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Determination of Mutual Diffusion Coefficients at Nonsymmetric Polymer/Polymer Interfaces from Rheometry

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ABSTRACT: A novel method for determining the mutual diffusion coefficient using rheometry is presented. The method includes mathematical modeling for mutual diffusion at polymer/polymer interfaces and experimental determination of material parameters for the model. The model combines the concepts of the reptation theory and the fast-mode model applied to miscible dissimilar polymers brought into intimate contact in the molten state. The material parameters for the model are obtained from experiments in which the dynamic complex shear modulus, G^*, is measured in parallel-plate geometry under small amplitude of deformation as a function of time and frequency for a sandwich-like assembly. The technique was applied to the poly(methyl methacrylate) (PMMA)/poly(styrene acrylonitrile) (SAN) system, and the measured mutual diffusion coefficient was found to be in agreement with the values reported in the literature for the same system.

1. Introduction

While diffusion of small molecules in a homogeneous medium formed by small molecules is well understood through the simple Fickian model, the diffusion in polymer networks is nonobvious and still an open subject. Our present understanding of this kind of mass transport has much taken benefit from the original theoretical ideas of de Gennes[1,2] and from the later work of Doi−Edwards[3] on molecular dynamics. From the motion of a single chain in a dense entangled network, one can capture the physics behind many phenomena of polymer solutions and polymer melts both under thermodynamic equilibrium and under time-dependent conditions. Diffusion at symmetric and nonsymmetric interfaces is a particular problem that is related to such picture about molecular dynamics. For instance, when two miscible or partially miscible polymers are brought into intimate contact at temperatures above the glass transition temperature, the initial macroscopic interface gradually disappears, and the strength of adhesion increases with the time of contact. Such phenomenon has been attributed to the interlacing of the surface macromolecules followed by a mass transfer of polymer chains across the interface. Different mechanisms have been proposed to explain the diffusion phenomena at polymeric interfaces. Brochard et al.[4] have derived the diffusive slow-mode model assuming that the two polymers diffuse with equal and opposite fluxes. The model predicts that the mutual diffusion is dominated by the slower-moving component. Kramer et al.[5] considered unequal fluxes balanced by a net flux of vacancies across a moving interface and derived what is known as the fast-mode model. This diffusive−convective model assumes that the overall mobility is a linear function of the component mobilities, which results in a mutual diffusion process that is controlled by the fast-moving component toward which the macroscopic interface moves. Several experimental studies have been found to be in favor of the fast-mode model.[6] Later, Brochard and de Gennes[7] revised the earlier slow-mode model and developed an hybrid slow-fast model that recovers for short time and length scales the results of the fast-mode model, whereas for long distances of penetration, the diffusion process is controlled by the slow-mode motion. Brochard[8] also revised the initial theory and removed the initial assumption about the fixed network and retrieved the basic results of the fast-mode model and, to some extent, the prediction of the asymmetric broadening of the interface that has been observed in many experiments. This subject was a matter of interesting discussions in the 1980s between the group of Cornell University and the group of de Gennes (College de France), but this debate is out of the scope of this paper.

Several spectroscopic techniques have been widely used to probe the mutual diffusion at polymer/polymer interfaces. The most popular ones include forward recoil spectrometry,[9] X-ray microanalysis in scanning electron microscopy,[10] secondary ion mass spectroscopy,[11] transmission FTIR spectroscopy,[12] dynamic light scattering,[13] neutron scattering,[14,15] pulsed field gradient NMR spectroscopy,[16] and Rutherford backscattering spectrometry.[17] These techniques require however different spectroscopic absorbencies for the components, and in some cases they require a labeling with a heavy element that may slow down the mass transport process.[18] Moreover, these techniques are conducted under quiescent conditions, and thus they do not represent some of the diffusion problems that occur in the presence of flow, such as the generation of weld lines during multigate injection molding or coextrusion processes, in which the diffusion process is superimposed to flow.

In this work we have developed a novel experimental technique and a theoretical background permitting for the first time to probe both self-and mutual diffusion at both symmetric and nonsymmetric polymer/polymer interfaces. The technique does not require any labeling, and the spirit here is based on the coupling between flow and mass transport. If the flow is of small amplitude of deformation, we have a semicoupling that allows probing pure Brownian motion and determing self-diffusion and mutual diffusion coefficients of symmetric

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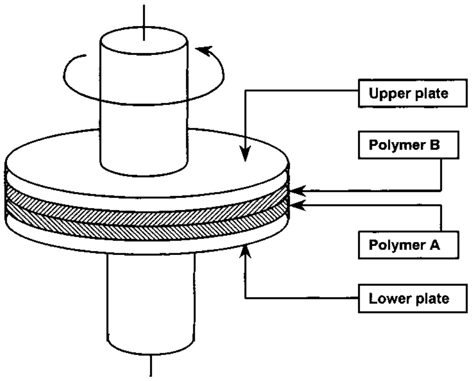

Figure 1. Sample setup for rheological testing.

and nonsymmetric polymer pairs. In our previous studies[19−21] we have shown that small-amplitude oscillatory rheometry may be a useful tool for probing the diffusion at symmetric polymer/polymer interfaces. The technique was applied on a polystyrene/polystyrene system, and the obtained self-diffusion coefficient was found to be in the range of the values reported in the literature. However, in our previous work we were limited to symmetric surfaces, and because of the absence of the theory in this field (diffusion-flow coupling), we were unable to extend our approach to the most important practical case of nonsymmetric systems. In the present work, we overcame the limitation by carrying out a new approach for modeling that gives us more insight into the diffusion process of unlike macromolecules. In this paper we restrict however our analysis to small amplitude of deformations (linear viscoelasticity), and we treat only the semicoupling case.

2. Experimental Section

2.1. Materials. The poly(methyl methacrylate) (PMMA) was supplied by Atohaas Americas Inc., and poly(styrene acrylonitrile)-29 (SAN-29, containing 29 wt % of acrylonitrile) was supplied by Bayer Corporation. The weight-average molecular weight M_w and polymolecularity index were 131 700 and 1.3 for the PMMA and 109 700 and 1.58 for the SAN29, respectively, as measured by the gel permeation chromatography (GPC) system (Dawn DSP, Waters Associates) with tetrahydrofuran as the solvent and μStyragel columns with 10^6, 10^5, and 10^3 Å pore sizes and 1 mL/min flow rate. The glass transition temperatures (T_g) measured by differential scanning calorimetery (DSC, Mettler toledo star system) were 107 and 104 °C for PMMA and SAN-29, respectively.

2.2. Sample Preparation and Viscoelastic Measurements. The experimental technique consists of measuring the dynamic moduli of a PMMA/SAN sandwich-like assembly as a function of time of welding at a given frequency (see sample setup shown in Figure 1). The samples for rheological testing were prepared by compression molding at 200 °C in the form of 25 mm diameter disks using a homemade mold with polished plate surfaces (mirror quality surfaces). The samples were then annealed at 85 °C under vacuum for 1 week to remove eventual surface contamination and to allow relaxation of oriented chains at the surface due to compression. The sandwich samples were prepared by bringing two round disks with smooth surfaces into intimate contact and placing them into the oven under vacuum at 120 °C for different welding times.

In our experiments, the more viscous polymer (PMMA) was put at the bottom, while the low viscous one (SAN) was mounted on the top. This avoids the flattening of the low viscous component during the experiments. The reverse configuration was also tried, but the results were not accurate due to the additional compression introduced by the upper sample. This also causes the flow of the low viscous polymer out from the parallel plates. Depending on the degree of miscibility of A/B polymer system, the number of layers in the sandwich can be also increased to increase the contribution of the interface/interphase. The complex shear modulus, G^*, of the sandwich was then measured as a function of time after 20 min of thermal equilibrium on a CVO-Bohlin controlled stress rheometer. More details about sample preparation and experimental procedure can be found in our previous work.[21]

2.3. Determination of Concentration Profile. Two physical situations should be distinguished: (i) the two polymer melts have quite identical viscosity; (ii) one of the components (the upper sample) is less viscous than the one put at the bottom. In the first case, both of the two components contribute to the overall rheological properties measured at the initial time, unless the two components are not well molten, and in this case the initial rheological properties reflect rather the slippage at the interface. In the second case (which is our case), the initial rheological properties of the sandwich-type assembly are mainly controlled by the properties of the less viscous polymer (upper sample)—due to its high viscosity, the lower sample belongs somehow to the plate of the rheometer. In both cases, as the diffusion proceeds, the two components interpenetrate and the initial sharp interface disappears, and it is gradually replaced by a diffuse interphase that thickens with the contact time. This interphase can be considered as a blend for which the composition varies with the time due to the difference in self-diffusion coefficients of the two components. Any increase in G^* with respect to the measured initial value is only due to the diffusion and the thickening of the interphase that now involves both the low and the high viscous components. Thus, only the relative variation of G^* with respect to the initial value is needed to determine the mutual diffusion coefficient. This relative value of G^* is expressed through an adequate choice of composition at the interphase (normalization procedure). The composition of the effective blend was determined as follows: First, a calibration curve was obtained by measuring the viscosity or G^* of the PMMA/SAN blends with various compositions ranging from 90/10 to 10/90 by a step of 10. Then the viscosity or G^* of the sandwich-type assembly was measured and compared to those of the blends. After normalization, as will be described later, the volume fraction of PMMA in the effective blend at the interphase was then obtained from the calibration curve.

3. Theory

In our previous work,[19−22] we have illustrated in details the direct semicoupling between diffusion at the polymer/polymer interfaces and viscoelastic properties. For the sake of clarity, we recall here the basic concept of our approach. When a single chain is put at a given interface that is continuously deformed, the diffusion process due to Brownian motion (the density of chains that may cross the interface) will be affected by the conditions of the flow (the magnitude of stresses and strains involved). Conversely, the rheological properties at such interface vary in time as a consequence of the diffusion process. Thus, there is a direct coupling between the flow and the mass transport at such interface. If, however, the applied stresses and strains are of small amplitude, the diffusion process is not affected by the flow, and in this particular situation the variation of the rheological material functions can be used to follow the diffusion process in time. This is the case of small-amplitude oscillatory shear measurements carried out on a multilayer sandwich-type assembly. From the measurement of the dynamic shear viscosity or dynamic complex shear modulus with time, one can determine the diffusion coefficient. In our previous work,[21,22] we have shown that such a technique is adequate for measuring with reasonable accuracy the diffusion coefficients for both symmetric and nonsym-

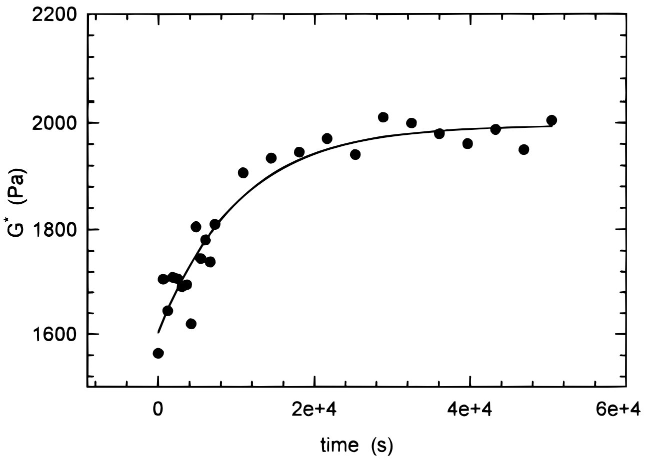

Figure 2. Complex modulus $G^*(\omega,t_h)$ versus welding time for a sandwich-like sample of PMMA/SAN at given frequency 6.0 × 10^{-7} rad/s ($<1/\tau_{\mathrm{rep,b}}$) and temperature 120 °C.

metric systems. In the case of nonsymmetric systems such as PS/PVME, we have shown by both ATR-FTIR (attenuated total reflection infrared spectroscopy) and rheometry that as the diffusion proceeds, the interface gradually thickens with the contact time. After a certain time, the two-layer system becomes a three-layer system with a central layer (the interphase) that can be considered as a blend of the two components with a given proportion of two polymers in contact and with its own viscosity and thickness. Using the three-layer model, we have particularly shown that the diffusion process cannot be described by a simple Fickian model, and a large contribution of case II diffusion was necessary to take into account for the nonsymmetric broadening of the interface.[22]

In the present paper, a different approach is used, and the nonsymmetric broadening of the interface is described following the physical insight given by the fast-mode model.

The typical results of G^* evolution with time at the interface of PMMA/SAN are shown in Figure 2. Clearly, G^* first increases monotonically and then reaches, within experimental errors, a steady-state plateau for long times of welding. The increase in G^* is a signature of the diffusion processes across the interface. As the mass transport proceeds, the initial weak interface strengthens with time due to the interpenetration of polymer chains that are continuously delivered by the polymer bulk reservoirs of the two sides of the interface. The question now is how to relate this rheological macroscopic information to the diffusion process that occurs at microscopic level—in other words, how to convert the measured G^* to a mutual diffusion coefficient that describes the kinetic of mass transport across the SAN and PMMA interface.

To solve the problem, we use the central equation of linear viscoelasticity given by Boltzmann's integral form

$$\tau(t) = \int_{-\infty}^{t} G(t-t')\,\dot{\gamma}(t')\,\mathrm{d}t' \qquad (1)$$

which stipulates that the stress measured at the time t is function of the whole rate of deformation history experienced by the sample at anterior times t', the information about the past history being contained in the relaxation modulus $G(t-t')$ or in what is known as the memory function $m(t-t') = \partial G(t-t')/\partial t'$. Under small-amplitude oscillatory shear flow, eq 1 gives the complex shear modulus

$$G^*(\omega) = i\omega\int_{0}^{\infty} G(t)\mathrm{e}^{-i\omega t}\,\mathrm{d}t \qquad (2)$$

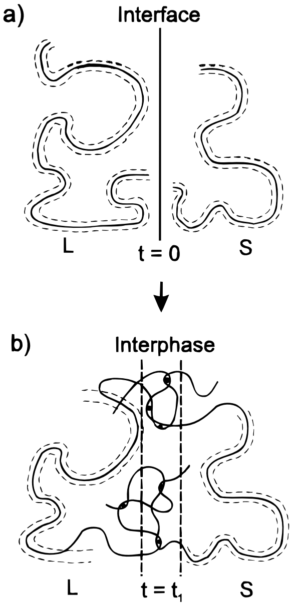

Figure 3. Schematic diagram of the mutual diffusion couple consisting of long (L) and short (S) chain molecules intimately contacted. (a) The initial case and (b) the situation after certain time t_1. Only a single chain for each polymer diffusing by the reptation mechanism is shown for clarity.

From the reptation theory we have[1,3]

$$G(t) = G_N^0 \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left(\frac{-(2n+1)^2\pi^2 k_{\mathrm{B}} T e^2 t}{\xi N^3 b^4}\right) \qquad (3)$$

where G_N^0 is the plateau modulus, N is the number of repeat units, b is the effective bond length, and e is the mesh size of the network.

To relate the results of eqs 1 and 2 to the diffusion process, we use the concept of irreversible thermodynamics. The physical situation of interest is pictured in Figure 3. Consider free long chains (L, say here PMMA) put, at time $t = 0$, into intimate contact with short chains (S, say here SAN); both have dimensions larger than the critical dimension of entanglement ($M > M_e$). After a certain time t_1, the two chains invade the interface mainly by reptation and entangle within a macroscopic interphase. For simplicity purposes, we assume that the segments of the two polymer chains have identical mobilities,[4,23] and we ignore the local reflection at the interface, which is not essential for the analysis considered here.[24] For the case of two components diffusing with unequal finite fluxes and for zero chemical potential of vacancies (tubes) in molten state, the fast-mode model expresses the mutual coefficient as[5]

$$D_{\mathrm{m}} = \Omega k_{\mathrm{B}} T\left(\frac{1-\phi}{\phi}\Lambda_{\mathrm{L}} + \frac{\phi}{1-\phi}\Lambda_{\mathrm{S}}\right)\left(\frac{1-\phi}{N_{\mathrm{L}}} + \frac{\phi}{N_{\mathrm{S}}} - 2\chi\phi(1-\phi) + 2\frac{\partial\chi}{\partial\phi}\phi(1-\phi)(1-2\phi) + \frac{\partial^2\chi}{\partial\phi^2}\phi^2(1-\phi)^2\right) \qquad (4)$$

where D_m is the mutual diffusion coefficient, Ω is the volume of quasi-lattice site assumed to be the same for both L and S molecules, k_BT is the temperature expressed in energy units, ϕ is the volume fraction of L chain molecules, Λ_L, Λ_S, N_L, and N_S are the Onsager coefficients and the numbers of repeat units of L and S, respectively, and χ is the Flory–Huggins interaction parameter which is considered here to be dependent on composition.

For $M > M_e$, the Onsager coefficients Λ_L and Λ_S can be expressed as functions of polymer segmental mobilities B_L and B_S by

$$\Lambda_L = B_{0,L}\frac{N_b^e\phi}{N_L\Omega} \tag{5}$$

$$\Lambda_S = B_{0,S}\frac{N_b^e(1-\phi)}{N_S\Omega} \tag{6}$$

where $B_{0,L}$ and $B_{0,S}$ are the monomer mobilities of L and S, respectively. As the diffusion proceeds, the initially sharp interface is replaced by a diffuse interphase that can be conceived a macroscopic equivalent blend of L and S molecules (as pictured in Figure 3). The overall time evolution of the macroscopic viscoelastic properties of the sandwich is essentially governed by the time evolution of such interphase. We then replace N_L^e and N_S^e in the expressions of Λ_L and Λ_S by the average number of repeat units between entanglement, N_b^e, for the interphase considered as a blend with ϕ fraction of L[25]

$$\frac{1}{(M_{0,b}N_b^e)^{1/2}} = \frac{\phi}{(M_{0,L}N_L^e)^{1/2}} + \frac{1-\phi}{(M_{0,S}N_S^e)^{1/2}} \tag{7}$$

where $M_{0,L}$, $M_{0,S}$, and $M_{0,b}$ are the monomer molecular weights of L, S, and of the blend in the interphase, respectively. N_L^e and N_S^e are the numbers of segments per entanglement length of L and S, respectively. Here $M_{0,b}$ is assumed to be arithmetic mean of $M_{0,L}$ and $M_{0,S}$.

By omitting the higher terms in eq 3 and substituting into eq 2, we obtain the expression for the monomer friction coefficient, $\xi_b = 1/B_b$, of the equivalent macroscopic miscible blend as a function of the dynamic complex shear modulus, $G^*(\omega)$,

$$\xi_b = \frac{\pi^2 k_B e_b^2 T}{N_b^3 b_b^4}\frac{1}{K^{1/2}} \tag{8}$$

where subscript b stands for the blend in the interphase and K is related to the complex shear modulus by

$$K = \omega^2\left[\left(\frac{8G_N^0}{\pi^2 G^*(\omega)}\right)^2 - 1\right] \tag{9}$$

Considering the average number of repeat units in the interphase

$$N_b = \frac{1}{M_{0,b}}[\phi M_L + (1-\phi)M_S] \tag{10}$$

and substituting eqs 8 and 9 and the expressions of Λ_L and Λ_S into eq 4 gives

$$D_m = \frac{N_b{}^e N_b^3 b_b^4 K^{1/2}}{\pi^2 e_b^2}\left(\frac{1-\phi}{N_L} + \frac{\phi}{N_S}\right)\left(\frac{1-\phi}{N_L} + \frac{\phi}{N_S} - 2\chi\phi(1-\phi) + 2\frac{\partial\chi}{\partial\phi}\phi(1-\phi)(1-2\phi) + \frac{\partial^2\chi}{\partial\phi^2}\phi^2(1-\phi)^2\right) \tag{11}$$

The above equation explicitly makes a direct coupling between the mutual diffusion coefficient (mass transport speed) and the linear viscoelastic material function, G^*.

4. Results and Discussion

Since the rheological material functions of the sandwich vary with the evolution of the interphase in time, $G^*(\omega)$ given by eq 9 should be replaced by a function of frequency and welding time $G^*(\omega,t_h)$. In the linear viscoelastic regime, the increment in $G^*(\omega,t_h)$ with the welding time only originates from the diffusion of chains in the interphase. This leads to an apparent diffusion coefficient. However, for long times of contact, $G^*(\omega,t_h)$ reaches an equilibrium constant value, $G^*_e(\omega)$, and thus the function K in eq 9 can be rewritten as

$$K = \omega^2\left[\left(\frac{8G_N^0}{\pi^2 G_e^*(\omega)}\right)^2 - 1\right] \tag{12}$$

The mutual diffusion coefficient given by expression 11 with K of eq 12 is a frequency-dependent function, which is a priori meaningless since it is a property of the material. As discussed in our previous work on self-diffusion process,[21] the dependency on frequency reveals that the local diffusion depends on the relaxation time of the different moving chains. Since a spectrum of relaxation can be obtained from G^*, a spectrum of diffusion coefficients can be also, in principle, obtained from the frequency-dependent G^*. At high frequencies, the measured dynamic modulus reflects the relaxation of short chains, whereas at low frequencies, $\omega < 1/\tau_{rep}$ (terminal zone), the measured material functions describe the dynamics of all chains, shorter and longer, but from a kinematics viewpoint the relaxation mechanism is dominated by the longer ones. Thus, in this frequency zone, one can define a mean value of mutual diffusion coefficient for a given polymer pair. This is mainly obtained in the region $\omega\tau_{rep} \ll 1$, where G^* is given by

$$G^*(\omega) \approx \sum_{n=0}^{\infty}\frac{8G_N^0}{(2n+1)^2\pi^2}\sum_{n=0}^{\infty}\frac{\omega\xi N^3 b^4}{(2n+1)^2\pi^2 k_B e^2 T} \tag{13}$$

Substituting eq 13 (taking the leading term $n = 0$) into eq 12 for the reptation model ($\omega\tau_{rep} \ll 1$) leads to the following expression

$$K = \left(\frac{\pi^2 k_B e^2 T}{\xi N^3 b^4}\right) = \frac{1}{\lambda^2} \tag{14}$$

where λ is a characteristic time. The mutual diffusion coefficient is then given by

$$D_{\mathrm{m}} = \frac{N_{\mathrm{b}}^{\mathrm{e}} N_{\mathrm{b}}^{3} b_{\mathrm{b}}^{4}}{\pi^{2} e_{\mathrm{b}}^{2} \lambda}\left(\frac{1-\phi}{N_{\mathrm{L}}} + \frac{\phi}{N_{\mathrm{S}}}\right)\left[\frac{1-\phi}{N_{\mathrm{L}}} + \frac{\phi}{N_{\mathrm{S}}} - 2\chi\phi(1-\phi) + 2\frac{\partial\chi}{\partial\phi}\phi(1-\phi)(1-2\phi) + \frac{\partial^{2}\chi}{\partial\phi^{2}}\phi^{2}(1-\phi)^{2}\right] \tag{15}$$

The above equation was used here to convert the terminal zone rheological material functions to mutual diffusion coefficient of the PMMA/SAN system.

The concentration, ϕ, of PMMA in the interphase was determined from a comparison of G^* of PMMA/SAN sandwich with a calibration curve established by measuring G^* of PMMA/SAN blends with various compositions ranging from 10/90 to 90/10 by a step of 10. The experimental results showed that the dynamic complex shear modulus of the sandwich sample at $t_{\mathrm{h}} = 0$ min was equal to that of a blend of a composition 50/50 (volume fraction of PMMA, $\phi_{\mathrm{PMMA}} = 0.5$). With the increase of the welding time, the complex shear modulus of the sandwich increases and then reaches, for long times of welding and within experimental errors, a steady-state equilibrium plateau characterized by $\phi_{\mathrm{PMMA}} = 0.7$. It should be, however, noted that at the initial time of diffusion, $t_{\mathrm{h}} = 0$, the volume fraction of PMMA in the equivalent blend should be close to zero, rather than 0.5. This is because the measured G^* reflects the contribution of the whole components of the sandwich that involves the effects of the bulks of SAN and PMMA. Here we are only interested in the relative increase of G^* due to the interphase with respect to the initial value. To account for such relative increase, we normalize the concentration profile of PMMA in the equivalent macroscopic blend by

$$\phi = \frac{C(t) - C_0}{C_1 - C_0} \tag{16}$$

where $C(t)$ and C_0 are the volume fraction of PMMA in the sandwich at the welding times t_{h} and zero ($C_0 = 0.5$ in this case), respectively, and $C_1 = 1$. Figure 4 shows the variation of the volume fraction of PMMA with the welding time. The raw data have been normalized by eq 16, thereby removing the influence of polymer bulks in the sandwich assembly. In Figure 4, ϕ increases rapidly for a short lapse of time and then reaches, within experimental errors, a steady value of about 0.4. It is worth to mention that the equivalent equilibrium blend is rich in SAN phase (60%), the faster moving component, which is in accord with the prediction of the fast-mode theory.[5]

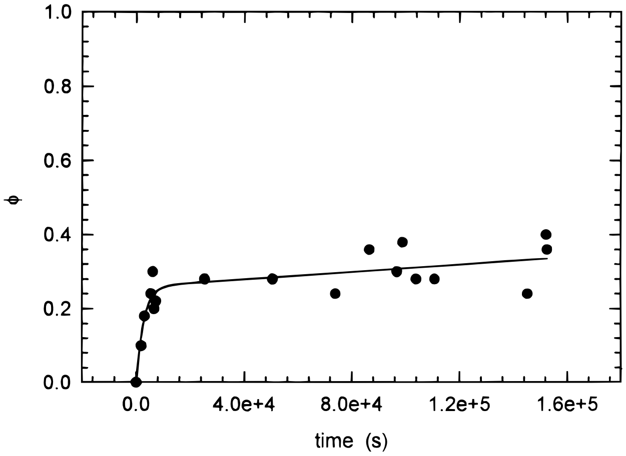

Figure 4. Time evolution of the concentration profile for the PMMA/SAN couple at 120 °C. The points are experimental data. The line represents a least-squares fit to the experimental data.

The phenomenon of rapid increase of ϕ at early diffusion times has also been reported in the literature.[26−29] Sivaniah et al.[26] investigated the interdiffusion in polystyrene using neutron reflectometry to follow the relaxation of the composition modulation in an isotopic polymer multilayer. They found that an abrupt increase in the interfacial width took place at early diffusion stage. Geoghegan et al.[27] measured the interdiffusion coefficient as a function of concentration and temperature for two blends of deuterated polystyrene and poly(α-methylstyrene), and their results clearly showed that the volume fraction of deuterated polystyrene has a steep increase at very small depth. Jones et al.[28,29] studied the spinodal decomposition of mixtures of poly(ethylenepropylene) and perdeuterated poly(ethylenepropylene) near the surface using forward−recoil spectrometry and measured the segment density profile near the interface of end-functionalized deuterated polystyrene and hydrogenated polystyrene. Both cases showed that the interfacial width rapidly increases at very short healing times. Shearmur et al.[30] studied the interdiffusion of deuterated and protonated PMMA using nuclear reaction analysis and showed that the volume fraction of deuterated PMMA rapidly increased at small depths, and the position of the interface moved toward the lower molecular weight component.

Another parameter we should determine for calculating the mutual diffusion is the $G^*(\omega,t_{\mathrm{h}})$ at low frequencies $\omega < 1/\tau_{\mathrm{rep}}$. In this frequency region, the chain dynamics is governed by reptation. The use of the $G^*(\omega,t_{\mathrm{h}})$ in this frequency range will cancel the frequency as shown in eq 15 and will amount to an average mutual diffusion coefficient that represents the contribution of all chains with different relaxation times. The data in the low-frequency region can be obtained by time−temperature principle by shifting $G^*(\omega_1,t_{\mathrm{h}})$ at $\omega_1 > \tau_{\mathrm{R0}}$, τ_{R0} being the Rouse time denoting the onset of the effect of tube constraints, to the $G^*(\omega_2,t_{\mathrm{h}})$ at $\omega_2 < \tau_{\mathrm{rep}}$. The data at temperature T can be obtained from those at temperature T_0 by a shift on the frequency scale

$$G^*(\omega,T) = \frac{T\rho}{T_0\rho_0} G^*(\omega \alpha_{T\to T_0}, T_0) \tag{17}$$

where $\alpha_{T\to T_0}$ is the shift factor.

From Doi and Edwards theory,[3] we have

$$G^* = G_{\mathrm{N}}^{0}(\pi\omega\tau_{\mathrm{R0}})^{1/2} \qquad \text{for } \omega \geq 1/\tau_{\mathrm{R0}}$$

and

$$G^* = \sum_{n=0}^{\infty} \frac{8G_N^0}{(2n+1)^2\pi^2} \frac{1}{1 + [\omega\tau_{\mathrm{rep}}/(2n+1)^2]^2} \times \sum_{n=0}^{\infty} \frac{\omega\tau_{\mathrm{rep}}}{(2n+1)^2}\left[\left(\frac{\omega\tau_{\mathrm{rep}}}{(2n+1)^2}\right)^2 + 1\right]^{1/2} \qquad \text{for } \omega < 1/\tau_{\mathrm{rep}} \tag{18}$$

Since $G^*(\omega_1,T_1,t_{\mathrm{h}})$ and $G^*(\omega_2,T_2,t_{\mathrm{h}})$ could be described by eq 18 at $\omega > \tau_{\mathrm{R0}}$ and $\omega < \tau_{\mathrm{rep}}$, respectively, the

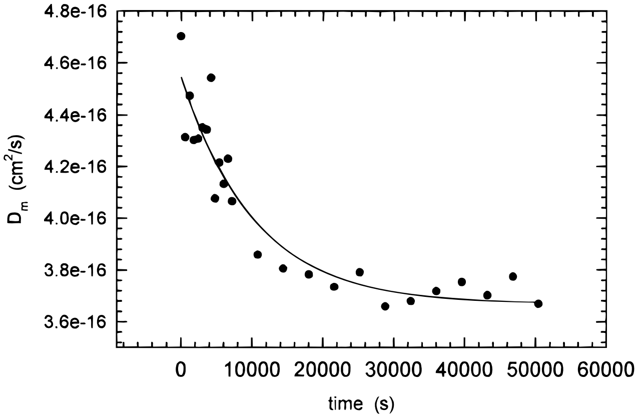

Figure 5. Apparent mutual diffusion coefficients as a function of welding time for PMMA/SAN sandwich-like sample at 120 °C. The points are experimental data. The line represents a least-squares fit to the experimental data.

following expression is obtained by taking the leading term ($n = 0$) for eq 18

$$G^*(\omega_2,T_2,t_h) = G^*(\omega_1,T_1,t_h) \times \frac{\rho_2 T_2}{\rho_1 T_1}\frac{8\omega_2 \alpha_{T_2\to T_0}\tau_{rep}}{[1+(\omega_2\alpha_{T_2\to T_0}\tau_{rep})^2]^{1/2}(\pi^5\omega_1\alpha_{T_1\to T_0}\tau_{R0})^{1/2}} \qquad (19)$$

In the case of $T_2 = T_1$, the above equation allows to convert the data of G^* from (ω_1, t_h) to (ω_2, t_h) at the same temperature. Equation 19 was found to nicely describe the results of PMMA/SAN system by comparing the calculated $G^*(\omega<\tau_{rep},t_h)$ to that obtained at low frequencies by superimposing the data obtained in the temperature range 120−230 °C at reference temperature of 120 °C. With the value of G^* in the low-frequency region is then possible to determine the average mutual diffusion coefficient provided that Flory−Huggins interaction parameter, χ, is known. For our experiments, χ was determined from the following dependencies on temperature and AN content in SAN: $\chi = 0.0202 + 3.06/T$[31] and $\chi = -0.0008 - 0.0209\phi$.[32−35] Figure 5 shows the variation of the calculated D_m with the welding time. This average apparent mutual diffusion coefficient varies in the same manner as does G^* but in the inverse sense; decreasing rapidly before reaching an equilibrium value, D_e, at long times. The time dependence of the apparent mutual diffusion coefficient could be explained in terms of Doi and Edwards theory[3] in the same manner as for the self-diffusion coefficient.[21] Apparent self-diffusion coefficient, D_a, usually varies as $t^{-\alpha}$ for $t < \tau_{rep}$ and reaches an steady-state value for $t \geq \tau_{rep}$.

To compare our results to the data reported in the literature, we shifted all data to the conditions of our experiments using the relation[36] $D \propto M^{-1}$ and WLF equation[37]

$$\log\left(\frac{D_0 T}{D T_0}\right) = \frac{-C_1^0(T - T_0)}{C_2^0 + T - T_0} \qquad (20)$$

with $C_1^0 = 9.97$ and $C_2^0 = 88.23$ as obtained from the time−temperature superposition of PMMA/SAN viscoelastic properties in the temperature range 120−230 °C at reference temperature 120 °C. Kim et al.[35] and Yukioka et al.[38,39] have measured the mutual diffusion coefficient for PMMA/SAN using forward recoil spectrometry and ellipsometry, respectively. Kim et al. reported a value of 1.6×10^{-13} cm^2/s at temperature 187 °C for a blend with 40 wt % in PMMA with molecular weights of SAN and PMMA of 17 600 and 31 700, respectively, while Yukioka et al. found a value of about 7×10^{-16} cm^2/s at 130 °C for the PMMA/SAN system with 25 wt % of AN in SAN. Using the results of Kim et al. for the variation of D_m with weight percent of AN in SAN and shifting the data with respect to molecular weight and temperature, we obtain 1.1×10^{-17} cm^2/s for the results of Kim et al. and 1×10^{-16} cm^2/s for the results of Yukioka et al., respectively. Our results ($D_m \cong 3.7 \times 10^{-16}$ cm^2/s) are about 1 order of magnitude larger than those of Kim et al. and are in good agreement with the results of Yukioka et al.

5. Concluding Remarks

The novel technique developed in this work makes for the first time a direct link between mass transfer at similar and dissimilar polymer/polymer surfaces and linear viscoelastic material functions. It allows the determination of both self-diffusion and mutual diffusion coefficients that, unlike the classical techniques, does not require any labeling or specific absorbencies, as it is the case for most of spectroscopic techniques. Different scenarios can be imagined and studied by means of this technique. This may consist, for instance, of A/A and A/B polymers, A/B surfaces with chemical reaction, sandwich of A/copolymer/B, cross-linked, and non-cross-linked surfaces and gels. Depending on the degree of miscibility of A/B polymer system, the number of layers may also be increased to increase the contribution of the effect of the interface/interphase. The concept, with some refining, may be also transposed to a nanoscale using surface force devices.

In this work, we have however ignored, at a first approximation, polymer polydispersity, and the analysis was only limited to a semicoupling between flow and diffusion in the sense that the small-amplitude flow does not perturb the dynamics of the chains during their excursion across the interface. A full coupling requires more insight into the theory to account for dual influence of diffusion and high deformation flows.

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