

NOTE

Temperature and Molecular Weight Dependence of the Zero Shear-Rate Viscosity of an Entangled Polymer Melt from Simulation and Theory

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INTRODUCTION

In a previous article, we described how the frequency-dependent complex shear modulus and the time-dependent shear stress relaxation modulus for a highly entangled polybutadiene (PBD) melt can be obtained from molecular dynamics (MD) simulations of an unentangled PBD melt.¹ In that work, we obtained from simulations of an unentangled melt all properties required for the prediction of the dynamic shear modulus with three reptation theories for the dynamics of entangled melts of linear, monodisperse polymers.^{2–5} More recently, we showed how the high-frequency (glassy) behavior of PBD can be obtained directly from MD simulations.⁶ The calculated complex and stress relaxation shear moduli for a PBD melt with a molecular weight of $1.3 \cdot 10^5$ Da at 298 K were found to be in excellent agreement with experimental data.^{1,6} In this work, we investigate the ability of MD simulations of the unentangled melt, in conjunction with reptation theory, to reproduce the molecular weight and temperature dependence of the viscoelastic properties of PBD.

Here we concentrate on the low-frequency/long-time dynamics that determine the zero shear-rate viscosity, a property that has been extensively studied for PBD as a function of molecular weight and temperature.^{7–14}

THEORY AND SIMULATIONS

Reptation Theory

The reptation theory of polymer dynamics in monodisperse, linear polymers, which originated with de Gennes^{15,16} and was developed by Doi and Edwards⁵ into a full description of the linear and nonlinear rheology of entangled melts, leads to discrete spectra of relaxation modes for the shear modulus given by

$$G(t) = \sum_p^N G_p \exp\left(-\frac{t}{\tau_p}\right) \quad (1)$$

The complex shear modulus $G^*(\omega)$ is defined as a Laplace transform of the time-dependent shear stress modulus $G(t)$:

$$G^*(\omega) = i\omega \int_0^\infty e^{-i\omega t} G(t) dt = G'(\omega) + iG''(\omega) \quad (2)$$

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Table I. Scaling Behavior for η_0 from Reptation Theory

	DE	MDE	Milner–McLeish
$f(n) = \frac{\eta_0}{\tau_d G_N}$	$\frac{\pi^2}{12}$	$\frac{1}{3}(1 - n^{-1/2})^3 + \frac{1}{15}n^{-3/2}$	$\frac{8}{\pi^2} \cdot [1 - s_d(n)]^2 \sum_{p, \text{odd}}^n \frac{1}{p^4}$
$\log(\eta_0)/\log(M_w)$ slope ^a	3.00	3.22	3.07
			$S_d(n) = \frac{\sqrt{1 + 4\left(\frac{225}{256}\pi^3 n\right)^{1/2}} - 1}{2\left(\frac{225}{256}\pi^3 n\right)^{1/2}}$

^a Obtained from a power-law fit in a molecular weight range of $M_w = 10^3$ to 10^6 Da. (See Figure 1)

Reptation theories involve a linear superposition of $p = 1$ to N Maxwell modes of strength G_p and relaxation time τ_p . The sum is subdivided into several relaxation processes in which the number of modes for each process depends on the particular modification of the original reptation model but generally includes Rouse and reptation regimes with different expressions for G_p and τ_p . Previously, we applied three reptation models to the prediction of the dynamic shear modulus of PBD: (1) the original Doi–Edwards theory (DE),^{2–5} (2) a modified version of DE (MDE) that accounts for fluctuations of the chain contour-length,¹⁷ and (3) an additional reptation model, presented by Milner and McLeish,¹⁸ that accounts for contour-length fluctuations. The full formulation of these models is summarized in our previous work.¹

Zero Shear-Rate Viscosity

The viscosity at a zero shear-rate or steady-flow viscosity η_0 is given as an integral over the entire time domain of $G(t)$.⁵

$$\eta_0 = \int_0^\infty G(t)dt = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega} \quad (3)$$

Although the original reptation model^{2–5} has successfully explained many characteristic features of the viscoelastic behavior of concentrated polymer solutions and polymer melts, it does not give a correct quantitative prediction for the molecular weight dependence of the zero shear-rate viscosity. The original DE theory predicts η_0 to be proportional to the cube of the molecular weight, $\eta_0 \sim M_w^3$, whereas experimental evidence indicates that for highly entangled chains, $\eta_0 \sim M_w^\alpha$, where the empirical exponent α ranges from 3.14 to 4.0.¹⁹ It has been understood for some time that the physical origin of the $\alpha > 3$ scaling is that the relax-

ation of some portion of the stress occurs by faster process(es) than reptation, for example, contour-length fluctuations, which would decrease the viscosity relative to the asymptotic result.^{5,18,20} It is convenient to express the zero shear-rate viscosity obtained from reptation theories as

$$\eta_0(n) = G_N \tau_d(n) \cdot f(n) \quad (4)$$

where $n = N/N_e$ is the number of entanglements along the polymer chain (N_e is the number of segments between the entanglements), τ_d is a reptation relaxation time proportional to n^3 , G_N is the molecular weight independent plateau modulus, and $f(n)$ is a function accounting for contour-length fluctuations. These functions are outlined in Table I for the three reptation models considered. Although all three models yield an asymptotic molecular weight scaling of the viscosity equal to 3, the models that include effects of contour-length fluctuations yield a scaling exponent greater than 3 in the molecular weight range of available experimental data, as shown in Table I.

Temperature Dependence of the Viscoelastic Relaxation

Experimental data for numerous polymers indicate that the processes comprising the terminal flow region and the glass–rubber transition change with temperature in a similar manner.^{12,19} One of the important implications of this fact is the validity of the time–temperature or frequency–temperature superposition principle. Particularly suitable for the description of this common temperature dependence is the shift parameter a_T , which is given by²¹

$$a_T = \log \frac{\eta_0(T)}{\eta_0(T_R)} \quad (5)$$

Table II. Properties of PBD Chains as Functions of Temperature (T) Obtained from MD Simulations

T (K)	$D(T)$ ($\text{\AA}^2/\text{ps}$)	ρ (kg/m^3)	C_∞	τ_R^a (ns)
293	$3.5 \cdot 10^{-4}$	920	5.44	126.59
323	$1.2 \cdot 10^{-3}$	900	5.4	32.55
353	$3.2 \cdot 10^{-3}$	880	5.45	14.24
400	$7.5 \cdot 10^{-3}$	851	5.47	6.07

^a τ_R is end-to-end vector relaxation time of the polymer chains (Rouse time).

which relates the dynamics at temperature T to the dynamics at reference temperature T_R . The time–temperature superposition principle allows us to determine the influence of temperature on dynamics for all length (and time) scales based on knowledge of the dynamics on a single arbitrary length scale. A convenient length scale to examine the temperature dependence of dynamics in MD simulations is that of the statistical (Kuhn) segment. In the context of the Rouse model, the temperature-dependent segmental frictional coefficient or monomer friction coefficient $\zeta(T)$ is inversely proportional to the center-of-mass diffusion coefficient $D(T)$ of the polymer molecule:⁵

$$\zeta(T) = \frac{k_B T}{D(T)N} \quad (6)$$

where k_B is the Boltzmann constant and N is the number of statistical segments comprising the chain. The diffusion coefficient of unentangled polymer chains can be determined straightforwardly from MD simulations for temperatures well above the glass-transition temperature (T_g).^{22–24} For the majority of polymer melts, the temperature dependence of the monomer friction coefficient can be represented reasonably well by the Vogel–Fulcher law:²⁵

$$\ln \zeta(T) = A + B/(T - T_0) \quad (7)$$

where T_0 is a Vogel temperature. The temperature-dependent shift factor a_T is given by

$$a_T = \log e \ln \zeta(T)/\zeta(T_R) = -C_1 \frac{T - T_R}{T - T_R + C_2} \quad (8)$$

which is the well-known Williams–Landel–Ferry (WLF) equation, where C_1 and C_2 are constants characterizing a given polymer.²¹

Simulation Methodology

The MD simulations of an unentangled PBD melt are described in detail elsewhere.^{1,22,26,27} Briefly, we per-

formed MD simulations of a PBD melt, using a carefully validated quantum chemistry-based potential described in previous publications.^{22,26} An ensemble of 40 random copolymer chains each consisting of 30 units with a microstructure of 40%/50%/10% 1,4-cis/1,4-trans/1,2-vinyl monomers was generated. Each chain consisted of 114 backbone carbons, which is slightly below the entanglement molecular weight for this polymer.²⁸ All the simulations considered here were performed in an NVT ensemble, yielding an average pressure of 1 atm. Simulations were performed at $T = 293$, 323, 353, and 400 K.

RESULTS AND COMPARISON WITH EXPERIMENT

Molecular Weight Dependence

The zero shear-rate viscosity of PBD melts as a function of molecular weight at 298 K was calculated with eq 4. Properties needed to determine the entanglement molecular weight (chain dimensions represented by the characteristic ratio, C_∞ , and density of the polymer melt, ρ) and the terminal relaxation time (entanglement molecular weight and monomer friction coefficient) were determined from simulations of the unentangled melt. These data are listed in the Table II. To compare how different reptation models reproduce η_0 , we performed calculations for all three models mentioned. The results are compared with experimental data in Figure 1. Excellent agreement can be seen between the Milner–McLeish model and experimental results over the entire range of molecular weights, whereas the MDE model underestimates the viscosity for all molecular weights of PBD. The original DE model exhibits better agreement with experimental

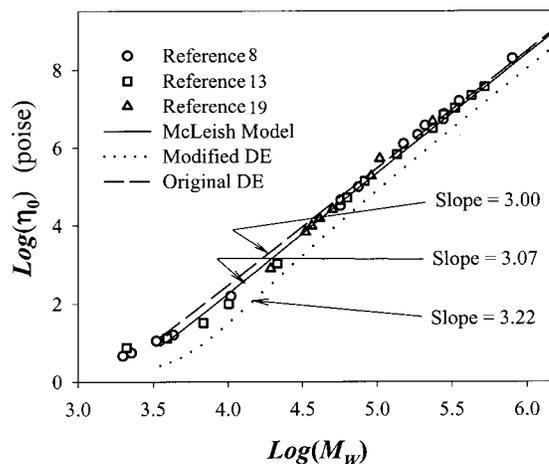


Figure 1. η_0 as a function of the weight-average molecular weight (M_w) for PBD calculated with three reptation models and compared with experimental data.

data at higher molecular weights, where the contour-fluctuation contribution becomes less important, whereas at lower molecular weights, it somewhat overestimate the viscosity, consistent with a comparison of the DE theory with other empirical data.^{5,17} The superiority of the Milner–McLeish model is consistent with the better agreement obtained with the experimental complex shear modulus for PBD in our previous work.¹

Temperature Dependence

Figure 2 shows the monomer friction coefficient $\zeta(T)$ obtained from the self-diffusion coefficient of the unentangled chains with eq 6. A fit of the Vogel–Fulcher equation, shown in Figure 2, yields $T_o = 135$ K. This value is in a good agreement with that obtained for local dynamics from simulations of PBD²⁹ and the experimentally measured T_g of 181 K.¹⁹ In Figure 3, the empirical shift factors obtained from experimental measurements of viscosity of PBD melts³⁰ for a variety of molecular weights are shown. Values of a_T obtained from a WLF fit (eq 8) to the monomer friction coefficient from simulation are in good agreement with the experimental values over the entire temperature range, except for the low-temperature region. At temperatures less than 210 K, a_T predicted from MD simulation starts to deviate from experimental data. This discrepancy may be due to (1) an error in the WLF extrapolation obtained from simulation due to statistical uncertainties in the monomer friction coefficient obtained from simulation, (2) a small difference in T_g between the low molecular weight ensemble used in the simulations and higher molecular weight systems studied experimentally, (3) an imperfect description of nonbonded and conformational energetics provided by the potential

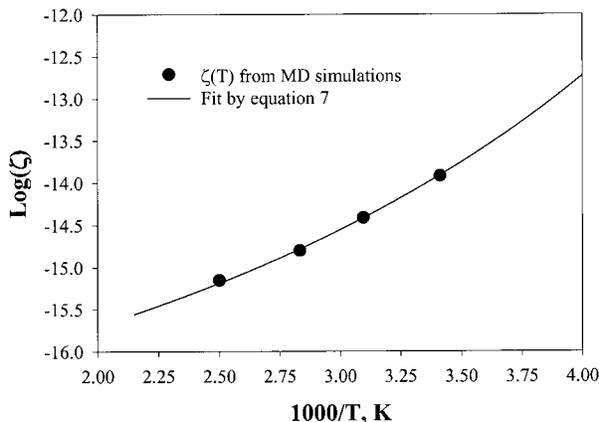


Figure 2. Temperature dependence of the monomer friction coefficient $\zeta(T)$ obtained from the self-diffusion coefficient of unentangled PBD chains. Simulation results and a Vogel–Fulcher fit are shown.

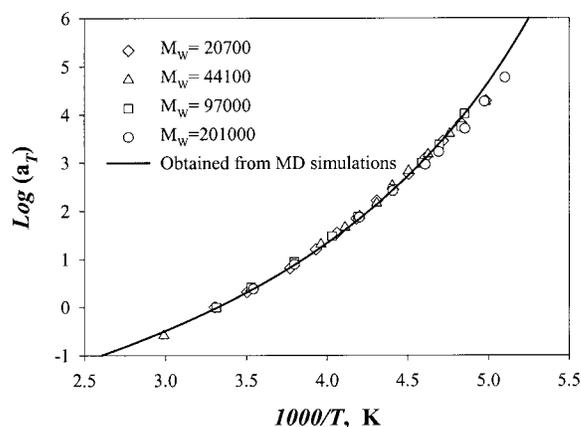


Figure 3. Temperature-dependent shift factor a_T from simulations of the unentangled PBD melt. The solid line is a WLF fit to the monomer friction coefficient obtained from simulations. T_R is 301 K. Shown for comparison are experimental values obtained from viscosity measurements for a number of molecular weights.

function, and/or (4) deviation from WLF behavior near T_g .

CONCLUSIONS

The quality of agreement between simulation and experiment for the molecular weight dependence of the viscosity and temperature-dependent shift factor for PBD, along with the previously reported agreement for the complex shear modulus for an entangled PBD melt, is strong evidence that MD simulations of unentangled melts using high-quality, validated potentials, in conjunction with reptation theory, can be used to predict the linear viscoelastic properties of polymer melts over a wide range of molecular weights and temperatures.

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