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A Creep Compliance Simulation Study of the Viscosity of Entangled Polymer Melts

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ABSTRACT: A new Monte-Carlo model is proposed in which the viscosity of entangled polymer melts is obtained directly from their creep compliance. In the model, the melt is represented by a dense array of chains which interact through entanglements placed on the sites of a diamond lattice. The chains are allowed to slip through entanglements by use of a thermally activated process. For chains of monodisperse length M, we find that the viscosity scales as $\eta_0 \sim M^{3.46\pm0.05}$, in agreement with experimental observation.

1. Introduction

The reptation model introduced by de Gennes[1] and further refined by Doi and Edwards[2] has been very successful in describing the dynamics of entangled polymer melts. In that approach, the polymer chain is assumed to "slither" through a tube formed by its neighbors which are assumed to be fixed. The model correctly describes the dependence of the self-diffusion coefficient D on chain molecular weight M as $D \sim \mathrm{M}^{-2}$. For the zero shear rate viscosity η_0, however, reptation predicts $\eta_0 \sim \mathrm{M}^3$, whereas the experimentally measured scaling exponent is 3.4 ± 0.1.[3] That discrepancy remains one of the most intriguing problems in polymer physics.

In a further refinement of the reptation model, Doi[4] has suggested that the higher viscosity exponent found experimentally is due to fluctuations in the length of the tube at small molecular weights, lowering the viscosity. That point of view was later challenged by Needs and des Cloizeaux[5,6] who contend that tube fluctuations are too small to account for a 3.4 power law. The reptation dynamics has also been solved numerically in a few simple "repton models"[7,8] but none has been completely successful at unambiguously reproducing the experimentally observed power law. Molecular dynamics simulations[9] have shown that, as long as a single chain is considered, its motion is confined to a tube, in accordance with the reptation model. More recent work by O'Connor and Ball[10] has determined that the experimental 3.4 power law can be traced to Rouse fluctuation effects in the Doi−Edwards model. Finally, using a totally different approach from reptation theory, Fixman[11] has shown that a similar proper power law can be obtained through use of the phenomenological Langevin equation.

Monte-Carlo simulation studies have also been used to investigate the dynamics of polymer melts.[12−18] In those studies, the polymer is represented by a set of random walks on a lattice whose unit length equals the statistical segment length. The polymer segments are then moved on the lattice using a set of elementary motions, e.g. crankshaft like motion, and entanglement effects are automatically taken into account by a self-avoiding condition which prevents bond cutting during the segment rotations. The viscoelastic properties are then estimated from the terminal relaxation time calculated from the decay of the end-to-end vector correlation function. These simulations were meant to check the validity of the reptation concept and did not attempt to calculate the viscosity power law.

In the present work, we propose a new Monte-Carlo lattice model in which the viscoelastic properties of polymer chains are calculated directly from their creep compliance. An essential feature of our lattice representation is that it explicitly takes into account the configurational rearrangements of the tube as well as the fluctuations in the number of entanglements per chain, which have been neglected in reptation theory. Unlike all previous approaches, our model does not require an independent estimation of the entanglement length. Rather, entanglements are explicitly incorporated into the lattice and treated as friction points between two chains. In spite of its simplicity, that representation has been found to provide an accurate description of the effects of temperature and rate of deformation on the drawability of polymers in the solid state.[19] More elaborate definitions of chain entanglements have been proposed in the literature.[20−22]

2. Model

In our approach, the polymer melt, *prior to deformation*, is represented by a dense array of chains which interact through entanglements placed on the sites of a diamond lattice. We start with a regular array in which all the chains are in an ordered conformation; see Figure 1a which represents a typical repeating unit cell. In Figure 1a, the chains between entanglement sites are represented by vectors which are given different line types in order to easily visualize the different chains and their connectivity. These chains are then randomized using a collective slithering end−end motion.[23−24] In that process, the end of a chain (i) is picked at random and elongated by one lattice unit coming from the end of a neighboring chain (i + 1), again picked at random. To compensate for that loss, the other end of the chain (i + 1) is elongated by a similar technique and the motion proceeds until the starting chain i recovers its original length. A two-dimensional representation of that process is given in Figure 1b for a molecular weight $M = 8$ (henceforth in units of the molecular weight between entanglements, M_e). A second cycle of motions is then initiated from another chain i, and so on and so forth, until equilibrium is reached. We found that the end-to-end vector lengths, R, of the chains reach a stationary value after $\sim 20M^3$ visits per chain.[23,24] In order to speed up the convergence of the calculations, a crankshaft relaxation pro-

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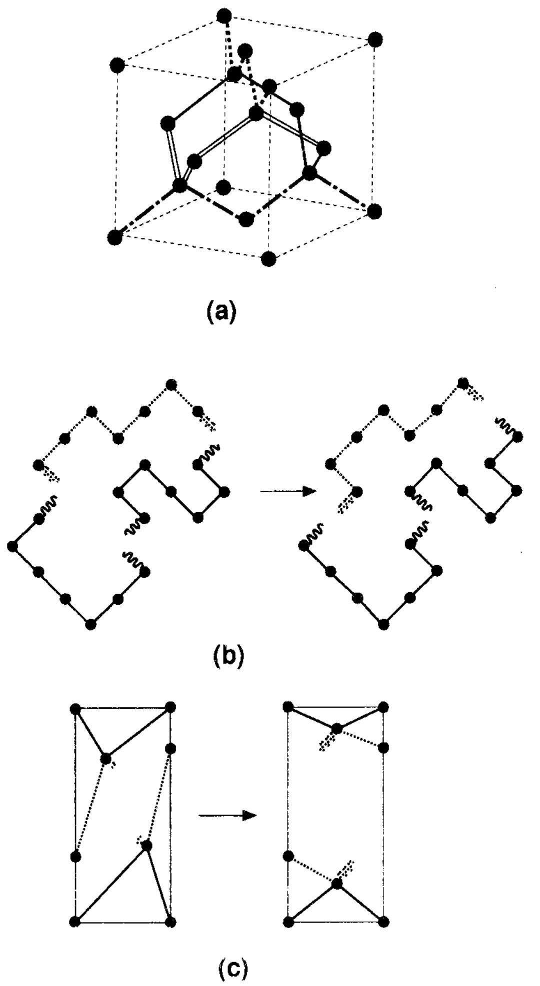

Figure 1. Model representation of a dense undeformed polymer melt. Heavy dots denote entanglement points. (a) Repeat unit cell on a diamond lattice, illustrating the starting ordered conformation. (b) Two-dimensional representation of the collective slithering end−end motion. The figure is for $M = 8$; chain ends are denoted by wiggling lines. (c) Disentanglement/reentanglement process.

cess has been added to the slithering end−end motion. For the range of molecular weights investigated, $8 < M < 40$, simulations on a diamond lattice with unit length d lead to $R^2/(d^2M)$ values in the range 1.1−1.2.

After completion of the construction of the network for a given molecular weight M, the viscoelastic properties are tested in a creep compliance test. In such a test, a *constant* tensile stress σ is applied to the sample and an elongational viscosity is obtained from[25]

$$\eta = \sigma/(\mathrm{d}\epsilon/\mathrm{d}t) \qquad (1)$$

where $\mathrm{d}\epsilon/\mathrm{d}t$ denotes the strain rate. No periodic boundary conditions are imposed along the direction of applied stress. For small σ, the elongational viscosity approaches 3 times the shear viscosity.[26] In our approach, the stress σ_i on a particular chain strand i between two lattice sites (or entanglements) is calculated by using the classical treatment of rubber elasticity in the Gaussian approximation[27]

$$\sigma_i = (3kT/l)(r_i/n_il) - \sigma_0 \qquad (2)$$

in which r_i and n_i denote, respectively, the length of the end-to-end vector and the number of statistical segments (of length l) for strand i. σ_0 in eq 2 denotes the local stress in the absence of strain, i.e. that for which $r_i = n_i^{1/2}l$. Stretching the network to a particular stress value σ is performed by straining the sample, i.e displacing the top row of lattice sites, in a series of very small strain increments $\delta\epsilon$. For each increment, the network of remaining sites is relaxed internally to its minimum energy configuration using a series of fast computer algorithms which steadily reduce the net residual force acting on each entanglement site.[28,29] That process is realized in a sequence of steps. At each step, an entanglement point is visited and its position is adjusted so as to bring to zero the resultant of the forces (eq 2) along the four connected chain strands. To save computer time, only displacements along the draw axis are explicitly calculated.[28,29] After these relaxation steps, the axial stress acting on the top row of lattice sites is calculated and the sequence of straining and relaxation processes is repeated until the desired stress value σ is attained.

Upon attainment of the desired σ value, our model allows for the following four processes to occur.

(i) Chain Slippage. In that process, a chain around an entanglement is selected at random and it is allowed to slip by one statistical segment according to a Monte-Carlo lottery.[30] Slippage occurs along the direction which minimizes the stress gradient in the chain across the entanglement (for more details, see ref 30). This effectively leads to an increase (by one unit) in the number of statistical segments in the most stressed strand of the chain, at the expense of a decrease (by one unit) in the less stressed strand. At the end of each visit and regardless of whether slippage has occurred, the time t is incremented by $1/[n(t)]$ in which $n(t)$ denotes the total number of entanglements at time t.[30]

(ii) Chain Disentanglement. Chain slippage leads to local changes in the number of statistical segments between entanglements and, occasionally, to disentanglement at chain ends.

(iii) Chain Reentanglement. Upon disentanglement, a chain end is allowed to immediately reentangle at the middle point of a neighboring chain strand picked at random.[31] That process is clearly displayed in Figure 1c in which all six newly formed chain strands on the right-hand side are at mechanical equilibrium, i.e. $r_i = n_i^{1/2}l$. We note that, in our model, reentanglement is assumed to be a very fast process as compared to the rate of disentanglement so that the total number of entanglements in the network remains approximately constant at all times.

(iv) Network Relaxation and Increase in the Overall Strain. Upon completion of processes i−iii for a small time interval δt, the network is relaxed towards mechanical equilibrium and the strain is increased back to its initial value, σ.

The sequence of four processes described above is repeated over and over again until a linear dependence of strain on time (see eq 1) is obtained. It is to be noted that these processes lead to a very nonaffine deformation of the polymer network which quickly loses the regularity of the starting configuration of Figure 1a (for illustration, see for example ref 29).

In all our simulations we took, without any loss of generality, a number of statistical segments between entanglements in the melt $n_e = 60$. The value of (kT/l), which is related to the modulus, is set equal to 5. The simulations have been made for two stress values $\sigma = 0.01$ and $\sigma = 0.02$ which correspond to initial elongations around 0.5 and 1%, respectively. These values are quite

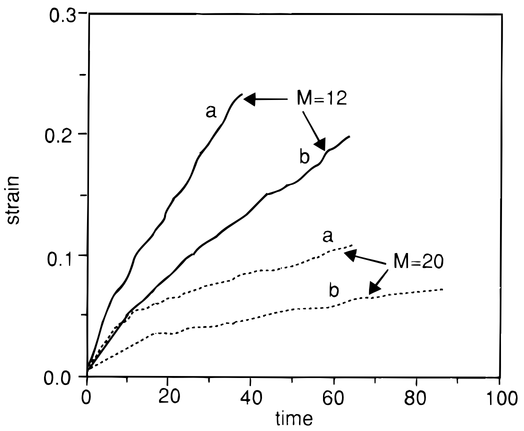

Figure 2. Time dependence of the strain, ϵ, for two monodisperse systems with $M = 12$ and $M = 20$. The external stress values σ are as follows: (a) $\sigma = 0.02$; (b) $\sigma = 0.01$.

small compared to that for the maximum extensibility of the chain strands between entanglements which is of the order of $n_e^{1/2}$, i.e around 800%. The results, to be presented below, are for diamond lattices of up to 5000 entanglement sites and molecular weight values M ranging from 8 to 40 entanglement lengths.

3. Results and Discussion

Figure 2 shows the dependence of strain, ϵ, on time for two monodisperse systems with $M = 12$ and $M = 20$. We start by studying the case $M = 12$ with $\sigma = 0.02$ (curve a) and $\sigma = 0.01$ (curve b). Our data show the presence of a stationary linear regime after a transient time $t_c \approx 5-10$. Within that linear regime, the amount of chain disentanglement is exactly compensated by the number of chain reentanglements and the curves have a slope proportional to the external stress σ. Thus, at $\sigma = 0.02$ and 0.01, we find $d\epsilon/dt = 0.0027$ and $d\epsilon/dt = 0.0055$, respectively. That proportionality in the limit of small external stresses allows one to uniquely define a viscosity value η from the use of eq 1. Comparing the curves for $M = 12$ to those for $M = 20$, we first note that the critical times for the onset of a linear regime increase with M ($t_c \approx 10-20$ for $M = 20$). This is because high molecular weight networks have a low density of chain ends and a significant amount of slippage is required before disentanglement occurs. Even more important is the observation that the rates $d\epsilon/dt$ in those linear regions are strongly dependent on M. That dependence, which is at the basis of our calculation of a viscosity exponent (see later), typically occurs in the regime of "constraint release" which was neglected in the reptation models of refs 7 and 8.

Figure 3 summarizes our results for the dependence of the viscosity η_0 on M for a monodisperse molecular weight distribution (symbol ○). Our data denote average values over two measurements made for $\sigma = 0.01$ and $\sigma = 0.02$. The size of the symbols is larger than the length of the error bars. We find $\eta_0 \sim M^{3.46\pm0.05}$, in agreement with experimental observation. It is important to stress that this agreement has been obtained from a model which explicitly takes into account the configurational rearrangement of the tube (Figure 1c), which has been neglected in reptation theory.[32] Our model results therefore seem to indicate that tube renewal is essential for reproducing the high viscosity exponent value measured experimentally. That conclusion is in accordance with the results of the modified Doi–Edwards model of ref 10 in which the disengaged tube is modeled as a plasticizer. Finally, it should be noted that our model approach may be quite helpful in understanding the effect of polydispersity on viscosity. Further work in that direction is in progress.

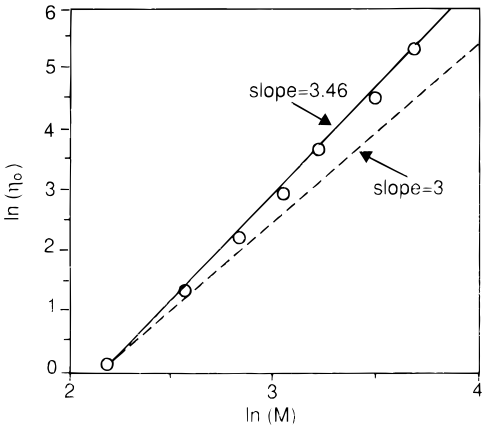

Figure 3. Calculated dependence of the viscosity η_0 on molecular weight M. The values (symbol ○) are averages over two measurements made for $\sigma = 0.01$ and $\sigma = 0.02$. The size of the symbols is larger than the length of the error bars.

Admittedly, our model predictions are for a relatively small range of molecular weight values with chains having no more than 40 entanglements along their contour. As exemplified in Figure 2, however, the onset of a linear regime in the strain *vs* time curves is significantly delayed at high molecular weights and the amount of computer time becomes prohibitively too large. Thus, present calculations for $M = 40$ entanglement lengths ($t_c \approx 100$) take up to 300 h CPU time on a single 200 MHz R4400 processor of a Silicon Graphics Challenge. In addition, the present simulations were for arrays of up to 5000 entanglements which were deemed sufficiently large to ensure a good reproducibility of the results for chains having up to 40 entanglement lengths. It is quite likely that larger networks will be required at higher molecular weights. In that regard, it is worth noting that experimental viscosity data for up to 2000 entanglement lengths still show the $M^{3.4}$ regime.[33]

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