polymer communications

Relaxation behaviour of highly polydisperse polymer melts

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We examine the problem of a highly polydisperse polymer melt within the framework of the tube model. Recent ideas on tube dilation in branched polymers are applied to linear melts when polydispersity is very strong. The weight distribution function $P(M)$ and the relaxation modulus $G(t)$ are related by a non-linear integral equation. The case of power-law polydispersity, $P(M) \sim M^{-\tau}$, is examined in detail and relaxation moduli, $G(t)$, calculated. When $1 < \tau < 2$, $G(t) \sim t^{-2\gamma}$ where γ is related to the polydispersity index τ via $\gamma = (\tau - 1)/(2 - \tau)$.

(Keywords: rheology; melts; polydispersity)

Introduction

Dense polymeric fluids provide us with a rich set of physical examples of strongly interacting systems and have attracted considerable interest among condensed-matter physicists as well as polymer scientists[1]. In particular their dynamical behaviour is rich, encompassing an enormously wide range of time-scales from picosecond monomeric collisions to configurational changes of entire molecules that may take seconds or longer. The slower motions are governed by the topological interactions between the polymer chains and are usually understood via a dynamical mean-field picture known as the tube model[2]. In this model the predominant dynamical mode of polymer chains at long times is curvilinear diffusion (reptation) along their own contours. Lateral motion perpendicular to the contour is restricted by an effective topological interaction to the radius of the tube, a, which is the main parameter of the model. (An equivalent measure of the tube often quoted is the effective molecular weight between topological constraints of 'entanglement molecular weight', M_e.) The tube size amounts to a coarse-graining of the polymer to an effective topological length, and seems to be a highly co-operative phenomenon as tube sizes of 30–100 Å indicate. This size range emerges from measurements of the plateau modulus and numerical simulation (though the latter is hard because of the large time-scale range)[3]. If a bulk strain is communicated affinely to the tubes, stress-decay in the melt can be understood by the loss of strained chain configurations as the chains diffuse out of their original tubes[1,2]. For monodisperse linear polymers consisting of N effective monomers of size b each contributing a local friction constant of ζ, this model predicts near single exponential behaviour:

$$G(t) = G_0\mu(t) = G_0 \frac{8}{\pi^2} \sum_{p\ \mathrm{odd}}^{\infty} \frac{1}{p^2} \exp\left(\frac{-p^2 t}{T_{\mathrm{rept}}}\right) \quad (1)$$

with a characteristic 'reptation time' $T_{\mathrm{rept}} = \zeta N^3 b^4 / \pi^2 kTa^2$ and a plateau modulus $G_0 = 4cb^2kT/5a^2$ (where c is the volume concentration of chains). Experimentally we find that $T_{\mathrm{char}} \sim N^{3.4}$ and that monodisperse polymer melts do exhibit a near-exponential stress-decay.

However, most polymeric fluids encountered in nature and in the laboratory are highly polydisperse and consequently their relaxation spectra are very broad. The form of the relaxation of polydisperse melts is not even qualitatively understood except in the comparatively simple case of a binary blend of two monodisperse fractions[4]. In this paper we report results of applying techniques first developed for branched polymer melts to the problem of highly polydisperse linear polymers.

Since the early success of the model in explaining viscoelasticity in this ideal system, including some aspects of the non-linear response, effort has been directed in three related directions: fluctuations in the effective entangled length[5]; predictions for branched polymers[6,7]; self-consistency in the dynamics of the tube-potential itself[4,7]. These three problems are closely related because the extra topological constraints in branched polymers suppress reptation completely and all stress is lost by fluctuation of the entangled path length. Moreover, tube segments near a branch point relax very much slower than segments near an end. At the characteristic relaxation time of one of these slow segments, fast segments in the neighbourhood cannot act as effective topological constraints because their configuration is changing so rapidly and any constraints are released faster than they are encountered. Instead, fast segments act as a solvent for the slow segments and the effective tube diameter seen by the slower segments is dilated to a larger value. Although both length fluctuation and constraint release are important in linear polymers, their effects are dominant in branched polymers and also easier to study because time-scales for tube relaxation differ so widely.

It is necessary to know the dependence of the tube diameter on polymer concentration in order to calculate its self-consistent value at any time-scale. In melts and concentrated solutions experiments on the concentration dependence of the modulus agree with assuming that the entanglement spacing depends only on the line density of the polymer chain[2] (though dimensional arguments have to be used with caution when more than one length scale exists[8]). Universal behaviour is found such that

$$a \sim \phi^{-\alpha} \quad (2)$$

where α is close to 1/2. Combining this dependence with the assumption that the effective volume concentration ϕ is given by the fraction of unrelaxed polymer allows a

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very simple solution to the problem of monodisperse star polymers[7]. Each tube segment a distance s (in units of molecular weight) from the free end has a characteristic relaxation time $t(s)$. The fluctuations in arm length can be viewed as an activated diffusion against an entropic potential[6] $U(s) = kTvs^2/M_eM$, though a self-consistent, dynamic value of M_e must be used so that $M_e \sim \phi_{\mathrm{eff}}^{-1} \sim [1 - s(t)/M]^{-1}$ giving an ordinary differential equation:

$$\frac{\mathrm{d}t}{\mathrm{d}s} = t(s)\frac{\mathrm{d}}{\mathrm{d}s}U_{\mathrm{eff}}(s) = t(s)\frac{2v}{M_{e0}}\left(\frac{s}{M}\right)\left(1 - \frac{s}{M}\right) \quad (3)$$

as an approximation to the partial differential equation for the distribution function of released segments. The relaxation modulus $G(t)$ is then easily calculated from $s(t)$ since $G(t) \sim \phi_{\mathrm{eff}}^2$. When time-scales for relaxation of different parts of a molecule differ widely, this approach has been quite successfully applied to a number of problems, including the gelation ensemble of branched lattice-animals[9].

This 'tube dilation' approach is not applicable to linear polymers in most cases because all tube segments in a linear molecule relax on the same characteristic time-scale T_{rept}. A more appropriate picture is to consider that individual constraint release events allow the tube itself to behave like a free Gaussian polymer chain undergoing Rouse dynamics[4] with a relaxation function $R(t)$. The final relaxation modulus is the independent superposition of reptation and constraint release so that $G(t) \sim \mu(t)R(t)$. The monomeric hopping times for the tube must be consistent with the terminal relaxation times of the constraining polymers responsible for it. Even in the monodisperse case this is a complex problem, and is richer still in the case of the binary blend. The binary blend also allows us to ask when the reptation time of the shorter chains is short enough for the terminal relaxation to be correctly given by the 'dilated tube' picture in which the short chains act as effective solvent for the long. Doi *et al.*[4] assume that the critical condition is that the initial Rouse motion of the tube due to constraint release by the short chains must outpace the curvilinear motion of the long chains and find:

$$\frac{M_S}{M_e} < \left(\frac{M_L}{M_e}\phi_L\right)^{1/3} \quad (4)$$

in the parameter space of the two molecular weights M_L and M_S and the volume fraction of long chains ϕ_L. Recently Rubinstein, Colby and Viovy[4] have modified the picture in favour of a more local criterion for entanglement. The difficulty arises in the self-consistent calculation of the tube segment waiting times. Depending on the molecular weights and relative concentrations of the two polymers, the terminal relaxation of the longer chains may either be dominated by reptative or by Rouse dynamics. Again the qualitative form of the relaxation modulus can be calculated but it seems prohibitively difficult at present to extend the method to cases of broad distributions of waiting times such as polydisperse or branched polymers. However, in the limit of well-separated time-scales of the two components as in (4) above (the authors' 'tube reptation' regime), the model reduces to the tube dilation prediction. They picture the dynamics as equivalent to the original tube of 'fast' constraints undergoing reptation within a wider tube of 'slow' constraints. More general polydisperse systems seem at first sight intractable, but if one example of very broad polydispersity [binary blends satisfying (4)] admits to a tube dilation approach, it is possible that other more general examples may be treated approximately in the same way.

Polydisperse linear blends

When the weight fraction of chains of molecular weight M is $P(M)$ we are interested in the functional relationship between $P(M)$ and the relaxation modulus $G(t)$. This has for a long time been of considerable commercial interest, as it is known that polymer rheology is more sensitive to molecular weight distribution than gel permeation chromatography, especially with respect to high molecular weight fractions[10]. The problem is that the information on $P(M)$ is highly convoluted. Attempts have been made by Tuminello[10] to consider the problem using the idea of effective solvent but it is clear from the case of star polymers that more than a simple superposition is involved and that chain dynamics need to be calculated self-consistently. Moreover in the experiments of Tuminello, rheological data treated with the hypothesis of simple superposition consistently gave narrower molecular weight distributions than direct methods (in this case light scattering). This is just what would be expected if a continuous renormalization of relaxation times was the result of co-operative disentanglement: the reptation time of short chains is unaffected by the polydispersity but the long chains relax faster than they would in a monodisperse melt.

In polydisperse linear melts the separation of time-scales will not come from the activated character of fluctuations in entangled path length as in branched polymers but instead from the broad distribution of chain lengths. For a starting point we look for the analogue of the self-consistent equation (3) when the system consists of polydisperse linear polymers rather than branched polymers with an inherently broad distribution of relaxation times.

We first look for the general consequences of the assumption that the effective tube radius at a time t after a step strain depends on the effective concentration of unrelaxed segments, then consider some specific examples. Let $g(M, t)$ be the fraction of original tube length of polymers of molecular weight M unrelaxed at time t. If monodisperse, this exhibits near exponential decay with a characteristic time $T_{\mathrm{rept}}(M) \sim M^3/a^2$. From (2) we may write, taking our measure of time such that $T_{\mathrm{rept}}(1) = 1$ in the monodisperse case:

$$\frac{\mathrm{d}}{\mathrm{d}t}g(M, t) = -\frac{g(M, t)}{M^3}\phi_{\mathrm{eff}}(t) \quad (5)$$

This is the analogy which we sought of the branched polymer equation (3) in this case, but needs to be accompanied by an expression for the effective dynamic concentration ϕ_{eff}. If we take the limiting assumption of widely separated time-scales (which needs careful examination but is in all cases an upper bound to the relaxation rate) then all relaxed polymer counts as solvent and we have

$$\phi_{\mathrm{eff}}(t) = \int_0^\infty g(M, t)P(M)\,\mathrm{d}M \quad (6)$$

Solving for $g(M, t)$ from (5) and recasting (6) in terms of the variable $\lambda = 1/M^3$ gives a non-linear integral equation connecting $P(M)$ and $\phi_{\mathrm{eff}}(t)$:

$$\phi_{\text{eff}}(t) = \frac{1}{3}\int_0^\infty \lambda^{-4/3}P(\lambda^{-1})\exp\left[-\lambda\int_0^t \phi_{\text{eff}}(t')\,\mathrm{d}t'\right]\mathrm{d}\lambda \tag{7}$$

The relaxation modulus follows directly from $G(t) = G_0(\phi_{\text{eff}})^2$. Solving the integral equation is eased by noting that if $\mathscr{P}(s)$ is the Laplace transform of the function $\lambda^{-4/3}P(\lambda^{-1})$ with λ and s as conjugate variables and $\mathscr{P}'$ its derivative then (7) may itself be recast as a non-linear first-order differential equation for $\phi_{\text{eff}}(t)$:

$$\frac{\mathrm{d}\phi_{\text{eff}}(t)}{\mathrm{d}t} = \frac{1}{3}\phi_{\text{eff}}(t)\mathscr{P}'[\mathscr{P}^{-1}(3\phi_{\text{eff}}(t))] \tag{8}$$

We now examine the validity and results of this approach taking the explicit example of power-law polydispersity. In this case we have $P(M) = (1-\tau)M_0^{(\tau-1)}M^{-\tau}$ where the normalization is written in terms of a low-molecular-weight cut-off M_0. Clearly $\tau > 1$ for integrability of the distribution function (the case of $\tau < 1$ requires a high-molecular-weight cut-off). The first question to check is the applicability of entanglement dynamics self-consistently throughout the distribution. The degree of entanglement is $M/M_e(t) \sim (\tau - 1)^{-1}M^{(2-\tau)}$ since the effective entanglement molecular weight varies inversely with the effective concentration. So for the system to remain entangled we must have $1 < \tau < 2$ and remark that in this regime the polydispersity is extreme in the sense that a weight-average molecular weight M_w is not defined and that the usual polydispersity index M_w/M_n diverges. For $\tau > 2$ the model may still be appropriate for short and intermediate time-scales but the very longest modes will represent effectively unconstrained relaxation of the largest molecules. The molecular weight characteristic of the transition from entangled to unentangled behaviour M_t depends on both entanglement and cut-off molecular weights: $M_t = [(1-\tau)M_eM_0^{(1-\tau)}]^{1/(2-\tau)}$.

As to the class of distribution functions for which the limiting case of dilution might approximate the co-operative constraint release, it is not straightforward to apply the criteria of Doi *et al.*[4] from the simple binary blend, but a simple condition that must be satisfied for a short polymer to act as effective solvent for a longer is that

$$T_{\text{rept}}(M_S) < K'T_{\text{rept}}(M_L) \tag{9}$$

where K' is some large number, at least of the order of 10. Using the concentration dependence of the reptation time we find that for power-law polydispersity $M_S < K'^{-1/(4-\tau)}$, i.e. the separation in the scale of molecular weight required is not as severe as that in time-scale and the approximation which considers *all* relaxed polymer as effective solvent improves with increased polydispersity as the exponent $\tau \to 1$. In the range where entanglement dynamics applies throughout, $1 < \tau < 2$, we expect the approximation to apply.

To solve for the relaxation function we use known Laplace transforms to find the appropriate form of (8):

$$\frac{\mathrm{d}\phi_{\text{eff}}(t)}{\mathrm{d}t} = \left(\frac{1-\tau}{3}\right)K^{(\tau+2)/(\tau-1)}[\phi_{\text{eff}}(t)]^{(1+2\tau)/(\tau-1)} \tag{10}$$

which may be integrated directly. The constant K depends on the polydispersity exponent via $K = (1/3)\Gamma[(\tau-1)/3]$. There are three cases:

$$\begin{aligned}
&\tau < 2 \quad \phi_{\text{eff}}(t) = [1 + A(\tau)t]^{-\gamma};\\
&\qquad\qquad \gamma = \left(\frac{\tau-1}{2-\tau}\right) > 0; \qquad A(\tau) > 0\\
&\tau > 2 \quad \phi_{\text{eff}}(t) = [1 + A(\tau)t]^{-\gamma};\\
&\qquad\qquad \gamma = \left(\frac{\tau-1}{2-\tau}\right) < 0; \quad A(\tau) < 0 \qquad (11)\\
&\tau = 2 \quad \phi_{\text{eff}}(t) = \exp(-K^4t)
\end{aligned}$$

with the surprising result that we may mimic exponential decay in one case! The constant A, which depends only on the exponent τ, changes sign as τ passes through 2: $A = K^{(\tau+2)/(\tau-1)}(2-\tau)/3$. This permits the entanglement-dominated range of relaxation to diverge naturally as the disentanglement transition diverges. The regime of power-law distributions considered here is also attractive because behaviour is not necessarily dominated by high- or low-molecular weight cut-offs. Cut-off effects are explicit in the range $0 < \tau < 1$ for example.

Dynamical spectra on simultaneously well-characterized but broadly polydisperse polymer melts are not at present to hand. However, near-power-law relaxation moduli are commonly observed in melts for which M_w/M_n is large. For example, a commercial high-density polyethylene with $M_w/M_n = 8$ follows $G(t) \sim t^{-2/5}$ over three decades in time[11]. This is not inconsistent with a value of $\tau < 2$ since in practice a high-molecular-weight cut-off is always present which will prevent divergence of the weight-average molecular weight even for gentle power-laws in the range of interest.

We mention in conclusion the application of this approach to analysis. The relation between $P(M)$ and $G(t)$ is straightforwardly inverted and may be able to furnish an additional quantitative ability to dynamical methods of evaluating molecular-weight distributions.

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