Anomalous Molecular Weight Dependence of Chain Dynamics in Unentangled Polymer Blends with Strong Dynamic Asymmetry

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We address the general question of how the molecular weight dependence of chain dynamics in unentangled polymers is modified by blending. By dielectric spectroscopy we measure the normal mode relaxation of polyisoprene in blends with a slower component of poly(ter-butylstyrene). Unentangled polyisoprene in the blend exhibits strong deviations from Rouse scaling, approaching ‘entangled-like’ behavior at low temperatures in concomitance with the increase of the dynamic asymmetry in the blend. The obtained results are discussed in the framework of the generalized Langevin equation formalism. On this basis, a non trivial relationship between the molecular weight dependence of the longest chain relaxation time and the nonexponentiality of the corresponding Rouse correlator is found. This result is confirmed by molecular dynamics simulations.

The chain dynamics of polymer systems is one of the basic and classical problems of polymer physics [1, 2] and thereby it has been the subject of intensive investigation over many years. It is generally assumed that the Rouse model [1] provides a suitable description of the chain dynamics of the so-called unentangled polymers, i.e., chains of molecular weight M lower than a certain limit M_e ('entanglement mass'). At higher molecular weights $M > M_e$ topological constraints ('entanglement effects') start to play a role and the chain dynamics strongly deviates from Rouse expectations. Tube models [1] are generally used to explain these deviations. One of the key questions in this field is how the chain dynamics depends on the molecular weight, or on the number of 'beads' N , of the chain. The Rouse model predicts that the longest relaxation time of the chain —usually called the Rouse time τ_R — depends on N (or M) as $\tau_R \propto N^2$. For $N > N_e$, the reptation theory predicts a change in this dependence to $\tau_R \propto N^3$. From an experimental point of view it is difficult to isolate τ_R because, usually, other chain modes with wavelengths lower than N also contribute to the measured magnitudes. Dielectric spectroscopy on the so-called type A-polymers, as polyisoprene (PI), allows however to follow directly the behavior of τ_R . These polymers contain dipole moments along the chain backbone that do not cancel when they are summed over the whole chain, giving rise to an 'end-to-end' net polarization vector. The fluctuations of this vector produce a relaxation peak in the imaginary part $\epsilon''(\omega)$ of the dielectric permittivity spectrum. This peak, which is called 'normal mode' (NM) relaxation, appears at lower frequencies than the segmental relaxation peak (α -relaxation), which is due to the fluctuations of the dipole component perpendicular to the chain backbone. As the NM relaxation is dominated by the longest wavelength chain fluctuations [1], the frequency of the maximum, $\omega_{\max}$, of this peak defines a time $\tau_{\text{NM}} = \omega_{\max}^{-1}$ which essentially coincides with τ_R . The molecular weight dependence of τ_{NM} for PI has been deeply investigated (see e.g., [3–5]). Below $M_e \approx 6500$ Da Rouse behavior is obtained. On the contrary, reptation-like M -dependence is observed for $M > M_e$.

Recent molecular dynamics (MD) simulations in both bead-spring [6] and real blends [7], as well as experimental investigations [8–10] have put in evidence that the chain dynamics of linear unentangled polymers is drastically modified when they form part of dynamically asymmetric polymer blends. These are miscible polymer systems where the two components display very different segmental mobility (or glass transition temperatures T_g). MD simulations [6] show that this dynamic asymmetry between the two components induces

for the fast component in the blend strong nonexponentiality of the Rouse mode correlators and a clear breakdown of the Rouse scaling. A scaling law $\tau_p \sim (N/p)^{x(T)}$ was reported, where τ_p is the relaxation time corresponding to the Rouse correlator $\langle \mathbf{X}_p(t) \cdot \mathbf{X}_p(0) \rangle$. The chain Rouse mode, $\mathbf{X}_p(t)$, of index $p = 1, \dots, N-1$ (wavelength N/p) is defined as $\mathbf{X}_p(t) = N^{-1} \sum_{j=1}^N \mathbf{r}_j(t) \cos[(j-1/2)p\pi/N]$, with $\mathbf{r}_j$ the vector giving the position of the j -bead in the chain. The parameter x giving the wavelength dependence of τ_p strongly depends on temperature T , varying from $x \approx 2$ (Rouse prediction) at high T —where the dynamic contrast between the two blend components is very small— to $x \approx 3.5$ at rather low T , where the slowing down of the slow component gives rise to high dynamic contrast. The values of x reported in Ref. [6] are included in Fig. 1. These simulation results for a generic bead-spring model suggest that the molecular weight dependence of $\tau_{\text{NM}} \approx \tau_{\text{R}}$ ($p = 1$) should also depend on temperature and be given by $x(T)$ as $\tau_{\text{NM}} \sim M^{x(T)}$, though this has never been confirmed experimentally.

In this letter we address this question for the first time by measuring the normal mode relaxation of unentangled PI with different molecular weights in blends with poly(tert-butylstyrene) — denoted as PtBS. We find a molecular weight dependence of τ_{NM} for PI in the blend very different from that of pure PI, and qualitatively similar to that suggested by the simulations [6]. We discuss the obtained results in a simple theoretical framework based on the generalized Langevin equation (GLE) formalism [11]. In this framework we obtain a direct and nontrivial correlation between the $x(T)$ parameter giving the molecular weight dependence of the Rouse time $\tau_{\text{R}} \approx \tau_{\text{NM}}$ and the nonexponential parameter of the first Rouse mode correlator ($p = 1$). This correlation is nicely corroborated by the MD simulation results.

We have investigated LCST miscible blends of PI and PtBS with a 35 % (weight) concentration of PI. The molecular weight of PI was varied in the range $1100 \text{ Da} \leq M_{\text{n}} \leq 6510 \text{ Da}$, i.e., below the entanglement mass for PI, whereas for PtBS we used $M_{\text{n}} = 2300 \text{ Da}$ (below $M_{\text{e}} \approx 37600 \text{ Da}$ for this polymer). The polydispersity index $M_{\text{w}}/M_{\text{n}}$ of all components was rather low, in the range of 1.05. The samples were prepared by solution casting from toluene solutions and were vacuum dried at temperature above T_{g} to eliminate any trace of solvent. The average T_{g} of the blend samples ranges between 240 and 250 K, depending on the M_{n} of PI. Due to the high concentration of PtBS, these T_{g} 's mainly reflect the freezing-in of PtBS in the blend. A broadband dielectric spectrometer, Novocontrol Alpha-A analyzer,

FIG. 1: Inverse T -dependence of the parameters (circles and squares) characterizing the Rouse correlators of the fast component in the simulated blend of Ref. [6] (see units there). Circles: exponent x for the wavelength dependence of the relaxation times $\tau_p \sim (N/p)^x$. Squares: ratio $2/\langle\beta\rangle$, with $\langle\beta\rangle$ the stretching exponent of the correlator for $p = 1$ (see text). Error bars, related to the dispersion in the N -dependence of $2/\beta$ (see text) are indicated. Diamonds: For PI in the blend, inverse T -dependence of the exponent x for the M_n -dependence, $\tau_{NM}/\tau_\alpha \propto M_n^x$, of the NM relaxation time normalized by the α -time. A typical error bar is shown. The lines, included as guides for the eyes, are empirical fits to $x(T) = 3.5 - a \exp[-(E/T)^{4.8}]$, with $a = 1.3$, $E = 0.45$ for MD results, and $a = 1.5$, $E = 300$ for PI in the blend.

was used to isothermally measure the complex dielectric function $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$, with $\omega = 2\pi f$, between 260 K and 350 K and in the 10^{-1} Hz to 10^6 Hz frequency range. The dielectric losses of PI are almost two orders of magnitude larger than those of PtBS, thereby the response of PI in the blend dominates the measured dielectric signal. More experimental and sample details can be found in Ref. [8].

Fig. 2 shows as an example the normalized imaginary part of the dielectric permittivity for PI of $M_n = 2700$ Da and its blend with PtBS at the lowest investigated temperature.

FIG. 2: Experimental results at $T = 260$ K for $\epsilon''(f)$ (normalized to its maximum $\epsilon''_{\max}$) of PI with $M_n = 2700$ Da in the blend (circles) and in the pure state (squares). The positions of the NM and α -relaxation in both systems are indicated. The horizontal double arrows indicate the time scale separation between NM and α -relaxation in pure PI (right) and PI in the blend (left).

By blending with the slow PtBS-component, both the NM and the α -relaxation of PI are slowed down and broadened in comparison with pure PI. Moreover, the time scale separation between these two relaxations increases in the blend and becomes larger the lower the temperature. It is worth noting that the slowing down of the NM when increasing M_n is more pronounced for PI in the blend than for the pure polymer. This is already an indication that the Rouse scaling giving the M_n -dependence of the NM's characteristic time, τ_{NM} , in pure PI will not be able to explain the behavior of the NM of PI in the blend system.

The analysis of the dielectric losses of pure PI with different M_n 's and of the respective blends with PtBS was performed by following the procedure of Refs. [4, 8], providing values for the characteristic times at the maxima of the NM- and α -relaxations. As expected, all the blends showed similar dielectric strength for the NM-relaxation of PI, compatible with a 35% of the strength in pure PI. The obtained values of τ_{NM} were normalized to those of the segmental α -relaxation (τ_α) in order to correct for the M_n -dependence of the α -relaxation

FIG. 3: Molecular weight dependence, at $T = 260$ K, of the quantity $(\tau_{\text{NM}}/\tau_{\alpha})/M_n^2$ for PI, with τ_{NM} the NM relaxation time, τ_{α} the α -relaxation time and M_n the molecular weight. Circles and squares are data for PI in the blend and pure states respectively. Typical error bars are shown for PI in the blend. For pure PI the error bars are given by the symbol size. The horizontal dashed line for pure PI in the range $M < M_e \lesssim 6500$ Da reflects Rouse behavior in the unentangled regime. Solid lines indicate entangled-like behavior $\tau_{\text{NM}}/\tau_{\alpha} \propto M_n^x$, with $x = 3.4$ and $x = 3.2$ for PI in the blend and in the pure state respectively. The effective entanglement length (see text) $M'_e \approx 370$ Da for PI in the blend is indicated.

(i.e., the M_n -dependence of T_g) [12]. Fig. 3 shows as an example the so-obtained results, also at the lowest investigated T , for both pure PI and PI in the blend. Data of pure PI with $M_n > M_e$ have also been included for comparison. Moreover, all data of $\tau_{\text{NM}}/\tau_{\alpha}$ have been divided by M_n^2 to further stress the differences with respect to the Rouse behavior (which in this representation is given by a horizontal line). In the case of pure PI we obtain similar results to those previously reported [4]. Thus Rouse ($x = 2$) and entangled-like ($x = 3.2$) scaling is found respectively below and above $M_e \approx 6500$ Da. For PI in the blend at this T we obtain $\tau_{\text{NM}}/\tau_{\alpha} \sim M_n^x$ with $x \approx 3.4$. This is a remarkable result, since for PI in the blend we are only exploring the *unentangled* range $M < M_e$, which in pure PI displays

simple Rouse behavior. Having noted this, the values of the effective exponent x strongly depend on temperature. These are included in Fig. 1, showing values close to 3.5 at the lowest investigated T (close to T_g 's of the blends) but approaching at high T the values obtained for pure unentangled PI (i.e., Rouse scaling $x = 2$). This experimentally confirms the simulation results (see Fig. 1) of the generic bead-spring model of Ref. [6], although due to experimental limitations in the high-frequency range we cannot access the high- T limit ($x \rightarrow 2$) probed by the simulations.

The anomalous dynamic behavior of the fast component in asymmetric polymer blends with compositions rich in the slow component has usually been associated to the slowing down, as T decreases, of the slow component, that freezes in the T_g -range of the system. For the PI/PtBS blend here investigated the value $x \approx 3.4$ found at 260 K — in the glass transition range of the system — is similar to that obtained for bulk PI in the entangled regime (see Fig. 3). Indeed, the simple picture of short PI-chains moving through a frozen matrix of PtBS invokes the original problem of reptation [1]. By assuming a reptation-like mechanism at this low- T limit, we estimate an effective entanglement mass (M'_e) for PI in the blend as the molecular mass at which the extrapolated law $\tau_{NM} \sim M_n^{3.4}$ crosses over the Rouse behavior of the PI homopolymer (see Fig. 3). This gives $M'_e \approx 370$ Da [13]. From the chain dimensions of PI ($\langle R_g^2 \rangle / M_n \approx 0.6 \text{ \AA}^2 \text{ mol g}^{-1}$ at 298 K, with $\langle R_g^2 \rangle$ the average radius of gyration [14]), we estimate a value of the corresponding ‘tube diameter’ [1] of $d_t = [M'_e \langle R_g^2 \rangle / M_n]^{1/2} \approx 15 \text{ \AA}$. This is consistent with the expected channel width for the motion of the PI chains in the frozen matrix of PtBS. This can be roughly estimated as $\rho^{-1/3} \sim 18 \text{ \AA}$, with ρ the number density of PtBS chains in the blend.

However, this interpretation in the limit of frozen component cannot be easily extended to the broad temperature range for the crossover in the exponent x shown in Fig. 1. In the framework of tube models one might invoke constraint-release mechanisms [2] to account for ‘dilution’ of the entanglement network as T increases [15]. This approach seems at least questionable for the problem investigated here. The reason is that, unlike for the usual situations addressed by tube models, the time scale for constraint-release would be in this case the α -relaxation time of the slow component. This time scale is indeed coarse-grained in tube models, that therefore cannot capture the physical mechanisms arising in the proximity of the glass transition of the slow component.

The results in Ref. [6] suggested instead that a theoretical framework based on a GLE

could be appropriate to describe the crossover behavior in the exponent $x(T)$. Following the scheme proposed by Schweizer in Ref. [11], we can express the integrodifferential equation for the autocorrelation function of the Rouse mode $p = 1$ for the fast component of the blend, $C_1(t) = \langle \mathbf{X}_1(t) \cdot \mathbf{X}_1(0) \rangle$, as:

$$\dot{C}_1(t) + \xi_0^{-1} \int_0^t dt' \Gamma(t-t') \dot{C}_1(t') = -(\tau_R^0)^{-1} C_1(t), \quad (1)$$

(see [11] for details). Here $\Gamma(t)$ would be a memory function driven by the structural relaxation of the slow component of the blend, which would produce an extra friction nonlocal in time. In this expression τ_R^0 is the Rouse time ($p = 1$) and ξ_0 the corresponding constant friction coefficient for standard Rouse behavior, which is recovered in the limit that the memory function $\Gamma(t)$ decays to zero at microscopic times [11]. For the fast component in polymer blends with strong dynamic asymmetry the decay of $\Gamma(t)$ will be controlled by the structural relaxation of the slow component and thereby will be fast at high temperature but will become slower as the temperature approaches T_g . If we assume that $\Gamma(t)$ always decays faster than the global motion of the chain, we can invoke a ‘pseudo-Markovian’ approximation (see Ref. [11] and references therein), and replace the convolution integral of Eq. (1) by a time local product $\left[\int_0^t dt' \Gamma(t') \right] \dot{C}_1(t)$. In the framework of this approximation and defining a time dependent effective friction coefficient $\xi(t) = \int_0^t dt' \Gamma(t')$, the solution of Eq. (1) can be expressed as [11]:

$$\Phi_1(t) = \frac{C_1(t)}{C_1(0)} = \exp \left[-\frac{\xi_0}{\tau_R^0} \int_0^t \frac{dt'}{\xi_0 + \xi(t')} \right]. \quad (2)$$

In order to deduce the functional form of the normalized Rouse correlator $\Phi_1(t)$ we would need to know the time dependence of $\xi(t)$. This would imply to construct a microscopic model for the memory function in this particular case as it has been done, e.g., in the case of the renormalized Rouse models for entangled homopolymers [11]. Though this is beyond the scope of this work, some nontrivial predictions can be made on the basis of Eq. (2) and compared with results from our simulations of dynamically asymmetric blends [6, 7]. These simulations show that $\Phi_1(t)$ is nonexponential in general and that the nonexponentiality increases as the temperature decreases (concomitant with the broadening of the normal mode relaxation experimentally observed in the frequency domain [8]). In an intermediate time range $\Phi_1(t)$ can be well approximated by an stretched exponential function $\Phi_1(t) \approx \exp[-(t/\hat{\tau}_R)^\beta]$ (see [6] for details) where $\hat{\tau}_R$ is a generalized Rouse time and $\beta < 1$ an

stretching exponent which depends on temperature but results to be hardly dependent on N . In the former framework the time dependence of Eq. (2), given by the integral expression, should be just proportional to t^β and thereby we could express the generalized Rouse time as $\hat{\tau}_R = [\gamma\tau_R^0]^{1/\beta}$, where γ is a constant with the right dimensionality. As $\tau_R^0 \propto N^2$ (Rouse behavior) the N -dependence of $\hat{\tau}_R$ results to be $\hat{\tau}_R \propto N^x$ with $x(T) = 2/\beta(T)$.

This expression establishes a direct and nontrivial correlation between the molecular weight dependence of the generalized Rouse time and the nonexponentiality of the corresponding Rouse correlator. If this correlation does exist, we should be able to deduce the $x(T)$ values shown in Fig. 1 just from the knowledge of $\beta(T)$ corresponding to a description of $\Phi_1(t)$ in terms of an stretched exponential function. The β -values calculated from the simulations [6] at each temperature show some dispersion for different values of N but not a systematic dependence. Therefore we have calculated the average β -value $\langle\beta\rangle$ at each T and taken into account the scattering of β as an error bar. The so-obtained values of $x(T) = 2/\langle\beta(T)\rangle$ are represented in Fig. 1 (squares) together with the values of x discussed before (circles). The agreement is almost perfect taking into account the approximations and uncertainties involved. In particular, the pseudo-Markovian approximation should break as soon as the time scale of the memory function — which in this approach is related to the structural α -relaxation of the slow component in the blend — becomes of the order or longer than $\hat{\tau}_R$. Therefore, deviations from the simple law $x(T) = 2/\beta(T)$ could be expected in the low- T limit. Moreover, it is noteworthy that in our treatment we implicitly assume that $\Gamma(T)$ does not depend on N . The fact that the β -values found by MD simulations for $\Phi_1(t)$ hardly depend on N seems to be consistent with this assumption, at least for the simulated system.

In summary, we have experimentally demonstrated that the molecular weight dependence of the chain dynamics of the fast component in dynamically asymmetric unentangled polymer blends strongly deviates from the Rouse scaling. These deviations increase as the temperature decreases in concomitance with the slowing down of the structural relaxation of the slow component of the blend. The fact that we find the same behavior for a real system and for simulations of a simple bead-spring model confirms that this is a general feature of dynamically asymmetric blends. The GLE formalism seems to be a suitable theoretical framework for this problem.

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