Elongational Flow of Blends of Long and Short Polymers: Effective Stretch Relaxation Time

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We study the onset of chain stretch and emergent extension hardening in the nonlinear rheological response of molten binary blends of long and short polymers. We predict that, upon dilution with short chains, the effective stretch relaxation time of the long chains initially increases in proportion to $\phi_L^{-\alpha}$ (where ϕ_L is the volume fraction of long chains and α is the dilution exponent for entanglements). We confirm this behavior experimentally, in a set of experiments that measure both the dilution exponent from linear rheology and the effective stretch relaxation time under extensional flow.

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Design of polymeric materials for the processing industry requires understanding of their melt behavior in complex, nonlinear flows. Two key concepts underpin many developments in this field: the universality of the physics of long-chain molecules [1] and the *tube model* for entangled polymers [1,2]. The latter stems from a realization that surrounding chains limit the motion of a test chain perpendicular to its contour but do not prohibit motion along it. Chains are confined to a tubelike region defined by their own contour, giving a principle relaxation mechanism of chain-diffusion along its tube (termed *reptation*). Just two material-specific parameters are required in the model: the tube diameter, a, which gives the typical confinement scale perpendicular to the chain contour, and the entanglement time, τ_e, which is the relaxation time scale for a subsection of chain with size equal to the tube diameter. This picture, however, is deceptively simple: there remain significant challenges in making quantitative predictions for linear and nonlinear flow of practical materials.

A complication arises because the surrounding chains, which form the tube, are also in motion. It might be that, before a test chain has escaped from its tube, one of the constraining chains moves out of the way, releasing the entanglement constraint. This *constraint release* process provides a second relaxation mechanism, commonly modeled as a local sideways hop of the tube at each constraint release event [3–6]. Accounting for constraint release has been essential in understanding the experimental lack of shear banding in strong flows of monodisperse melts [5,6]. It is also crucial in most industrial polymers, where polydispersity of chain length, and chain branching, result in a wide spectrum of constraint release rates.

This Letter reports a study of the simplest system exhibiting multiple constraint-release rates: a bimodal blend comprising long and short linear molecules of the same material. Though idealized, this system retains practical relevance: many industrial polymeric materials contain a high-molecular-weight (MW) component to improve stability in elongational flows. If the rate of an elongation flow exceeds the inverse of stretch relaxation time of the long molecules, they are stretched by the flow, so that their length along the tube contour grows. The macroscopic consequence of chain stretch is *elongation hardening* (the stress component in the direction of elongation grows above the linear viscoelastic prediction). So, a key quantity is the stretch relaxation time of the long chains. In monodisperse materials, this is given by the *Rouse time* of the chains [2], which is $\tau_R = \tau_e Z_L^2$ where Z_L is the number of entanglement segments along a long chain. In this Letter we investigate how the effective stretch relaxation time changes upon dilution with shorter chains.

The presence of two chain types (long and short) means that, for a test long-chain, there are two types of entanglement: those with short chains (short lived, fast constraint release rate) and with long chains (long lived, slow constraint release rate). It is thus convenient to picture *two* tubes surrounding the long chain—a "thin tube" representing *all* entanglements, and a "fat tube" representing entanglements with other long chains only. If the weight fraction of long chains is ϕ_L, then the diameter of the fat tube a_f is

$$a_f^2 = a^2 \phi_L^{-\alpha}, \qquad (1)$$

where the dilution exponent, α, bears alternative theoretical estimates of 4/3 and 1 [[7] and references therein]. Given sufficient dilution, this fat tube diameter exceeds the radius of gyration of the long chains, in which case they are not mutually entangled (here we consider only melts where the long chains are mutually entangled). Since both thin and fat tubes are coarse-grained random walks, Eq. (1) indicates that, there are $n = \phi_L^{-\alpha}$ thin tube segments, each of size a, within each fat tube segment of size a_f. The dilution exponent also affects the blend terminal modulus, $G_T \propto \phi_L^{1+\alpha}$, since at long times only the mutual long-chain

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entanglements can act as elastic constraints [4,7]. In this Letter we shall examine the dilution exponent, since (as we shall see) it is important for the effective stretch relaxation time also.

The physics of stretch relaxation in bimodal blends can be illustrated simply. The thin tube undergoes constraint release events occurring at a rate ν_S given by the short chains, allowing it to explore the fat tube. Two time scales are important. The first is the time for the n segments of thin tube within a single fat tube segment to explore locally the width of that fat tube segment (and so, locally, to equilibrate subject to the fat tube constraint). This time is the constraint release Rouse time for n thin tube segments,

$$\tau_{\mathrm{ef}} = 2n^2/3\pi^2\nu_S. \tag{2}$$

Here, we have used the same definition of constraint release rate ν_S as used by Graham *et al.* [6], and retain the same prefactors as suggested by their equation for constraint release events of a tube. The second time scale is the constraint release Rouse time for the whole thin tube (comprising Z_L thin tube segments), which is, similarly,

$$\tau_{R,\mathrm{CR}} = 2Z_L^2/3\pi^2\nu_S. \tag{3}$$

Suppose the (elongational) flow is at strain rate $\dot{\varepsilon}$ sufficiently slow that the thin tube has ample time to equilibrate locally within the fat tube (i.e., $\dot{\varepsilon}\tau_{\mathrm{ef}} < 1$). Then, the deformation of the chain (and thin tube) is entirely imposed by the fat tube constraint; so, the relevant *stretch* (as regards elongation hardening) is the stretch due to increases in length along the fat tube contour; the relaxation time scale for this stretch is hereafter referred to as the "effective stretch relaxation time." A possible mechanism for relaxing this stretch is *via* motion of the thin tube along the fat tube, made possible by constraint release, for which the relevant time scale must be $\tau_{R,\mathrm{CR}}$ [Eq. (3)]. However, this is often *much* longer than the bare Rouse time $\tau_R = \tau_e Z_L^2$ of the long chains. It seems implausible that this new effective stretch relaxation time becomes important (controlling the onset of elongation hardening) upon fractional dilution of long chains by the shorter chains. Is there a faster mechanism for relaxing stretch along the fat tube? We show in the following that there is.

Consider a single fat tube segment with end-to-end vector $\mathbf{R}$, containing n thin tube segments equilibrated subject to this fat tube constraint. The end-to-end vector $\mathbf{r}$ of one of the thin tube segments can be shown (assuming Gaussian chain statistics) to have a second-moment average given by

$$\langle r_\alpha r_\beta \rangle = n^{-2} R_\alpha R_\beta + \tfrac{1}{3}a^2(1 - n^{-1})\delta_{\alpha\beta}. \tag{4}$$

Stretches in the thin and fat tubes are defined as $\lambda_t = \sqrt{\langle r_\alpha r_\alpha \rangle / a^2}$ and $\lambda_f = \sqrt{\langle R_\alpha R_\alpha \rangle / a_f^2}$, respectively [6,8], so taking the trace of Eq. (4) and averaging over fat tube segments gives

$$\lambda_t^2 = \phi_L^\alpha \lambda_f^2 + (1 - \phi_L^\alpha), \tag{5}$$

or, for stretches close to 1, $\lambda_t - 1 \approx \phi_L^\alpha(\lambda_f - 1)$. If there is stretch in the fat tube, and the thin tube is equilibrated within it, then a stretch in the thin tube is induced. This drives a relaxation of stretch, *via motion along the thin tube*. A simple equation for the dynamics of thin tube stretch is

$$\dot{\lambda}_t = \tau_R^{-1}(\lambda_t - 1) + \text{(flow terms)}. \tag{6}$$

However, the thin tube stretch is slaved to the fat tube stretch via Eq. (5), so the flow terms are wholly due to fat-tube constraints. Hence, Eq. (6) should be recast in terms of the fat tube stretch. Noting that the fractional rates of stretch relaxation must be the same, i.e. $\lambda_t^{-1}\dot{\lambda}_t = \lambda_f^{-1}\dot{\lambda}_f$, and assuming stretches close to 1, we get

$$\dot{\lambda}_f = \phi_L^\alpha \tau_R^{-1}(\lambda_f - 1) + \text{(flow terms)}. \tag{7}$$

From this we can see that the effective stretch relaxation time increases smoothly, as $\phi_L^{-\alpha}\tau_R$ upon dilution of long chains with short chains. The novel mechanism for this is relaxation of stretch in the fat tube, via motion of the chain along the thin tube. We anticipate this behavior holds until one of two criteria are fulfilled. Either (a) stretch relaxation by constraint release with time scale $\tau_{R,\mathrm{CR}}$ becomes a faster mechanism for relaxing stretch, or (b) the time scale for stretch relaxation becomes faster than τ_{ef}, the time for the thin tube to explore the full width of the fat tube (since $\tau_{\mathrm{ef}} \sim \phi_L^{-2\alpha}$, such a crossover is inevitable). In either case, the effective stretch relaxation time would become constant upon further dilution. The critical volume fractions are found by equating $\phi_L^{-\alpha}\tau_R$ with $\tau_{R,\mathrm{CR}}$ and τ_{ef}, respectively,

$$\phi_a^\alpha = 3\pi^2\nu_S\tau_e/2, \qquad \phi_b^\alpha = 2/3\pi^2\nu_S\tau_e Z_L^2. \tag{8}$$

To test this, we investigated two series of bimodal blends of linear monodisperse polyisoprene: (i) PI-30k ($M_w = 33.6$ kg/mol, $M_w/M_n = 1.03$) blended with PI-400k ($M_w = 483.1$ kg/mol, $M_w/M_n = 1.03$), and (ii) PI-2k ($M_w = 2.4$ kg/mol, $M_w/M_n = 1.09$) blended with PI-1000k ($M_w = 1131$ kg/mol, $M_w/M_n = 1.05$), where M_w and M_n are the weight- and number-average molecular weights, respectively. The component polymers were prepared by anionic polymerization with narrow-molecular-weight distributions and a similar microstructure of mainly *cis*-1,4 units (for details, see [9]). Blends were prepared by dissolving the components separately in cyclohexane at about 40 °C in the presence of a little antioxidant (BHT, about 10 wt % vs polymer). When both polymers were perfectly dissolved, the low-MW solution was cautiously poured into the flask containing the high-MW solution. The resulting solution was allowed to stir at 40 °C for about 1 h. The blends were recovered by precipitation in cold methanol and dried under vacuum. The linear rheology was determined with an ARES rheometer (Rheometric Scientific) from oscillatory shear measure-
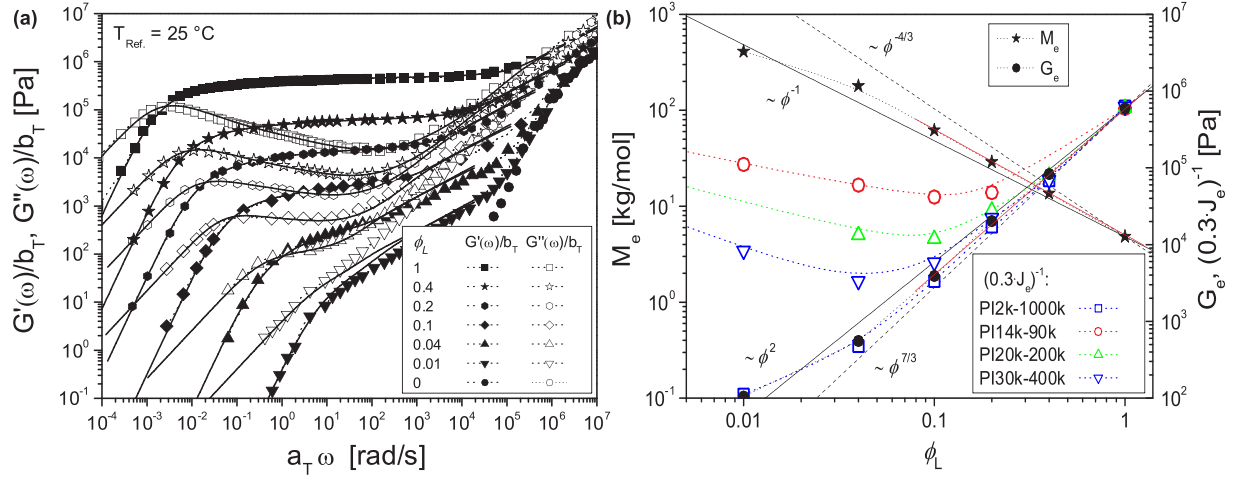
FIG. 1 (color online).   (a) Storage and loss modulus $G'(\omega)$ and $G''(\omega)$ from linear oscillatory shear measurements shifted to 25 °C (symbols) and fitted by the Likhtman-McLeish theory (curves) for blends of PI-2k with PI-1000k. (b) Fitted values of modulus G_e and entanglement molecular weight $M_e = M/Z$ vs weight fraction for PI-2k–PI-1000k blends, and inverse of steady-state recoverable compliance J_e^0 vs concentration for a series of blends. Error bars are within symbol size.

ments of the elastic $G'(\omega)$ and viscous $G''(\omega)$ modulus mastercurves, shifted to the reference temperature of 25 °C using a time-temperature superposition (TTS) method with a single set of parameters [9]. Nonlinear uniaxial start-up tests in elongation were performed using a SER rheometer add-on (X-Pansion Instruments) at constant strain rates $\dot{\varepsilon}$ in the range of 0.01 s^{-1} to 0.1 s^{-1} up to 4 strain units [i.e., extension ratio of exp(4)]. To access high strain rates, out of the instrumental range, the TTS procedure was also employed for the elongational flow with the same shift factors and method as reported in Auhl *et al.* [9–11].

The PI-2k is essentially unentangled and its series of blends with PI-1000k was used to examine the dilution exponent α. Figure 1(a) shows the storage and loss modu-

lus from linear oscillatory shear, together with fits to the low frequency end of the spectrum using Likhtman-McLeish theory for entangled linear chains [12]. These fits allow the extraction of independent effective parameters τ_e, G_e and Z for the self-entangled, but diluted, long chains (the effective ''entanglement molecular weight'' is obtained as $M_e = M_w/Z$). We anticipate $G_e \sim \phi_L^{1+\alpha}$ and $M_e \sim \phi_L^{-\alpha}$. As can be seen in Fig. 1(b), the fits indicate a value of α somewhere between 1 and 4/3, the best fit for $\phi_L \geq 0.1$ giving $\alpha = 1.1 \pm 0.1$ in case of M_e and $\alpha = 1.2 \pm 0.1$ in case of G_e. We obtained a similar conclusion by examining the steady-state recoverable compliance J_e^0 which, *in the well entangled regime*, is inversely proportional to the effective plateau modulus. Figure 1(b) indi-
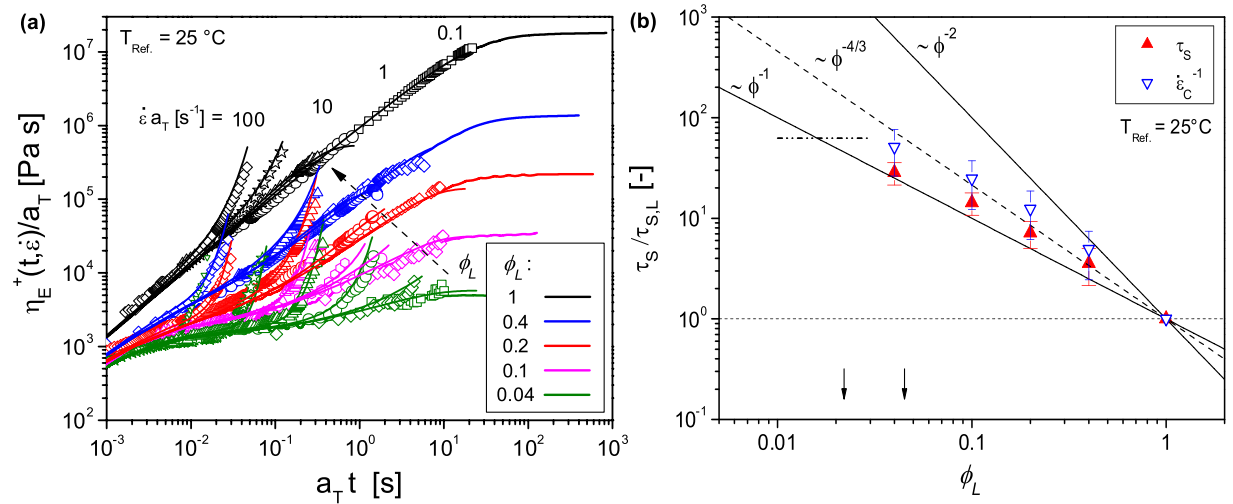

FIG. 2 (color online).   (a) Transient elongational viscosity $\eta^+(t, \dot{\varepsilon})$ for blends of PI-30k with PI-400k shifted to 25 °C from experiments (symbols) and multimode Rolie-Poly fits (lines). (b) Effective stretch relaxation time τ_S of the blends, normalized by that of the undiluted long chains as fitted to pure component extensional data (which is practically identical to the Rouse time predicted from linear rheology) and inverse strain rate $\dot{\varepsilon}_C^{-1}$ where strain hardening occurs, as a function of weight fraction.

cates that, for a series of blends, the inverse of compliance versus weight fraction asymptotes towards a slope close to 7/3 on a logarithmic plot, agreeing well with the scaling of modulus at high volume fractions (this is most evident for blends with the longest high-molecular weight chains). There is sufficient evidence to indicate that the dilution exponent is greater than 1, but not sufficient to confirm the suggested 4/3 exponent.

Figure 2(a) shows the transient elongational viscosity over a range of rates and dilutions for the series of PI-30k blended with PI-400k. With increasing dilution of the long component, hardening occurs at lower elongational rates: clearly, the effective stretch relaxation time is increasing with dilution. To quantify this, we employ two measures of the stretch relaxation time, as follows: (i) First, we define the stretch relaxation time as the inverse of the elongation rate $\dot{\varepsilon}_C$ at which hardening is first observed. This is a rough (but robust) criterion, since successive elongation rates are separated by a factor of approximately 3. (ii) Second, we perform a multimode fit to the linear and nonlinear data using the Rolie-Poly model [8], and define the effective stretch relaxation time from that of the slowest mode in the fit. Because of the noise in the elongational data, especially at the greatest dilutions, there remains some uncertainty in this value, but this gives tighter error bounds than the first method.

The effective stretch relaxation times from both methods are shown in Fig. 2(b) as a function of dilution. The enhancement in effective stretch relaxation time is potentially large: the greatest observed was a factor of 30. The stretch relaxation time varies smoothly with dilution (i.e. it does not jump suddenly to a new value given by the constraint release Rouse time $\tau_{R,CR}$ of the whole thin tube). At the smallest dilutions (largest ϕ_L), the behavior appears consistent with the power law predicted above, $\tau_S \sim \phi^{-\alpha} \tau_R$. The exponent α appears greater than 1, with a value of 4/3 being a good fit (though both are within error bars). At greater dilutions (smaller ϕ_L) there is some deviation. Equation (8) gives two bounds for the predicted power law behavior. We estimate the constraint release rate from the short chains as $\nu_S = c_\nu/\tau_{dS}$, where $c_\nu = 0.1$ is a parameter describing the effectiveness of constraint release events in inducing tube hops [6] and τ_{dS} is the reptation time of the short chains (3.04×10^{-3} s at 25 °C). The remaining parameters are $\tau_e = 1.3 \times 10^{-5}$ s and $Z_L = 100$ giving, for $\alpha = 4/3$, $\phi_a = 0.022$ and $\phi_b = 0.045$ [indicated by arrows in Fig. 2(b)]. Noting that a factor of 2 error in our estimate of ν_S could reverse the order of these two critical volume fractions, the data appear consistent with a transition towards a constant stretch relaxation time below (either of) these critical volume fractions. Our estimates favor the limiting mechanism being that the thin tube can no longer equilibrate locally in the fat tube during the time scale of stretch relaxation. These experimental results are fully consistent with our theoretical predictions.

In conclusion, we have predicted a novel mechanism whereby the effective stretch relaxation time of the long

chains in a bimodal blend is enhanced substantially above its value in the pure melt. This involves relaxation of stretch in the fat tube (representing entanglements with other long chains) *via* motion of the chain along the thin tube (representing entanglements with all other chains). The stretch relaxation time is related to the lowest deformation rate for strain hardening in steady elongational flow; we have positively tested our predictions via elongation experiments on binary blends of polyisoprene. On further increases of strain rate, beyond τ_{ef}^{-1}, we anticipate changes in the effective stretch relaxation time (though hardening still occurs), as the long chains no longer explore the full fat tube width. There is, additionally, a rich behavior to explore, with multiple relaxation processes (e.g. at the bare Rouse time), in nonsteady flows such as step strain.

Finally, we are hopeful that these findings will be significant for polydisperse industrial resins (noting that large enhancements in effective stretch relaxation time are possible). In this context, it is an important observation that the degree of enhancement $\phi^{-\alpha}$ of stretch relaxation time is independent of the matrix molecular weight [provided one remains clear of the bounds given by Eq. (8)]. This has the potential to simplify further theoretical development for polydisperse resins.

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