

Segmental Mobility of Polyolefin Melts¹

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Processes on different length scales affect the dynamics of chain molecules. Small-scale effects determine the mobility of individual chain segments and, with it, much of the temperature and density dependence of the transport properties of polymers. They are conveniently described by a local friction coefficient, which is inversely proportional to the probability for segmental motion. In this work, an exact enumeration scheme for the simulation of interactions and relative motion of two short chain sections on a lattice is combined with an equation of state to predict the variation of the friction coefficient with temperature, pressure, and small-scale chain structure. The method is applied here to polyolefins, i.e., hydrocarbon chains that differ mostly in small-scale architecture, and the theoretical results are compared with experimental data. For temperatures well above the glass transition temperature, the approach gives a good qualitative representation of the variation of the friction coefficient with chain structure and temperature. Furthermore, there is excellent agreement between calculated and experimental pressure variation of the viscosity at low to moderate pressures. A first estimate of the effects of chain flexibility on segmental mobility is also included.

KEY WORDS: exact enumeration; monomeric friction coefficient; polymer; pressure dependence; viscosity.

1. INTRODUCTION

The dynamics of chain molecules are affected by local interactions between individual chain segments as well as processes on the length scale of the whole chain and collective motions of chain segments. In this work, we focus on small scales and investigate the segmental mobility of polymers in the melt. The polyolefins depicted in Fig. 1 are a good starting point for the investigation. These polyolefins, all hydrocarbons with sum formula

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C_nH_{2n} , differ considerably in their viscoelastic properties [1–11] despite their chemical similarity.

An important ingredient in theories for polymer dynamics is a friction coefficient, ζ , which is employed in coarse-grained models to describe small-scale effects on the dynamics of the system [12]. The friction coefficient ζ is inversely proportional to the probability for segmental motion [13], a relationship that we exploit in this work. In an exact enumeration procedure we perform lattice simulations of relative motion and interactions of two short chain segments, where the surrounding medium is represented in an average way. The collected statistics are evaluated as described in Section 2 to yield the the average probability for segmental motion as a function of a reduced temperature and lattice filling fraction for each of the architectures in Fig. 1.

The combination of the simulation results with the recently developed Born–Green–Yvon lattice model for the thermodynamic properties of polymers [14–16] allows the investigation of the mobility of the polyolefins at a given temperature and pressure. The method of determining the friction coefficients presented here is not an absolute one, but using the probability for segmental motion of a linear chain (polyethylene in our case) at 413 K and atmospheric pressure as a reference value, we are able to calculate relative values of the friction coefficients as a function of temperature and pressure.

To compare the theoretical results with experimental data, we extract friction coefficients of the polyolefins of interest from experimental viscosity data as described in Section 4. For temperatures well above the glass transition temperature, we find that our approach gives a good qualitative

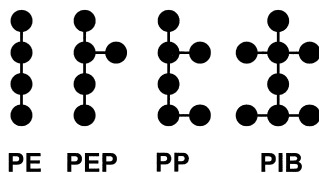


Fig. 1. United atom representation of the polyolefins considered in this work. Shown are the repeat units with four carbon atoms in the backbone for polyethylene (PE), an alternating copolymer of polyethylene and polypropylene (PEP), polypropylene (PP), and polyisobutylene (PIB).

representation of the variation of the friction coefficient with the temperature and chain architecture. We also compare the pressure dependence of the viscosity of polypropylene [17, 18] with our predictions and find excellent agreement for low to moderate pressures. The polyolefins discussed in this work are known to become less flexible as the temperature decreases [19, 20]. We include a first estimate of the effects of flexibility on the segmental mobility in Section 5, where we discuss the results presented here as well as future directions of the research.

2. SIMULATION OF LOCAL MOBILITY

The simulation procedure is based on the idea that the friction coefficient ζ is inversely proportional to the probability for segmental motion. To deduce this probability we perform an exact enumeration of all possible combined configurations and relative movements of two chain segments on a lattice. During the enumeration procedure we collect statistics on the characteristic parameters of each possible initial and final configuration and the connecting move. In the second step, these statistics are evaluated for conditions corresponding to different temperatures and densities. The advantage of this two-step procedure is that the time-consuming part, the exact enumerations, have to be performed only once to yield results that can be evaluated quickly for a variety of conditions. The simulation procedure, which is described in detail in Ref. 21, is illustrated in Fig. 2. The evaluation of the results may be summarized as follows; the probability P_m of a move m between an initial state of type i and a final state of type f is calculated according to

$$P_m = P_i f_{i|f} P_{\Delta E} P_\phi \quad (1)$$

where P_i is the probability for the initial state, $f_{i|f}$ is the relative frequency of reaching f from i , and $P_{\Delta E}$ accounts for the energy difference $\Delta E = E_f - E_i$ between the initial and the final state,

$$P_{\Delta E} = \begin{cases} e^{-\beta \Delta E} & \text{for } \Delta E > 0 \\ 1 & \text{otherwise} \end{cases} \quad \text{with } \beta = \frac{1}{k_B T} \quad (2)$$

P_ϕ is the probability that a sufficient number of contiguous sites is available to the moving segment in a lattice filled to a fraction ϕ .

$$P_\phi = \exp\left(-\frac{4s_n}{n_l(1-\phi)}\right) \quad (3)$$

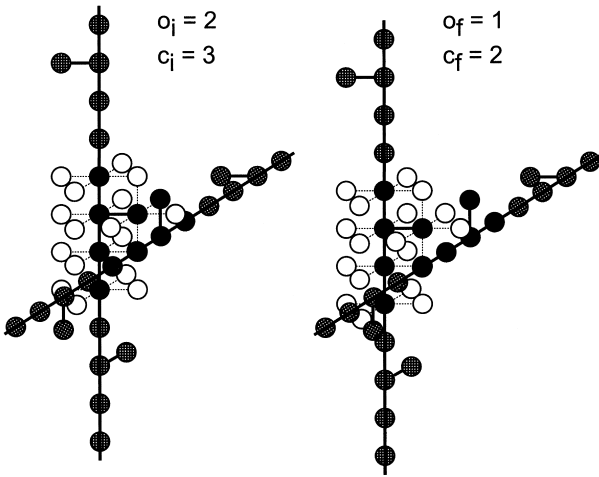


Fig. 2. Illustration of the simulation procedure. Left: An initial combined configuration of two PEP segments. There are $s_f = 5$ sites in the section of interest in each chain (indicated by the filled circles) and $n_i = 18$ identified nearest-neighbor (nn) sites of chain 1 (indicated by open circles). o_i and c_i indicate the number of nn sites occupied by chain 2 and the number of established contacts, respectively. Right: The new combined configuration after chain 1 has been moved one lattice site to the front. o_f and c_f give the occupied sites and established contacts, respectively. In the move, $s_n = 5$ sites were newly occupied by the first segment.

where n_i is the number of nearest neighbor sites of the segment of interest, and s_n is the number of newly occupied sites. Finally, the probability for any kind of move is $P = \sum_m P_m$.

3. CALCULATION OF FRICTION COEFFICIENTS

While the friction coefficient ζ is known [13] to be inversely proportional to the probability for segmental motion, $\zeta \propto P^{-1}$, the proportionality constant between P^{-1} and ζ is not easily determined. Hence, we choose a reference state for the linear chain and express our results for the friction coefficients as the ratio,

$$\frac{\zeta}{\zeta_{\text{ref}}} = \frac{P_{\text{ref}}}{P} \quad (4)$$

where P_{ref} and ζ_{ref} are the reference state values of the probability of segmental motion and the friction coefficient of the linear chain, respectively.

Table I. BGY Lattice-Model Parameters for the Polyolefins Considered in this Work [15]^a

Polymer	PE	PEP	aPP	PIB
ϵ (J · mol ⁻¹)	-1977.5	-2000.0	-2040.7	-2208.1
r	21068.4	19025.8	16511.7	18547.3
v (L · mol ⁻¹)	0.00876846	0.00972039	0.0113939	0.0094158

^a The values presented here correspond to a molar mass $M = 170,000$ for each of the polyolefins.

The reference state can be chosen freely; in our case, a temperature of $T_{\text{ref}} = 413.15$ K and a pressure of $p_{\text{ref}} = 0.1$ MPa turn out to be convenient. To make comparisons with experimental data, we employ equations of state based on the recently developed Born–Green–Yvon (BGY) lattice model [14, 22]. The BGY lattice model has three system-dependent parameters for a polymer melt, corresponding to the volume v per lattice site, the number r of sites occupied by each chain, and the interaction energy ϵ between nonbonded nearest neighbors. For each of the polymers considered in this work, values for the system-dependent parameters have been determined from a comparison with experimental temperature–density–pressure data [15] and are summarized in Table I. In Fig. 3 we present

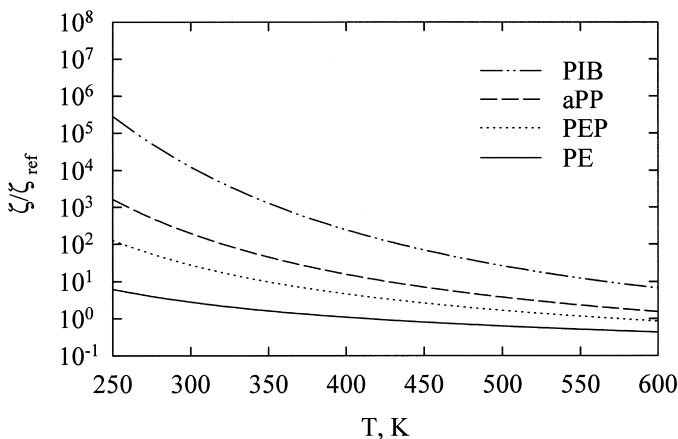


Fig. 3. Calculated friction coefficients, ζ/ζ_{ref} , as a function of temperature at constant pressure $p = 0.1$ MPa for the polyolefins considered in this work. The reference value is obtained for the linear chain (PE) at 413.15 K and 0.1 MPa.

calculated values for the relative friction coefficient ζ/ζ_{ref} as a function of temperature at a pressure of 0.1 MPa for the polyolefins considered in this work. As expected, the friction coefficients increase with decreasing temperature. Furthermore, the effect of the increasing number of side groups on the mobility is clearly visible. The linear chain (PE) has the highest probability of segmental motion, followed by PEP, PP, and PIB, which have one, two, and four side groups in the four-carbon backbone monomer, respectively.

4. COMPARISON WITH EXPERIMENTAL DATA

The friction coefficient ζ is not a directly measured quantity but can be extracted from measurements of dynamic properties like the viscosity or the self-diffusion coefficient. The most direct access to ζ is through the Rouse viscosity η_{R} [1, 12]. A friction coefficient per monomer can be defined as follows:

$$\zeta = \frac{N_{\text{R}}\zeta_{\text{R}}}{N} = m_0 \frac{\eta_{\text{R}}}{M} \left(\frac{N_{\text{A}}}{36} \rho \frac{R_0^2}{M} \right)^{-1} \quad (5)$$

where N is the degree of polymerization and m_0 is the mass of a monomer, which we take to be $n \times 14.03 \text{ g} \cdot \text{mol}^{-1}$, where n is the number of carbon atoms in the repeat unit depicted in Fig. 1. In addition to the Rouse viscosities η_{R}/M , evaluation of Eq. (5) requires values for R_0^2 , the mean-squared end-to-end distance of the chains, and for ρ , the mass density of the melt. In this work, we employ experimental values for these properties at a temperature of 413 K presented in a recent review by Fetters et al. [2] and included in Table II.

The Rouse model describes directly the viscosity for melts of low molecular mass $M \ll M_e$ (for example, $M_e \approx 1000$ for PE and $M_e \approx 7300$ for PIB [2]). Unfortunately, measurements of the melt viscosities for short chains are not only scarce, but chain-end effects have to be taken into account in their evaluation [1, 4]. We therefore decided to turn to high molecular weight viscosity data and an empirical scaling relation [23] to extract values for η_{R}/M . Motivated by the reptation model [12] and by experience with experimental data, Graessley and Edwards [23] suggested the following molecular mass dependence of viscosities in polymer melts:

$$\eta = \frac{\eta_{\text{R}}}{M} M \left[1 + \left(\frac{M}{M_c} \right)^{2.4} \right] \quad (6)$$

Table II. Experimental Parameters for the Polyolefins Considered in this Work^a

Polymer	PE	PEP	aPP	PIB
R_0^2/M ($\text{\AA}^2 \cdot \text{mol} \cdot \text{g}^{-1}$) [2]	1.21	0.834	0.67	0.57
ρ ($\text{g} \cdot \text{cm}^{-3}$) [2]	0.785	0.79	0.791	0.849
M_e [2]	976	2284	4623	7288
Viscosity data reference(s)	[4, 5]	[6]	[7]	[8]
Temperature range, T (K)	350–500	248–443	298–463	298–473
$\log[(\eta_R M^{-1})/(\text{P} \cdot \text{mol} \cdot \text{g}^{-1})]$	−4.1035	−3.6039	−3.3424	−2.7669
$\log[\zeta/(\text{P} \cdot \text{cm})]$	−8.5554	−7.8001	−7.3648	−6.6388
C_1	2.018	3.565	3.101	4.684
C_2 (K)	253	277	189	307
T_g (K)	188	211	268	202
T_g reference(s)	[11]	[6]	[7]	[1, 3]

^aThe values correspond to atmospheric pressure and a temperature of 413.15 K. The glass transition temperature for polyethylene (PE) is an estimate based on results for ethylene-butene copolymers [11].

with $M_e = 2.2M_e$ [23, 24]. In this work, we employ the experimental M_e values at 413 K reported by Fetters et al. [2] (cf. Table II), and determine η_R/M from a comparison of Eq. (6) with experimental data. Since values for the viscosity at 413 K are required in Eq. (6), we shift the viscosity values from the temperature of the measurements to 413 K using the temperature correlations provided with the experimental data [5–8]. The resulting correlations for the mass dependence of the viscosity give a satisfactory representation of the experimental data [21]. The values for η_R/M obtained in this way are included in Table II. Inserting them into Eq. (5) and employing the values for m_0 , R_0^2 , and ρ as discussed, we arrive at the values for the monomeric friction coefficient ζ at 413 K and atmospheric pressure presented in Table II. The value of the friction coefficient for PE at $T_{\text{ref}} = 413$ K and 0.1 MPa is the reference value for the experimental friction coefficients, and all further results are presented as $\zeta/\zeta_{\text{PE}}(T_{\text{ref}})$.

In measurements of viscoelastic properties of polymers, it is customary to describe the temperature dependence of the viscosity by Vogel–Tammann–Fulcher (VTF) or Williams–Landel–Ferry (WLF) equations [1]. Since the dominant contribution to the temperature variation of the viscosity is due to the friction coefficient, it is a reasonable approximation to assign the temperature dependence of the viscosity to the friction coefficient [1]. Some of the experimental studies quoted here provide slightly

different temperature correlations for the viscosity of samples of different molar masses. When shifting the experimental viscosity data to the reference temperature of 413 K, we employed the correlations appropriate for the molar mass under consideration. For the following comparisons with our work, on the other hand, we choose a representative correlation for each polyolefin and bring it into WLF form [see Eq. (7)] with a reference temperature of $T_{\text{ref}} = 413$ K. The corresponding parameters C_1 and C_2 are included in Table II.

The temperature-dependent friction coefficients are now obtained from

$$\log(\zeta(T)) = \log(\zeta(T_{\text{ref}})) - \frac{C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}} \quad (7)$$

with the $\zeta(T_{\text{ref}})$ values presented in Table II. In Fig. 4 we present the friction coefficients $\zeta(T)$ divided by the reference value $\zeta_{\text{PE}}(T_{\text{ref}})$ for the polyolefins considered in this work. The heavy lines in the graph indicate the temperature range in which experiments were performed. For each of the polyolefins, a strong increase in the friction coefficient is evident as the temperature is lowered. This increase is due to the slowing of the dynamics of the polymers as the glass transition is approached. The glass transition temperature T_g of polypropylene (aPP) is much higher (cf. Table II) than that of the other three polyolefins considered here. This is apparent in Fig. 4,

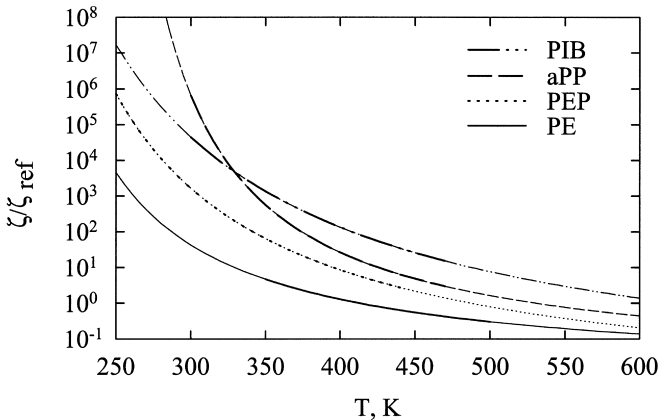


Fig. 4. Temperature dependence of the friction coefficients $\zeta(T)/\zeta_{\text{PE}}(413 \text{ K})$ extracted from experimental data. The heavy lines in the graph indicate the temperature range over which experiments were performed (cf. Table II).

where the friction coefficients of PE, PEP, and PIB have very similar temperature dependences, while the aPP friction coefficient curve starts turning up at a much higher temperature and crosses the curve of the friction coefficient for PIB.

Let us start the comparisons of the friction coefficients predicted from the simulation, Fig. 3, with those extracted from experimental viscosity data, Fig. 4, for temperatures well above the glass transition temperatures of the polymers. We note, first, that in both graphs the values of the friction coefficients increase for a given temperature when going from PE, which has the lowest friction coefficient, over PEP, PP, to PIB. As noted earlier, this can be understood as a result of the different small-scale architectures: the number of side groups in the repeat unit increases from PE (0)

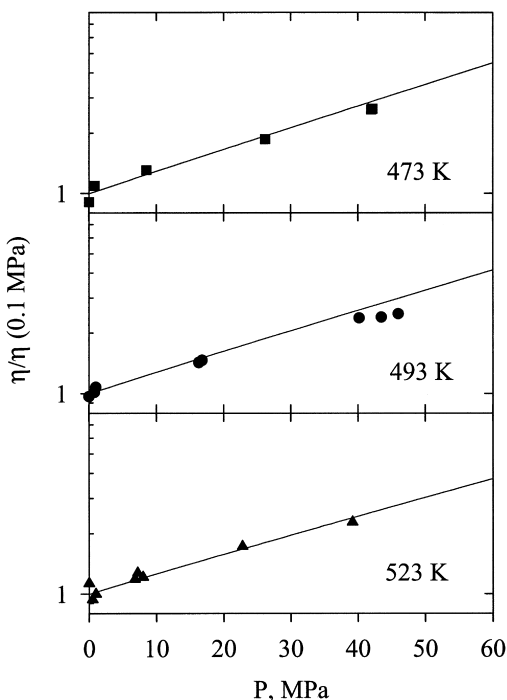


Fig. 5. Pressure dependence of the viscosity of polypropylene. For each of the three isotherms we present the viscosities divided by their value at atmospheric pressure. The lines represent results from our simulation procedure, the symbols indicate experimental data of Mattischek and Sobczak [17].

over PEP (1), PP (2), to PIB (4). The magnitude of the architecture effect is similar in the predicted and experimental friction coefficients. Furthermore, we note that the variation of the friction coefficients with temperature is of the same order of magnitude in the predicted and extracted curves for temperatures well above the glass transition temperature. The agreement between the simulation results and the ζ values extracted from experimental data diminishes as the glass transition temperature is approached. This is not surprising since we have focused on individual segmental motion rather than cooperative effects, and we have not included the variation of chain flexibility with temperature; these points are discussed below.

In Fig. 5 we compare the pressure dependence of the viscosity of polypropylene as predicted from our work with experimental data by Mattischek and Sobczak [17, 18]. To separate temperature and pressure effects, we use the values of the viscosity at atmospheric pressure to scale the viscosities along each isotherm. For low to moderate pressures (≤ 50 MPa), the agreement between experimental and predicted pressure variation is excellent. As the pressure is increased further, the predicted viscosities become larger than the experimental values. Compared to our earlier publication [21], we have used equation-of-state parameters here that give a better representation of high-pressure data. This accounts for the good representation of the data up to 50 MPa here, compared to a good representation up to about 20 MPa before. While the remaining discrepancy may be due to the equation of state, problems with the experimental measurements cannot be excluded [18].

5. DISCUSSION

In this work, we presented results of a recently developed [21] exact enumeration method for lattice simulations of chain segment mobility. The algorithm enumerates the attempted and successful moves for two short, straight sections of a polymer and is evaluated by taking relative frequency, energetics, and density effects into account. The result is the mean probability for segmental motion as a function of reduced temperature and the filling fraction of the lattice. We performed simulations for four small-scale architectures, obtaining results that show a sensible decrease in mobility with increasing density and number of side groups of a monomer.

Combining these results with equations of state for the corresponding polyolefins, we deduce monomeric friction coefficients as a function of temperature and pressure. Our method is not absolute, but by employing the friction coefficient of polyethylene at 413 K and atmospheric pressure as a reference value, we can predict the relative values of the friction

coefficients as a function of temperature and pressure for the polyolefins considered in this work. If we are interested in the properties of a single polyolefin, we can employ the value of the viscosity for a particular temperature and pressure as a reference value and predict the relative variation of the viscosity with temperature and pressure. The same is true for other transport properties that depend in a simple way on the friction coefficient; this will allow us to investigate diffusion coefficients, for example, in future work.

To compare our results with experimental data, we extracted Rouse viscosities and monomeric friction coefficients from high molecular mass viscosity data. Employing temperature correlations of the experimental data in the WLF form, we obtain "experimental" monomeric friction coefficients at atmospheric pressure over a range of temperatures, which we scale by the value for PE at 413 K. The comparison of these extracted friction coefficients with the results from our new simulation method is encouraging. For temperatures well above the glass transition temperature, the calculated probabilities give a good qualitative representation of the relative variation of the friction coefficient with temperature and monomer architecture. A comparison of calculated and experimental pressure variation of the viscosity of polypropylene shows excellent agreement for low to moderate pressures.

To extend the range of validity of the present theory to temperatures close to the glass transition, cooperative effects in the dynamics will have to be taken into account in a more sophisticated way. In this work, we have assumed a random distribution of voids over the lattice and have taken the system to be in an equilibrium state before each attempted move. One way to improve on this approximation would be to employ an iterative approach in which the distribution of configurations after a round of attempted moves is used as the input distribution of configurations for the next round of moves.

Of more immediate concern, however, are the effects of chain flexibility. Polyolefins become less flexible as the temperature is lowered [19, 20]. A measure for chain flexibility is the characteristic ratio C_∞ , which is defined as the ratio of the mean squared end-to-end distance R_0^2 of the actual chain to that of a completely flexible, Gaussian chain. Hence, a semiflexible chain can be modeled as a flexible chain composed of stiff segments with C_∞ backbone units [19]. While a more rigorous treatment of the effects of chain flexibility is currently under way, we would like to present here a first estimate for the effect. The simulation algorithm considers straight chain sections with four carbon atoms in the backbone. At high temperatures, four is a reasonable value for C_∞ for the polyolefins considered here [20]. As the temperature is lowered, however, C_∞ increases.

We can estimate C_∞ as a function of temperature for PE, PEP, and aPP from the values of $d \ln R_0^2/dT$ reported by Hattam et al. [20] together with C_∞ values reported by Fetters et al. [2]. For PE, for example, this yields $C_\infty = 4$ at 501 K, compared to $C_\infty = 7.3$ at 413 K. Unfortunately, we have to exclude PIB from consideration here since Hattam et al. did not report values of $d \ln R_0^2/dT$ for PIB, and literature values for this quantity vary by more than a factor of two (cf. Ref. 25).

An estimate for the mobility of chain sections with $C_\infty(T)$ atoms in the backbone can be obtained from our simulations with four-atom sections by raising P_ϕ , Eq. (3), to the power $C_\infty(T)/4$. The results of this estimate for the friction coefficients of PE, PEP, and aPP are presented in Fig. 6 together with the corresponding “experimental” friction coefficients. While the almost quantitative agreement of experiment and prediction is certainly fortuitous and should not be expected from such a rough estimate, the comparison confirms the importance of chain flexibility on dynamic properties (see, e.g., Ref. 26 and references therein).

So far, the simulation method described here has been applied only to straight chain sections of polymers on a cubic lattice with a single site-site interaction strength ϵ . It is, however, readily modified to include chain flexibility, chemical differences, and realistic bond angles, which allows a large range of polymeric systems to be investigated in this way. We plan to extend the theory in these directions and are currently focusing on the effects of chain flexibility.

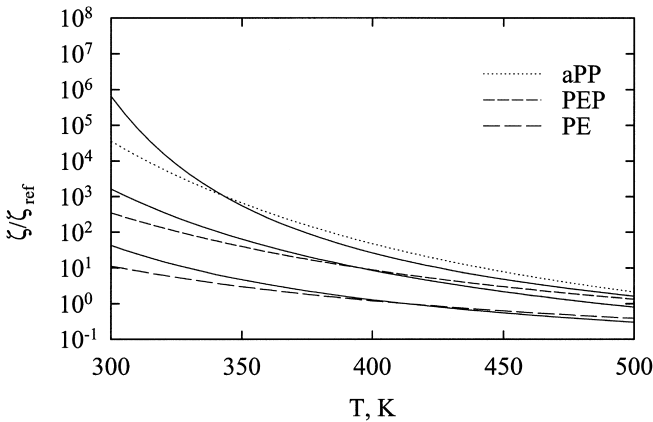


Fig. 6. First estimate of the temperature dependence of the friction coefficient including effects of chain flexibility. The dashed lines represent our theoretical estimates; the solid lines, the values extracted from experimental data.

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