Macromol. Symp. ***158,*** *155–168 (2000)*

Mutual diffusion at Polystyrene/Poly(vinyl methyl ether) as measured by ATR-FTIR and rheometry.

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SUMMARY: Mutual diffusion at PS/PVME (polystyrene/polyvinyl methyl ether) interface both below and above the glass transition temperature, T_g, of polystyrene was probed by Attenuated total reflection (ATR) and rheometry techniques. The results were analyzed with a simple three layer model and a combination of Fickian and Case-II diffusion models. The mutual diffusion coefficients obtained by the two techniques are compared and the importance of Case-II diffusion is discussed.

Introduction

Diffusion at polymer/polymer interfaces is involved in several situations of practical interest such as polymer processing, polymer/polymer lamination, and film formation from latex dispersion and phase behavior in multiphase systems. Various spectroscopic techniques have been used to quantify the diffusion process and to measure the mutual diffusion coefficients at A/B miscible polymer interfaces. The polystyrene/polyvinyl methyl ether (PS/PVME) couple has been widely used as a model system to study the phase behavior from both thermodynamic and kinetic viewpoints. While the classical thermodynamics deals with equilibrium, kinetics gives information on the dynamics of mass transport; i.e. the diffusion process between two equilibrium states. A new approach associating equilibrium and nonequilibrium thermodynamic (irreversible thermodynamic) has been recently developed and applied to particular problems of microscopic and mesoscopic diffusion in polymer media$^{1)}$.

CCC 1022-1360/00/$ 17.50+.50/0

The diffusion across highly entangled polymer networks is very complex and its mechanism depends greatly on the size of the diffusing agent, on the interaction parameter between the diffusion agent and the polymer and on the physical state of the polymer matrix. The diffusion process of small molecules in a molten amorphous polymer matrix generally proceeds in a Fickian fashion with a front moving as $\sqrt{t}$, whereas in the glassy state and at the onset of the rubbery state, the diffusion is highly non-Fickian due to the additional stresses generated by the penetration of the small molecules (solvent) that swell the network. This process is known as the case-II diffusion and is associated with stretching of polymer segments between entanglements that modifies the whole relaxation mechanism of the polymer network2) (perturbation of the equilibrium between the rate of destruction and rate of creation of junctions). The case-II diffusion has also been observed at polymer/polymer interfaces where a fast moving component swells the slower one3). This behavior was observed in various systems including PS/PVME using spectroscopic techniques.

Recently we have developed a new technique and mathematical modeling allowing for the quantification of the diffusion process at polymer/polymer interfaces and the determination of both self-and mutual diffusion coefficients using rheological analysis4-5). The technique consists of measuring the dynamic complex shear modulus, G*, (and thus the complex shear viscosity) of A/B sandwich type structure under small-amplitude oscillatory shear measurements. Form the time evolution and the equilibrium values of G*, an apparent and a mean value of the diffusion coefficient were determined. The self-diffusion coefficient was determined via a model that was derived using the reptation frame6-7) while the model for the mutual diffusion coefficient was obtained using a combination between the reptation model and the fast-mode model8). The obtained values were found to be in reasonable agreement with the values reported in the literature for the same systems.

The aim of this paper is to verify whether a simple analysis based on Fickian and Case-II models is adequate for describing the diffusion at PS/PVME interface as probed by rheological technique. The results obtained from rheometry are compared to those obtained from Attenuated Total Reflection Infrared Spectroscopy (ATR-FTIR).

Experimental section

Products: The polymers used in this work are polystyrene (PS) purchased from Polymer Source (Montreal, Canada) and polyvinyl methyl ether (PVME) obtained from Scientific Polymer Products. The weight-average molecular weight, Mw, and the polydispersity index (PI) were determined by Gel permeation chromatography, GPC, using tetrahydrofuran (THF) and the glass transition temperature, T_g, was determined by means of Differential scanning calorimetry, DSC. The PS was a primary standard with Mw of 108 880, IP of 1.05 and a T_g of 102°C. The secondary standard PVME was obtained as a 50% aqueous solution. Water was removed from PVME by heating up above 30°C, which induces a phase separation and the collected PVME was then dried under vacuum for one week. PVME had Mw of 73 200, IP of 1.83 and T_g of -24°C.

ATR experiment: Interdiffusion experiments were carried out on a FTIR spectrometer with ATR accessories using a germanium crystal, Ge. The polystyrene film was cast on the Ge crystal with a spin coater from a 3wt% solution in toluene at 1000 rpm. The thickness and surface roughness of the PS film were measured with a profilometer. The PVME layer was obtained by spin coating directly on the PS film from a 10wt% solution in isobutanol at 1000 rpm and the PVME thickness (of 1.6 μm) was evaluated from the gain in weight of the glass plate. ATR-FTIR spectra were collected with 250 averaged scans and a resolution of 4 cm^{-1}. The concentration profile of PVME was determined by comparing the time evolution of the spectra with those of a calibration curve obtained on different blends of PS/PVME with concentration ranging from 05/95 to 95/05 by a step of 5%. More details about ATR-FTIR experiments can be found elsewhere9).

Rheometry experiments: PS samples for rheological experiments were prepared by compression molding at 200°C using well-cleaned and polished molds (mirror quality surfaces). More details about sample preparation and rheological testing can be found in our previous work4,5). To prepare a bilayer sandwich sample of PS/PVME, a transparent glass cylinder with two open ends having an inner diameter of 37 mm and a height of 20 mm, was put on the lower 40-mm plate of the rheometer. The PVME was placed inside the glass cylinder and the heating chamber of the rheometer was then closed and kept on heating at the experimental temperature for about 2 hours so that the PVME may spread to form a thin film (of 0.8 mm in thickness) on the lower plate inside the glass cylinder. At this temperature and for this period of time, PVME was found to be stable as previously verified thermogravimetric tests. PS disc of 0.8 mm in thickness with a smooth surface was brought onto the top surface of PVME film and was well aligned with the parallel upper plate of the rheometer. The evolution the sandwich viscosity with time was determined under linear small-amplitude oscillatory shear measurements at a fixed frequency using the ARES controlled strain rheometer from Rheometric Scientific.

Rheometry and ATR-FTIR measurements were conducted both below (85°C) and above (105°C) T_g of PS. In both cases, PS and PVME are miscible as verified by previous experiments on the phase behavior conducted on several blends by optical microscopy9).

Theoretical Background

ATR experiments:

Fickian model: Figure 1 shows the ATR interdiffusion sample set-up, with a PS layer of thickness δ_1 and a PVME layer of thickness δ_2. The diffusion is along the z-axis, which is perpendicular to the PS/PVME interface and takes its origin at the surface of the ATR crystal.

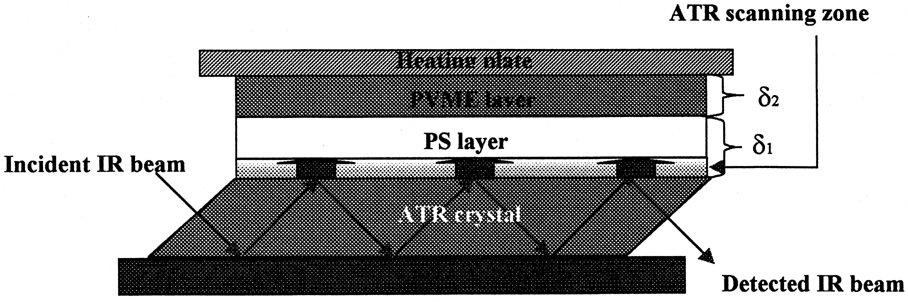


Fig. 1: ATR-FTIR interdiffusion sample set-up

The concentration profile given by Fick's law is

$$\frac{\partial C_{PS}}{\partial t} = \frac{\partial}{\partial z}\left(D_{ic}\frac{\partial C_{PS}}{\partial z}\right) \qquad (1)$$

in which the diffusion is proceeding along the z-axis at a constant rate. Here C_{PS} is the molar concentration of PS, D_{ic} is the interdiffusion coefficient, z is the distance from the PS/crystal interface and t is the interdiffusion time. Initial and boundary conditions for this system are given by

$$C_{PS} = C_0 \quad \text{for} \quad 0 \leq z \leq \delta_1 \quad \text{at} \quad t = 0 \qquad (2a)$$

$$C_{PS} = 0 \quad \text{for} \quad \delta_1 < z \leq \delta_1 + \delta_2 \quad \text{at} \quad t = 0 \qquad (2b)$$

$\delta C_{PS} / \delta z = 0$ for $z = 0$ at $t > 0$ (2c)

$\delta C_{PS} / \delta z = 0$ for $z = \delta_1 + \delta_2$ at $t > 0$ (2d)

where C_0 is the initial concentration of PS. Taking into account the conditions imposed by Equation 2, the solution of Equation 1 is given by

$$C_{PS}(z,t) = \frac{C_0}{2} \sum_{n=-\infty}^{n=\infty} \left(erf\left(\frac{\delta_1 + 2n(\delta_1 + \delta_2) - z}{2(D_{ic}t)^{1/2}} \right) + erf\left(\frac{\delta_1 + 2n(\delta_1 + \delta_2) + z}{2(D_{ic}t)^{1/2}} \right) \right) \tag{3}$$

The spatial and the temporal variation of PVME concentration is given by

$$C_{PV}(z,t) = C_0 - C_{PS}(z,t) \tag{4}$$

For comparing model predictions to experimental results, the exponential decrease in IR intensity has to be considered. The concentration of PVME at distance z from the crystal surface was multiplied by its corresponding relative intensity and integrated over the penetration depth of the IR radiation inside the polymer layer for each interdiffusion time. The cumulative concentration of PVME inside the penetration depth is given by the following Equation:

$$Q_{PV,F}(t) = \frac{\int_0^\infty C_{PV}(z,t) I_{rel}(z) dz}{\int_0^\infty I_{rel}(z) dz} \tag{5}$$

Case-II model. In its general form, Case-II diffusion model involves the modification of Fick's law by the introduction of additional stresses due to the penetration of the solvent (fast moving component) that swells the polymer network and stretches the chain segments between entanglements. One of the essential physical resultsof this modification is that the broadening of the interface is non-symmetric and the diffusion process is independent of the concentration profile, but depends on the relaxation of the polymer matrix. During the diffusion of the faster diffusing component (PVME), into the slower one (PS), the original interface moves as

$$z_{II} = \delta_1 - k_{II}t \tag{6}$$

When PVME diffuses in the PS with a relaxation constant k_{II}, an equilibrium composition of PS/PVME is formed behind the PVME front. The concentration profile is then given by:

$$C_{PV} = C_{PV}^{eq} \qquad z_{II} \leq z < \delta_1 \qquad t > 0 \tag{7a}$$

$$C_{PV} = 0 \qquad 0 \leq z < z_{II} \qquad t > 0 \tag{7b}$$

The equilibrium concentration C_{PV}^{eq} is given by

$$C_{PV}^{eq} = \frac{\delta_2 \rho_2 M_2^o}{\delta_2 \rho_2 M_2^o + \delta_1 \rho_1 M_1^o} \tag{8}$$

$M_1°$ and $M_2°$ are the monomer molecular weight of the PS and the PVME respectively, ρ_1 and ρ_2 are the densities of PS and PVME and δ_1 and δ_2 are the thickness of PS and PVME films, respectively. The cumulative concentration inside the penetration depth, d_p, is determined by replacing the concentration in Eq. 5 by the equilibrium concentration, which gives

$$Q_{PV,II}(t) = C_{PV}{}^{eq} \exp\left(\frac{-2(\delta_1 - k_{II}t)}{d_p} \right) \tag{9}$$

By using a linear combination of Fickian and Case-II diffusion for the PVME cumulative concentration, it is possible to take into account these two phenomena occurring simultaneously by

$$Q_{PVME}(t) = (1 - \phi_{II}) \frac{\int_0^\infty C_{PV}(z,t) I_{rel}(z) dz}{\int_0^\infty I_{rel}(z) dz} + \phi_{II} C_{PV}^{eq} \exp\left(\frac{-2(\delta_1 - k_{II}t)}{d_p} \right) \tag{10}$$

Rheometry: The situation of interest is pictured in Figure 2. At the initial state, the two-layer system can be characterized by$^{10)}$

$$\left(\frac{1}{\eta_s} \right)_0 = \frac{\phi_1}{\eta_1} + \frac{\phi_2}{\eta_2} \tag{11}$$

where ϕ_i and η_i are the volume fraction and the viscosity of the component i and η_s is the viscosity of the sandwich. As shown in Figure 2, the volume fraction ϕ_i is given by the ratio h_i/h. As the diffusion proceeds, 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 the volume fractions $\phi_1^{''}$ and $\phi_2^{''}$, ($\phi_1^{''}+\phi_2^{''}=1$). The viscosity of the sandwich at time *t* is then given by$^{10)}$

$$\left(\frac{1}{\eta_s} \right)_t = \frac{\phi_1^{'}}{\eta_1} + \frac{\phi_2^{'}}{\eta_2} + \frac{\phi_I^{'}}{\eta_I} = \frac{h_1^{'}/h}{\eta_1} + \frac{h_2^{'}/h}{\eta_2} + \frac{h_I^{'}/h}{\eta_I} \tag{12}$$

The viscosity of the interphase is given by a mean value

$$\eta_I = \phi_1\eta_1 + \phi_2\eta_2 \tag{13}$$

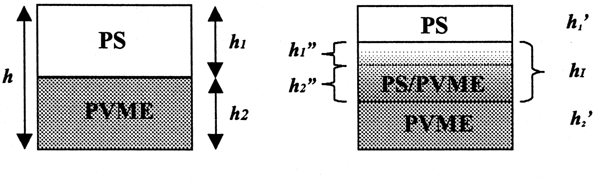
with

$$\begin{cases} \phi_1^{'} + \phi_2^{'} + \phi_I^{'} = 1 \\ \phi_1^{''} + \phi_2^{''} = h_1^{''}/h_I + h_2^{''}/h_I = 1 \\ h_i = h_i^{'} + h_i^{''} \quad i = 1,2 \end{cases}$$

From Equations11, 12 and 13, we derive the viscosity of the sandwich with at time t

$$\left(\frac{1}{\eta_s}\right)_t = \left(\frac{1}{\eta_s}\right)_0 + \left[\frac{1}{\phi_1^{''}(t)\eta_1 + (1-\phi_1^{''}(t))\eta_2} - \left(\frac{\phi_1^{''}}{\eta_1} + \frac{1-\phi_1^{''}}{\eta_2}\right)\right]\frac{2z(t)}{h} \tag{14}$$

The viscosity of the three-layer system depends on time through the dependency on time of the volume fraction, $\phi_1^{''}$, and the position of the interphase, z(t). The volume fraction can be calculated either from the Fickian model (Eq.3) or from the combination of Fickian model and Case-II model (Eq. 10).



At initial time *t₀*   At time *t*

Fig. 2: At initial time, the sandwich assembly is composed by two layers. During diffusion, an interphase with its own characteristics, viscosity and thickness, develops with the elapsed time.

Results and discussion

A typical example of the time evolution of the sandwich ATR spectra is shown in Figure 3. One band of PVME at 2820 cm^{-1} and two bands of PS at 2850 and 3025 cm^{-1} were used for quantitative analysis. The peaks were deconvoluted to convert the area under the three peaks to PS and PVME mole fractions using the calibration curve.

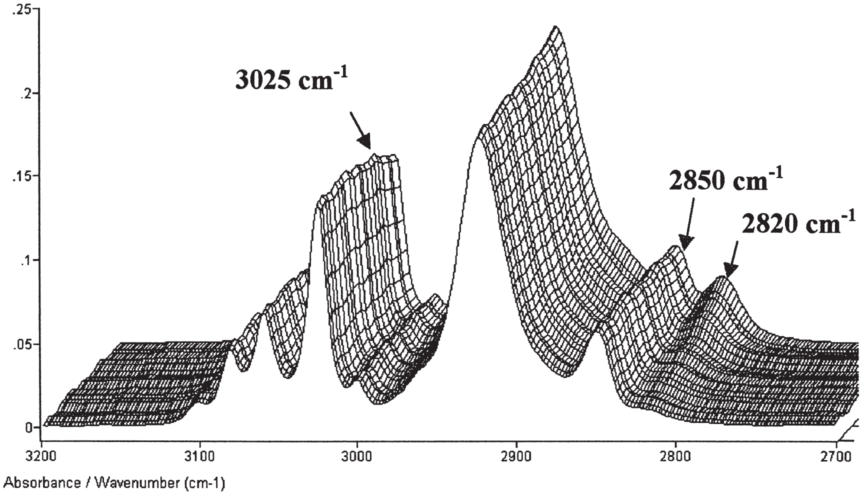


Fig. 3: Time evolution of ATR-FTIR spectra during the interdiffusion at the interface between PS and PVME. The indicated bands were used for quantitative treatment of the data.

The measured concentration profile of PVME across the interface at 85°C and 105°C is shown in Figure 4. At 105°C, which is above the T_g of PS, the diffusion process is fast and reaches equilibrium after only 3.5 hours, whereas at 85°C, which is 15°C below the T_g of PS, an induction time of 4 hours is needed before PVME is observed. The two curves were fitted by a combination of Fickian (Eq.3) and Case-II diffusion models (Eq. 10). At 85°C, the best fit was obtained by a combination of 79% of Fickian model with a mutual-diffusion coefficient of 3.4x10^{-14} cm^2/s and 21% of Case-II diffusion with a relaxation coefficient of 1.29x10^{-9}. At 105°C, the best fit was obtained with 90% of Fickian model with a mutual-diffusion coefficient of 9x10^{-13} cm^2/s and 10% of Case-II diffusion with a relaxation coefficient of 1.50x10^{-8}. These results indicate that below T_g, the diffusion process is mainly controlled by the fast moving component (PVME) that swells the network of the slower moving component (PS) and an important portion of Case-II diffusion is required to adequately describe the data. Above T_g of PS, only 10% of Case-II diffusion is required and the diffusion is almost of Fickian type. Similar results were obtained by Jabbari and Peppas3) on the same system and the values of the diffusion coefficients and the Case-II relaxation coefficients are of the same order of magnitude.

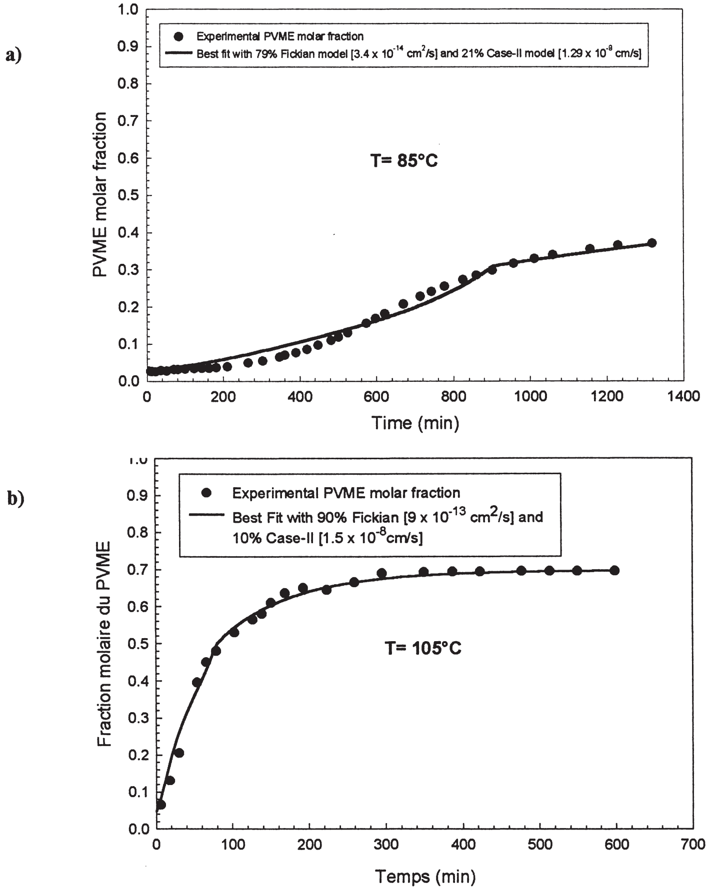


Fig. 4: PVME concentration profile determined from ATR-FTIR experiments at a) 85°C and b) 105°C.

Rheometry data at 85°C and 105°C are shown in Figure 5. On the same figures model predictions given by Equation 14 are also reported for comparison. The volume fraction, ϕ_1'', at a given position, z, was obtained either by simple Fickian model (Eq.3) or by a combination of Fickian and Case-II models. The results show that it is not possible in both cases to fit the data with a simple Fickian model. The diffusion process is mainly described by the Case-II diffusion. The mutual-diffusion coefficients obtained from rheometry are of the same order of magnitude as those obtained from ATR-FTIR measurements. However, a big difference is obtained in terms of the proportion of Fickian and Case-II diffusion models. This is because the two techniques measure different physical processes. In the case of ATR-FTIR measurements, the diffusion of PVME inside the PS matrix is detected at a given point imposed by the depth of IR radiation penetration. In contrast, rheometry measurements reflect the contribution of the whole sample sandwich. Initially, the rheological properties are mainly controlled by the weak interface and by the low-viscous component. As the diffusion proceeds, the interface strengthen giving rise to an interphase with its own thickness and rheological properties and the viscosity of the three-layers assembly is controlled by each of its layers and especially by the developed interphase. The interphase is formed mainly by the diffusion of the fast moving component (PVME) that controls the whole mechanical properties of the system. It is then not surprising that the diffusion processes probed by rheometry is essentially of Case-II diffusion type.

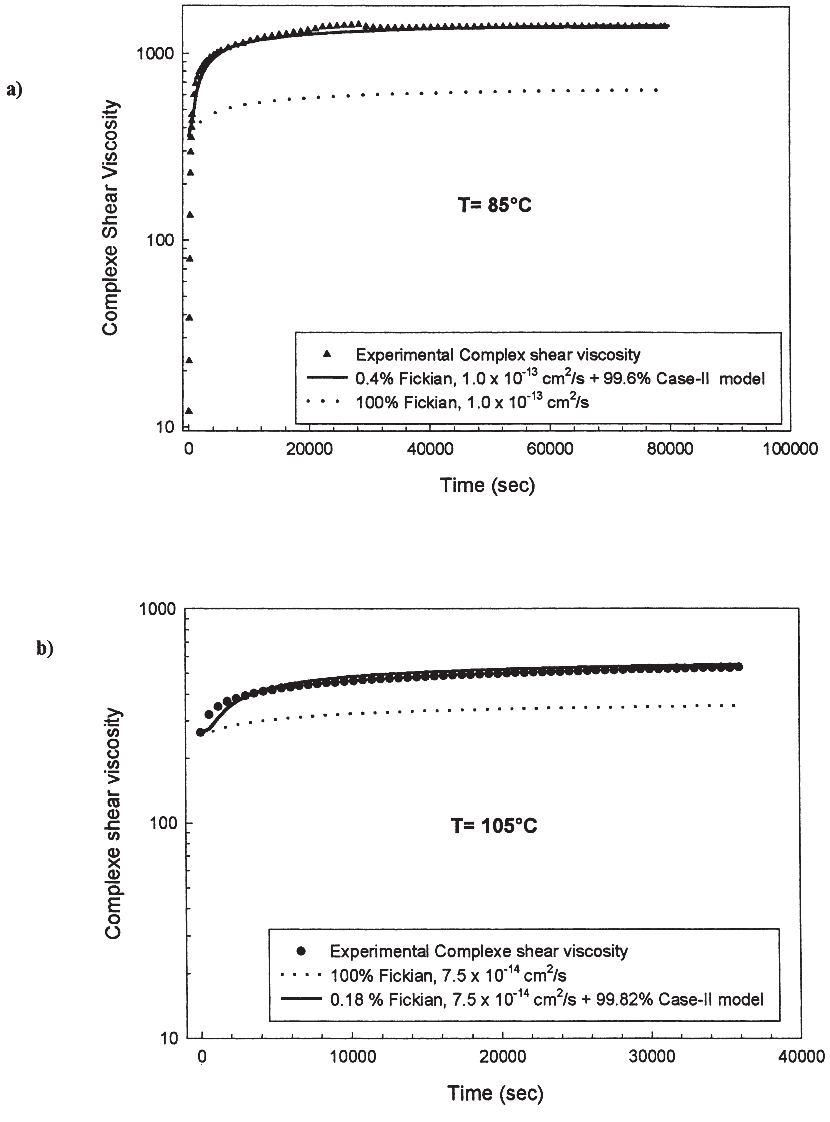


Fig.5: Time evolution of the sandwich complex shear viscosity during diffusion experiments at a) 85°C and b) 105°C.

Conclusion

The main results of this work are that the diffusion process at PS/PVME cannot be described by a simple Fickian model. The use of the contribution of the Case-II diffusion was found to be necessary both in ATR-FTIR and in rheometry measurements. This suggests that the diffusion mechanism is controlled by the faster-diffusion component that penetrates and swells the slower moving one.

Acknowledgments: This work was supported by the NSERC (Natural Sciences and Engineering Research Council of Canada) and the FCAR (Fonds pour la Formation de Chercheurs et l'Aide à la Recherche du Québec).

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