Quantifying chain reptation in entangled polymer melts: Topological and dynamical mapping of atomistic simulation results onto the tube model

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Summary Through a systematic methodology, we have calculated the segment-survival probability function $\psi(s,t)$ of the tube model directly from trajectories accumulated in the course of long molecular dynamics simulations for mono- and bi-disperse polymer melts. The computed $\psi(s,t)$ curves quantify reptation, contour length fluctuations (CLFs), and constraint release (CR). Linear viscoelastic properties thus obtained are found to be in reasonable agreement with experimental rheological data.

INTRODUCTION

The reptation (or tube) theory has been very successful in describing rheological behaviors of high molecular weight polymeric liquids typically encountered in practical polymer processing. In this theory, topological constraints arising from chain connectivity and chain uncrossability are of fundamental importance. Topological interactions, however, are very difficult to treat in a rigorous fashion due to the huge number of degrees of freedom associated with polymer configurations. The notion of a confining tube through which a chain can execute a motion that looks like reptation due to these constraints, developed by de Gennes [1] and Doi-Edwards [2], considerably simplifies the problem, since small-length scale fluctuations that are irrelevant to the large-scale rheological properties of the polymer are neglected. Since then, numerous research efforts have been made to improve the tube theory. Despite all the major theoretical and experimental advances, our current understanding of the role of topological constraints on the equilibrium dynamics and flow behavior of entangled polymers is still far from complete. A number of fundamental issues in molecular level underlying the application of tube models to actual systems remain unresolved. Clearly, we could tremendously benefit here if we could implement the tube theory into molecular simulations for dense polymer melts in order to get atomistic-level information for the dynamics of entangled polymers and the microscopic mechanisms underlying reptation and other relaxation mechanisms in these systems.

RESULTS

The most fundamental ingredient of all tube models is the survival probability $\psi(s,t)$ of a segment s of the primitive chain in the confining tube after time t. Once $\psi(s,t)$ is known, one can have a description of the dynamics and flow behavior of model entangled linear polymers from direct atomistic simulations in terms of diffusive primitive paths in the context of the tube model. We have recently developed a systematic methodology [3] which allows one to calculate the segment-survival probability function $\psi(s,t)$ describing the probability that at a time t, a segment s along the primitive path is still inside the initial (defined at t=0) tube, directly from trajectories accumulated in the course of long molecular dynamics simulations. The computed $\psi(s,t)$ curves account directly for reptation, chain local transverse fluctuations driven mainly from constraint release (CR) and regeneration mechanisms, and contour length fluctuations (CLFs). The CLF and CR mechanisms have been shown to facilitate relaxation in monodisperse melts, causing significant effects on the rheological properties.

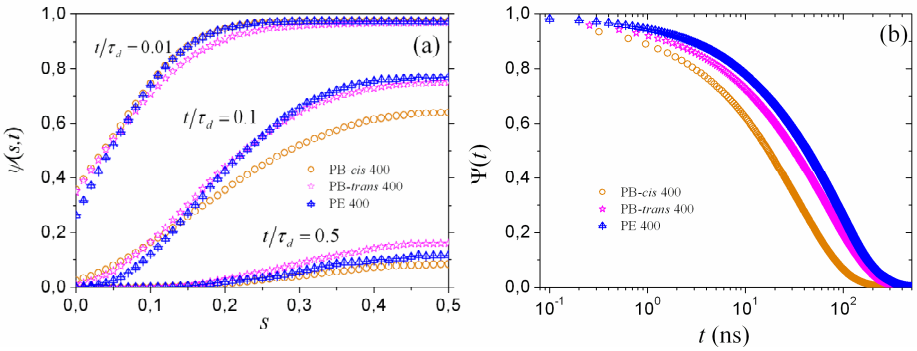

Figure 1. (a) Typical plots of the function $\psi(s,t)$ describing the probability that a primitive segment s remains in the initial tube after time t (scaled by the reptation time τ_d) , as computed from the new methodology for systems with the same number of monomers, but with different number of entanglements (Z=2.77, 3.36, and 5.26 for PB-*cis* 400, PB-*trans* 400, and PE 400, respectively). (b) Typical plots of the function $\Psi(t)$ representing the fraction of primitive chain that has remained in the initial tube after a time t for the same systems.

Figure 1 displays a comparison of the functions $\psi(s,t)$ and $\Psi(t)$ between different polymer melts having the same number of monomers but a different number of entanglements per chain due to their different chemical structure. As can be seen in Figure 1(a), for the very early times (t=0.01τ_d), most of the middle segments of the primitive chains remain inside the initial tube, whereas most of the outer segments (especially those closer to the chain ends) have escaped. As time elapses, the entire $\psi(s,t)$ curve is shown to decline to lower values. We further notice an inflection point near chain ends, which is attributed to CLF effects, also predicted by modern tube models. Furthermore, the chains are seen to have almost completely escaped the original tube after only half the reptation time, which is attributed to CR effects and consistent with the double reptation model. Figure 1(b) presents the corresponding results for the $\Psi(t) = \int_0^1 \psi(s,t)\,ds$ function for the same systems.

The CR mechanism is particularly important in bidisperse melts when the surrounding matrix chains are shorter than the probe chains. The CR mechanism is particularly important in bidisperse melts when the surrounding matrix chains are shorter than the probe chains [4]. Linear viscoelastic properties, such as the zero shear rate viscosity and the spectra of storage and loss moduli, obtained on the basis of the computed $\psi(s,t)$.

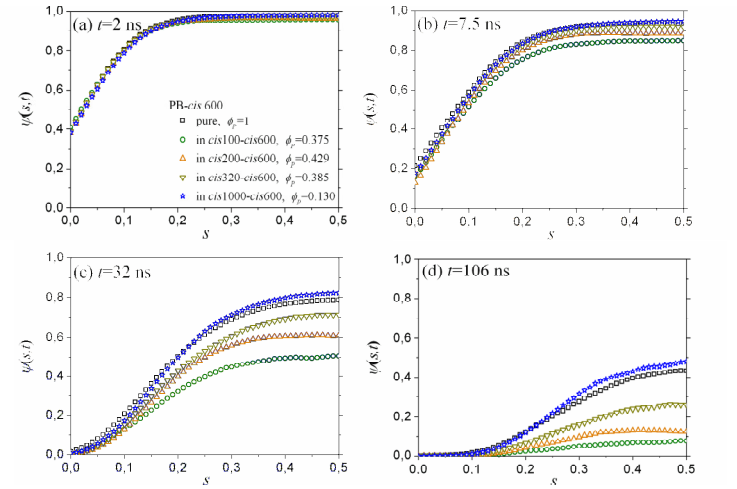

Figure 2. Dependence of the segment survival probability function for C_{600} *cis*-1,4-PB probe chains on matrix chain length in bidisperse system. Graphs of computed profiles at: (a) t = 2 ns (~τ_e), (b) t = 7.5 ns (~3τ_e), (c) t = 32 ns (~τ_R/3), and (d) t = 106 ns (~τ_d/4). τ_e, τ_d , and τ_R here denote the characteristic entanglement, disentanglement, and Rouse times, respectively, of the C_{600} *cis*-1,4-PB chains in their own melt at T=413 K and P=1 atm. Their numerical values are: τ_e=2.3±0.8 ns, τ_d=500±70 ns, and τ_R=90±15 ns.

As seen in Figure 2, the probe chains relax faster as the matrix chain length decreases, a direct manifestation of CR effects associated with the relaxation of the shorter matrix chains at this time scale; this is particularly noticeable in the *cis*100-*cis*600 system. At even longer times, the computed $\psi(s,t)$ curves in the various binary mixtures are observed to depart even more [Figures 2(c) and 2(d)], confirming again the significant role of CR on chain relaxation. It is also noticed in Figure 2 that C_{600} chains in the *cis*1000-*cis*600 system relax slightly slower than in their own melt, indicating that CR effects occur even in the strictly monodisperse C_{600} *cis*-1,4-PB melt due to the relaxation of neighboring chains around a tagged chain of exactly the same chain length.

CONCLUSIONS

We have provided computational results for the most fundamental quantity of the reptation theory, namely the segment survival probability function $\psi(s,t)$ and its average , from simulations with model monodisperse and bidisperse *cis*-1,4-PB systems. Computed results of $\psi(s,t)$ and $\Psi(t)$ quantifies CLF and CR effects, revealing their significant role in the rheological behavior of entangled polymer systems. Our results can be used to test a variety of modern tube models and justify their underlying assumptions [5]. A novel feature of our work is can be further extended to polymeric systems under flow to help understand the role of the so-called convective constraint release (CCR) mechanism [6] to melt dynamics, a key concept in all state-of the-art tube models

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