Notes

Self-Diffusion of Lamellar Diblock Copolymer Melts in the Order−Disorder Transition

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The self-diffusion of lamellar diblock copolymers in their melts has attracted considerable attention in recent years[1−8] because of the variety of structural and dynamic behavior these copolymers exhibit. The self-diffusion coefficients of these copolymers and the blends are usually described by the Williams−Landel−Ferry (WLF) equation[2−5] or the Vogel−Fulcher equation.[9] Use of the WLF equation for the copolymers involves choosing two parameter values by fitting data. Hamersky et al.[1] pointed out that the equation does not have predictive capability. In its place, they suggested four methods of predicting the copolymer mobility but with little success. Shull et al.[4] arrived at a conclusion that the WLF equation would not be expected to be valid for block copolymers when fluctuation effects are important.

In this note, we propose a method for predicting the self-diffusion coefficient on the basis of the friction coefficient. According to the reptation model, the pure component friction coefficient[10] is given by

$$\zeta_{re}(T) = \frac{M_0 kT}{MD_s}\left(\frac{4M_e}{15M}\right) \tag{1}$$

where D_s is the self-diffusion coefficient, M_0 is the monomer molecular weight, M_e is the entanglement molecular weight measured from the shear modulus or the plateau modulus, M is the molecular weight of the diffusant, k is the Boltzmann constant, and T is the temperature. For unentangled Rouse polymers,[10]

$$\zeta_{Ro}(T) = \frac{kTM_0}{D_s M} \tag{2}$$

For blends involving two homopolymers A and B, the entanglement molecular weight of the blend,[9,11] M_e^{AB}, is related to its constituent entanglement molecular weights as follows:

$$\frac{1}{[M_e^{AB}]^{1/2}} = \frac{f_A}{[M_e^{A}]^{1/2}} + \frac{f_B}{[M_e^{B}]^{1/2}} \tag{3}$$

where f_A and f_B are the compositions of the constituent homopolymers. The same relationship is applied to the copolymers here in our model. The inability of small molecules to form entanglements is accounted for by setting the corresponding M_e to infinity.[12] Accordingly, if homopolymer A is the unentangled polymer, eq 3 reduces to

$$M_e^{AB} = \frac{M_e^{B}}{f_B^{\,2}} \tag{4}$$

Hamersky et al.[1] suggest that an average local friction coefficient in polymer mixtures be estimated from

$$\log \zeta_{AB} = f_A \log \zeta_A + f_B \log \zeta_B \tag{5}$$

Substituting eq 1 into eq 5 and solving the resulting equation for D_{AB} with the aid of eq 3 lead to

$$\log D_{AB} = f_A \log D_A + f_B \log D_B + \alpha + \alpha_e \tag{6}$$

where

$$\alpha = \log\left[\frac{M_0^{AB}(M_A)^{f_A}(M_B)^{f_B}}{M_{AB}(M_0^{A})^{f_A}(M_0^{B})^{f_B}}\right] \tag{7}$$

$$\alpha_e = \log\left[\frac{(M^{AB}{}_e/M_{AB})}{(M^{A}{}_e/M_A)^{f_A}(M^{B}{}_e/M_B)^{f_B}}\right] \tag{8}$$

where the subscript 0 denotes monomer. When one of the homopolymers is the unentangled polymer, e.g., homopolymer A, eq 2 applies in place of eq 1 for homopolymer A and, therefore, eq 4 applies instead of eq 3. However, the same relationship (eq 6) holds with only α_e changed as follows:

$$\alpha_e = \log\left[\left(\frac{4M_e^{B}}{15}\right)^{f_A}\frac{(M_B)^{f_B}}{f_B^{\,2}M_{AB}}\right] \tag{9}$$

It should be noted here that there are a number of papers[15−20] on the diffusion based on the thermodynamic approach. In the approach, the thermodynamic interactions are often represented by χN, where χ is the interaction parameter and N is the degree of polymerization. The effect of N in our model is represented through the friction coefficients of the constituent homopolymers. The difference between ordered and disordered states is accounted for through the difference in the friction coefficient of the same polymer in different states. Near the order−disorder transition, the interaction parameter is usually quite small. Otherwise, there would be an interaction term in eq 5. Nevertheless, a limitation of the current model is that it is applicable to systems where the interaction parameter is small.

There are two parameters involved for predicting the self-diffusivity of the copolymers. These are α and α_e, which are not arbitrary but rather fixed by the proper-

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Table 1. Parameter Values for the Three Systems

figure	$10^{-4}M_{AB}$	f_A	M_e	α	α_e
1	2.3	0.4 (PS)	$M_e^{PI} = 5400$	0	−0.08
2	2.12	0.42 (PS)	$M_e^{PI} = 5400$	−0.007	−0.016
3	5.01	0.5	$M_e^{PEP} = 1500$, $M_e^{PEE} = 11\,000$	−0.004	−0.104

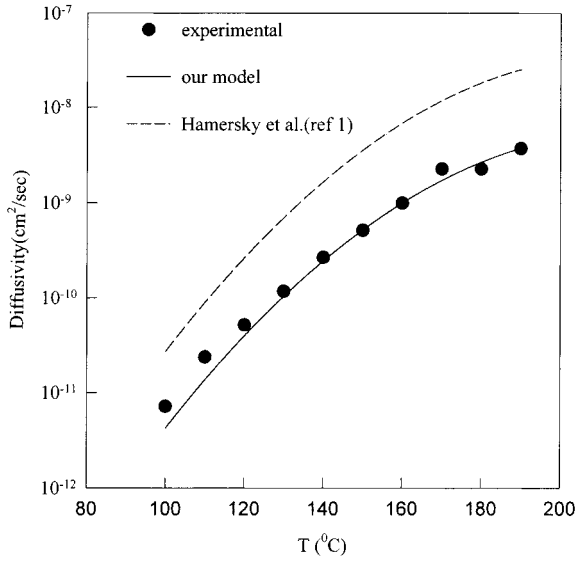

Figure 1. Diffusivity of the PS−PI block copolymer as a function of temperature.[1] The solid curve represents the prediction of our model; the dashed curve corresponds to Hamersky et al.'s method of predicting the copolymer diffusivity.

ties of the constituent homopolymers. The parameter α may be called an interaction factor; the parameter α_e may be called an entanglement factor by the nature of each parameter. The former represents a measure of interactions between the two homopolymers, whereas the latter results from chain entanglements.

Three sets of data are used to check the adequacy of the proposed model. Of these, two sets involve PS−PI (polystyrene−polyisoprene) block copolymers for which the PS block contributes little to the entanglements.[1,3] The other set has to do with PEP−PEE (poly(ethyleneepropylene)−poly(ethylethylene)) block copolymer for which both contribute to the entanglements. There are four parameter values needed to use the model for prediction along with the diffusivities of the constituent homopolymers. These are the composition of one of the constituent homopolymers f_A or f_B, the molecular weight of the block copolymer M_{AB}, and the entanglement molecular weights, M_e^B and M_e^A, of the constituent homopolymers that are usually available in handbooks, e.g., refs 13 and 14. The values of these parameters for the three systems are given in Table 1 along with the entanglement and interaction factors determined from these parameters.

Shown in Figure 1 is the self-diffusivity of the PS−PI copolymer as a function of temperature, compared with Hamersky et al.'s model[1] (dashed curve) and with our model prediction (solid line). The diffusivities of PS and PI homopolymers given by Hamersky et al. as a funcition of temperature at the same total degree of polymerization as the PS−PI copolymer were used for our prediction. Equation 9 was used for α_e since PS in the PS−PI specimens contributes little to the entanglements.[3,8]

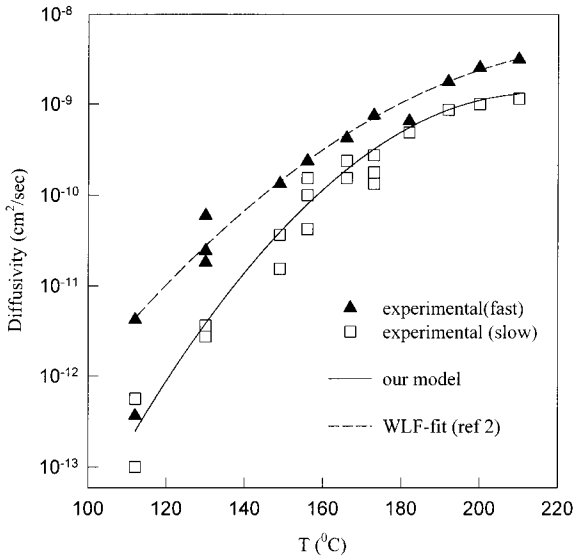

Figure 2. Diffusivity of the PS−PI copolymer as a function of temperature.[2] The solid curve corresponds to our model prediction, and the dashed curve represents fitting by the WLF equation.

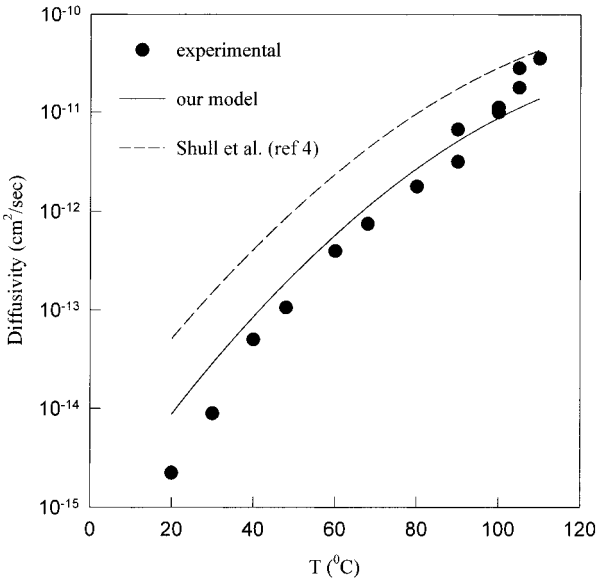

Figure 3. Diffusivity of the PEP−PEE block copolymer as a function of temperature.[4] The solid curve corresponds to our model prediction, and the dashed curve corresponds to Shull et al.'s result.

The data obtained by Ehlich et al.[2] are shown in Figure 2 along with their fit (dashed curve) and our model prediction (solid line) for a PS−PI block copolymer with a number-averaged molecular weight of 2.12×10^4 and a PS content of 42 wt %. The diffusivities of the constituent homopolymers are those given by Ehlich et al. The dashed curve represents the fit obtained by them by neglecting the contribution of PI and using the WLF equation for polystyrene for the copolymer with a change in the glass transition temperature. As shown in the figure, our prediction agrees well with the copolymer diffusivity determined from the slow components of the signal decay of the forced Rayleigh scattering intensity.

Shull et al.[4] obtained diffusivities of a PEP−PEE (poly(ethylenepropylene)−poly(ethylethylene)) block copolymer with a number-averaged molecular weight of 50 100. The PEP block contains 95% alternating eth-

ylene and propylene units with 5% randomly distributed polyisobutylene units. The PEE block is >98% poly(ethylethylene). Their prediction of the copolymer diffusivity is shown in Figure 3 (dashed curve). Also shown is our model prediction (solid curve). The diffusivities of PEP and PEE homopolymers with the same molecular weight as PEP−PEE copolymer were used in our prediction. The entanglement factor α_e was calculated from eq 8.

In summary, a model is proposed for predicting the self-diffusion coefficient in the order−disorder transition. The model does not involve any fitting parameter and yet predicts the diffusivity fairly accurately. The proposed model can predict the diffusivity involving unentangled copolymer, where the existing theories fail.

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