} \quad (9)$$

where $\beta = x/(x + 1)$.

Thus, we are led to a stretched exponential:

$$M(t) = B(t)\exp[(-S(t))] = B(t)\exp[-(f_1 t)^{\beta}] \quad (10)$$

where $B(t)$ is a slowly varying function and f_1 differs from f_0 only by a numerical factor of order unity.

At this moment, we have just repeated some classical theorems about Laplace transforms. What we must do now is to show that the form (6) for the distribution of relaxation rates is indeed plausible for our polydisperse melts.

3. The Two Major Limits

We shall assume that our chains, of polymerization index N, have a distribution of the form

$$P(N) = C(N)\exp(-N/\bar{N}) \quad (N > \bar{N}) \quad (11)$$

where $C(N)$ is a slowly varying function (a power law), while $\bar{N}$ is related to the average molecular weight. This form is indeed expected for radical polymerizations.[7]

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3.1. Entangled Chains ($N > N_e$). For a given value of N, the smallest reptation rate $f(N)$ is of the form[1]

$$f(N) = \frac{1}{\tau_0} N_e N^{-3} \quad (N \gg N_e) \tag{12}$$

where τ_0 is a microscopic jump time (independent of N) and N_e is the distance between entanglements. Using eq 9, we can convert the N distribution into a distribution of relaxation rates, writing

$$W(f)|\mathrm{d}f| = P(N)\,\mathrm{d}N$$

and we obtain, in the notation of eq 6,

$$W(f) = A(f)\exp\left[-\frac{1}{\bar{N}}\left(\frac{N_e}{f\tau_0}\right)^{1/3}\right] \tag{13}$$

Comparing this to eq 6, we see that, for the entangled case, we expect $x = {}^1/_3$ and (from eq 9) $\beta = {}^1/_4$.

3.2. Short Chains ($N < N_e$). Here, we expect the chains to follow Rouse dynamics,[1] and we have

$$f_N = \frac{1}{\tau_0} N^{-2} \tag{14}$$

This, by the same argument, gives $x = {}^1/_2$ and $\beta = {}^1/_3$.

4. Discussion

4.1. Possible Role of Double Reptation. The simple reptation picture which has been used here has been augmented by des Cloizeaux.[8,9] His model assumes that each entanglement is based on *two* chains (more complex knots are ignored). Then it may be argued that the memory function of interest $M(t)$ is not the naive reptation function $M_n(t)$ but is the square of it:

$$M(t) = M_n^{\,2}(t) \tag{15}$$

(where all M's are normalized to ensure $M(0) = 1$). This should hold even for polydisperse melts. If we accept eq 15, our prediction of stretched exponentials is maintained, and the β values are unchanged.

4.2. Role of Tube Renewal. A very long chain ($N = N_{\mathrm{long}}$), floating among shorter chains ($N = N_{\mathrm{short}}$), may relax by a process of tube renewal: this is known to influence significantly the rheological data:[3,10,11] a rough formula for the renewal time (τ_{ren}) is

$$\frac{1}{\tau_{\mathrm{ren}}} \cong \left(\frac{N_e}{N_{\mathrm{long}}}\right)^2 f(N_{\mathrm{short}}) \tag{16}$$

corresponding to a Rouse motion, where the jump frequency $f(N_{\mathrm{short}})$ is the reptation rate of the short chains (assumed here to be entangled). This might upset our results. To ascertain this, for a given N_{long}, we must compare the time τ_{ren} to the time t corresponding to the peak of S in eq 7:

$$t = f^{-1}(N_{\mathrm{long}})\frac{N_{\mathrm{long}}}{\bar{N}} \tag{17}$$

Our discussion holds only if $t < \tau_{\mathrm{ren}}$. Using eq 12 for $f(N)$, this gives

$$\frac{N_{\mathrm{short}}}{N_e} > \left(\frac{N_{\mathrm{long}}}{N_e}\right)^{2/3}\left(\frac{N_e}{\bar{N}}\right)^{1/3} \tag{18}$$

Typically, $N_e = 300$, $N_{\mathrm{long}}/N_e = 30$, $\bar{N}/N_e = 20$, and the inequality (18) imposes $N_{\mathrm{short}} > 4N_e$: most of the chain population should obey this. But if the ratio $\bar{N}/N_e$ was significantly smaller, our model would be inapplicable.

5. Conclusions

Polydisperse polymer melts should often display stretched exponentials in their mechanical memory functions. The exponent β should be temperature independent, but it should be different for short/long chains.

Can we relate these ideas to current rheological data?

(a) Ideally, we would want the long time tail of the memory function $M(t)$. But this is often derived from the frequency-dependent moduli $G(\omega)$ by Fourier transforms, which are somewhat hazardous at large times t.

(b) We may think of certain numerical checks: for instance, Ngai[12] and Plazek[13] showed that if $M(t)$ is a stretched exponential *at all times*, the product of the plateau modulus by the steady-state compliance is a number depending only on the index β (via gamma functions). However, in our picture, there is no reason for eq 4 to hold at intermediate times ($tf(\bar{N}) \lesssim 1$). Thus, we cannot use this trick.

(c) The same difficulty occurs with other discussions assuming stretched exponentials at all time: for instance, the analysis of experiments preformed in ref 13 gives $\beta \sim 0.5-0.6$, but the aim in this work was to describe the whole memory function.

On the whole, what we need is direct, precise, measurements of $M(t)$ at long times, in systems where the inequality (18) is well satisfied.

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References and Notes

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