Fit of a Nonreptative Model of Polymer Melt Dynamics to Experimental Melt Diffusion Constant Measurements

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Synopsis

A model of polymer melt diffusion recently proposed by Skolnick, Yariss, and Kolinski and which does not invoke reptation as the dominant mechanism of polymer melt motion is used to fit polymer self-diffusion constant data measured by Antonietti, Fölsch, and Sillescu for a homopolymeric melt as well as for a probe in a larger molecular weight matrix. The quality of fit of the data indicates that reptation theory cannot be verified by simple comparison to diffusion constant measurements.

INTRODUCTION

Recently a considerable amount of controversy has arisen over whether the molecules in a dense polymer system move via the "reptation" mechanism. A major claim of success of the reptation model comes from its explanation of the molecular weight dependence of the self-diffusion constant,

\[ D \propto M^{-1} \quad M < M_c \quad (1a) \]

\[ D \propto M^{-2} \quad M > M_c \quad (1b) \]

where \( M_c \) is the crossover value of the molecular weight.

Skolnick, Yariss, and Kolinski have published an alternative model based on the concept of dynamic entanglements suggested by their Monte Carlo simulations. Their model also explains the scaling behavior of \( D \) and, in fact, suggests that the crossover to \( M^{-2} \) behavior is merely indicative of the onset of some sort of constrained and not necessarily reptative motion.

Precise measurements of the molecular weight dependence of the diffusion constant of polystyrene in a matrix of equal molecular weight and in a matrix of higher molecular weight have recently been published by Antonietti, Fölsch, and Sillescu. They state that the exponents observed from their data are consistent with reptation theory. In this paper we show that the model of Skolnick et al., which does not invoke reptation, also accurately fits the data.
EQUATIONS AND PARAMETERS

The main assumptions in the model of Skolnick et al.\textsuperscript{3} are that the motion of a polymer chain on distance scales of the order of the radius of gyration is isotropic and that the slow down from the nonentangled limit arises from long-lived dynamic entanglements where a given chain drags another chain through the melt for times on the order of the longest relaxation time of the end-to-end vector. In the case of a polymer molecule in a matrix of equal molecular weight (and degree of polymerization), this leads to the equation

\[ D = D_0 \left[ 2(1 - \beta) \right] / \left\{ (1 - 2\beta + n/n_0) + \left[ 1 + 2(1 - 2\beta)n/n_0 + n^2/n_0^2 \right]^{1/2} \right\} \]

(2)

where \( n_0 \) is the average number of monomers between long-lived dynamic entanglements, and \( D_0 \) is the renormalized Rouse diffusion constant given by

\[ D_0 = \frac{kT}{\xi} = d_0, \]

with \( \xi \) the monomeric friction constant. The parameter \( \beta \) is a measure of the coupling of the internal (Rouse-like) coordinates to the center-of-mass motion. Numerically \( \beta \) should be close to zero unless the system is near a glass transition, at which point \( \beta = 1 \). If \( \beta = 0 \), eq. (2) reduces to

\[ D = \frac{d_0}{n(1 + n/n_0)}. \]

(3)

If the molecules of the matrix are larger than those of the probe, the probe's diffusion constant becomes (\( \beta = 0 \))

\[ D_p = \frac{d_0}{n_p} \left[ \frac{\gamma + (1 - \gamma)n_p/n_m}{\gamma + (1 - \gamma)n_p/n_m + n_p/n_0} \right], \]

(4)

where \( n_p \) (\( n_m \)) is the degree of polymerization of the probe (matrix), and \( \gamma \) is a parameter describing the fraction of the effect of a dynamical contact due to the probe. Numerically \( \gamma \) should be close to 1/2.

EMPIRICAL FITS

Using data published by Antonietti et al.,\textsuperscript{5} least squares fits with eqs. (3) and (4) using \( d_0, n_0, \) and \( \gamma \) as fitting parameters were performed. The probe molecular weight ranged over about one decade from 7200 (\( n = 69 \)) to 75,400 (\( n = 724 \)). The diffusion constant was measured in a matrix of the same molecular weight as the labeled polymer (homopolymeric mixture) and in a
matrix with molecular weight 111,000 ($n = 1066$). Both cases were measured at two temperatures: 185 and 212°C. Both temperatures are well above the glass transition temperature of polystyrene, so $\beta = 0$ should be a reasonable approximation. Furthermore, on the basis of the plateau modulus, which gives $n_e = 173$, these chains are in the crossover region, which is the most sensitive region in which to test the present theory.

The entanglement length initially used for the fits was obtained from the plateau modulus and had as mentioned above a numerical value of 18,000 ($n_e = 173$). Figure 1 shows the curves obtained by simultaneously fitting to the mixture and the homopolymer data at each temperature, with $d_0$ the only variable. The other parameters were fixed, i.e., $\beta = 0$, $\gamma = 0.5$, and $n_e = 173$. The results were $d_0$ (185°C) = $1.6 \times 10^{-10}$ cm$^2$/s and $d_0$ (212°C) = $9.9 \times 10^{-10}$ cm$^2$/s. The average deviation between the data and the curves was about 22%, with the fit to the mixture at 212°C being slightly better than the other three fits.

Figure 2 shows a similar fit to the same data except that $n_e$ is now allowed to vary. These results are $d_0$ (185°C) = $4.8 \times 10^{-8}$ cm$^2$/s and $d_0$ (212°C) = $2.9 \times 10^{-7}$ cm$^2$/s, with $n_e = 81$. The average relative error at 185°C was still about 23%, whereas that at 212°C dropped to 10%.

The energy of activation calculated from $d_0$ for both of these fits is about 29 kcal/mol. This seems to be rather large for monomer diffusion, but corresponds well to the same quantity calculated from the data. It is not an artifact of the fit.

Other fits were attempted by allowing more parameters to vary, but these became more sensitive to the experimental errors and in many cases gave unphysical values.
Fig. 2. Fits to the self-diffusion constants of the homopolymers (solid lines and triangles) and of the mixtures with a matrix of molecular weight 111,000 (dashed lines and circles). \( d_0 \) at each temperature and \( n_0 \) were the fitting parameters.

**CONCLUSIONS**

We find that the theory of polymer diffusion put forth by Skolnick, Yaris, and Kolinski,\(^3\) which does not make the reptation assumption, fits experimental data adequately. There is no basis in the quality of fits to prefer the reptation mechanism over that of a mechanism based on isotropic motion but where entanglements arise from long-lived dynamic contacts. Thus statements to the effect that the experimental data on self-diffusion can confirm the assumptions of reptation theory are invalid; rather the reptation model is but one of a class of possible motional mechanisms consistent with the scaling of the diffusion constant with molecular weight.

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**References**


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