

# Molecular Mechanisms of Interphase Evolution in the Liquid Polystyrene–Glassy Poly(phenylene oxide) System

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**ABSTRACT:** We report a diffusion study on a series of interphases formed between a polystyrene-rich (PS) liquid layer and a poly(phenylene oxide) (PPO) glassy matrix. Diffusion was promoted by annealing the polymer pair at several temperatures below the glass transition temperature of the PPO matrix, in experiments where the liquid component was supplied from an *unlimited* source. Depth PS concentration profiles were obtained via optical sectioning through the glassy layer with confocal Raman microspectroscopy. The PS profiles measured in all the samples had sharp diffusion fronts followed by a region with relatively uniform PS concentration. From the time evolution of the PS front advance, we directly obtained the time-scaling laws for interphase kinetics which are interpreted in the context of the Fickian and case II diffusion theories. Despite some recent studies reporting the occurrence of case II in this particular system, our results and analysis show conclusively that interphase kinetics are, on the contrary, markedly Fickian. Results previously published by other authors on this polymer pair are also analyzed with the aim of offering a unified view about the mechanism that controls interphase evolution at the molecular level.

## Introduction

Beyond its obvious importance in several technological fields, the diffusion of organic penetrants in glassy polymer matrices has been the focus of active research for many years. The penetration of *small* molecules, i.e., solvents, nonsolvents, and molecular dyes, into glassy polymers has been extensively studied, and the principles of this phenomenon are well understood. It has been well documented that, under certain conditions of temperature and concentration, penetration can be markedly non-Fickian, with some unique features labeled as case II diffusion. The application of ion-beam-based techniques by Kramer<sup>1,2</sup> has contributed to definitively understanding the foundations of this remarkable diffusion mechanism, confirming the ideas originally introduced by Thomas and Windle.<sup>3</sup> A more recent work by Argon updates some of the fundamentals, offering a more rigorous description of the driving forces involved in the process.<sup>4</sup>

Conventionally, studies of case II diffusion have been conducted by submerging a piece of the glassy polymer into an *infinite* source of small penetrant molecules; the theory around the phenomenon has also been developed under this condition. Driven by high levels of osmotic suction,<sup>5</sup> small molecules permeate through the surface of the glassy matrix filling first interstitial sites. The presence of small molecules creates a dilatational misfit and induces an effective (biaxial) stress field, mechanically counteracted by the constraint imposed by the glassy matrix. At a certain level of diluents, the induced stress field effectively overcomes the matrix yield stress and the glassy polymer is plastically deformed; this deformation rate controls further penetration of the small molecules, making it the rate-controlling step for the process. The condition of infinite supply of small molecules is not incidental as it guarantees a steady concentration of diluents driving the advance of the diffusion front. This whole set of conditions, i.e., high levels of osmotic

suction, infinite supply of small molecules, and diffusion controlled by mechanical relaxation, give rise to the most recognizable case II feature: its linear diffusion kinetics.<sup>3</sup>

The penetration of *large*, mostly liquid, molecules in glassy polymer matrices has started to be considered much more recently. The criterion used here to distinguish between *small* and *large* penetrants is based on the inverse relationship existing between molecular size and osmotic suction,<sup>5</sup> while we consider as *small* molecules those that produce levels of osmotic suction in the range of the glassy matrix yield stress, *large* molecules are those that, under similar conditions, generate osmotic suctions far below this limit. Under this criterion, bulky plasticizers, oligomers and polymers are considered here as *large* molecules. The first experiments of diffusion of liquid polymer molecules in glassy matrices were reported by Kramer and Composto on the liquid polystyrene/glassy poly(phenylene oxide) (l-PS/g-PPO) polymer pair<sup>6</sup> and separately by Sauer and Peppas on the liquid poly(vinyl methyl ether)/glassy polystyrene (l-PVME/g-PS) system.<sup>7,8</sup> These studies emerged as cases of interdiffusion between two miscible polymers with different glass transition temperatures ( $T_g$ ), conducted at temperatures intermediate between the  $T_g$ s of the components.

From a mechanistic point of view, the basis of the diffusion mechanisms involving large liquid molecules is not so well established as in the case of small-sized penetrants. Many authors brought the concepts learnt from case II to interpret the experimental evidence, i.e., liquid concentration profiles and apparent diffusion kinetics, implying that penetration of the liquid species are controlled by mechanical relaxation of the glassy polymer.<sup>7,8</sup> A different view offered by another group of authors describes the growing mechanism for these interphases as diffusion controlled, with characteristics similar to those observed in polymer diffusion in the melt state between species with different physical properties.<sup>9,10</sup> The extremely low osmotic suction associated with large-sized penetrants has been suggested as a factor that rules out case II diffusion in these systems.<sup>9</sup> Recent experiments on the l-PS/g-PPO and l-PVME/g-PS, carried out in the immediacy of  $T_g$  of the glassy polymer, have shown the absence of transition in the diffusion mode as

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the PS passes from glassy to liquid state, which seems to support the latter view.<sup>11</sup> On the other hand, Lin and co-workers recently reported case II diffusion kinetics in experiments carried out on the l-PS/g-PPO system, with PS samples of moderate-to-high molecular weight, and at temperatures well below the  $T_g$  of PPO.<sup>12</sup>

A remarkable similarity between diffusion experiments involving large liquid molecules is that most of them have been conducted in settings of *limited* liquid supply, i.e., a thin liquid layer that diffuses in the glassy matrix, in opposition to the conventional *infinite* supply condition inherent to case II. In conditions of limited supply, under the constraint of mass conservation, the concentration of liquid polymer throughout this thin layer depletes with diffusion time. Therefore, the local material properties behind the advancing diffusion front change continuously while diffusion evolves, which sometimes misleads attempts to establish a connection between molecular mechanisms and apparent diffusion kinetics.<sup>13</sup>

This paper reports a diffusion study on a series of liquid/glassy polymer interphases, carried out under conditions of *unlimited* liquid polymer supply. We have chosen the l-PS/g-PPO system in part motivated by recent work that reports for the first time evidence of case II in this polymer pair. The idea of carrying out experiments in a setting of *unlimited* liquid polymer, with liquid molecular weights in the lower end, i.e., higher levels of osmotic suction, has been to reproduce as close as possible those conditions under which case II manifests unequivocally their distinctive features. As an experimental tool, we employed optical sectioning by confocal Raman microscopy (CRM) in a configuration that delivers steady depth resolution, 1 order of magnitude improved with respect to that reported in our previous work. As the technique yields direct information on interphase concentration profiles, the results thus obtained can be straightforwardly analyzed in the context of Fickian and case II mechanisms. Results previously published by other authors for this polymer couple are also analyzed with the aim of offering a unified view about the dominating diffusion mechanism in these systems.

### Time Scaling Laws for Polymer Diffusion Kinetics

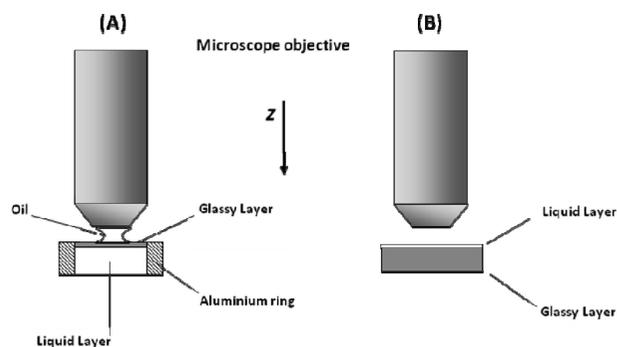
We start with a brief overview on time scaling laws for diffusion kinetics in the context of the diffusion mechanisms relevant to this work. In the first stages of polymer diffusion between two melt phases, the chains close to the interface, subjected to entropic confinement, recover their Gaussian chain statistics that they lost because of the proximity to the interface. At these early stages, chain diffusion is non-Fickian and is characterized by complex time scaling laws.<sup>14</sup> As the diffusion distances spanned by this regime are typically below the radius of gyration of the chains, well beyond the detection limit of the experimental techniques considered here, we will not consider it in detail.

For longer distances, center-of-mass diffusion prevails. Driven by Brownian motion, polymer diffusion consists of random thermal jumps of segments of polymer chains between adjacent voids or free volume elements. The process is naturally described by Fick's law, through a transport (diffusion) coefficient  $D$ . The simplest case is tracer diffusion, i.e., a low concentration of polymer chains moving in an essentially invariant polymer matrix. For a given temperature, the process can be described by a single molecular weight ( $M$ ) dependent diffusion coefficient, whose functionality with  $M$  can be expressed in terms of well-known regimes, i.e., Rouse, and reptation.<sup>15</sup> Concentration distributions of the diffusing species, mathematically described by combinations of error functions, have the characteristic sigmoidal shape. When diffusing species are present in appreciable amounts, thermodynamic factors start

to operate (interdiffusion).<sup>16</sup> In the most general case, the diffusing polymer and the matrix have dissimilar segmental mobilities, i.e., different viscosity. This arises from differences in chemical structure, commonly manifested through differences in  $T_g$ , and from differences in molecular weight. In this case, the low-viscosity polymer diffuses through an environment progressively enriched in the component of high viscosity, experiencing a continuous, sometimes dramatic, drop in molecular mobility. Fick's law with a concentration-dependent diffusion coefficient describes well this experiment.<sup>16</sup> A bulk flow contribution has to be included to account for the asymmetric intrinsic diffusivity between components.<sup>17</sup> The distribution profiles predicted by these models, experimentally supported by many experiments, are highly asymmetric. In most of these cases, a sharp diffusion front, i.e., concentration dropping abruptly in a narrow spatial region, is observed, with the steeper slope in regions of lower molecular mobility (higher local  $T_g$ ). A particular case is given when both liquid polymers are identical (self-diffusion); in this situation their molecular mobilities match, and a single diffusion coefficient describes the experiment.<sup>16</sup>

All the cases discussed above can be mathematically described by Fick's law. Focusing on the frequently studied one-dimensional diffusion case in planar geometry between two infinite layers, Fick's law predicts that the amount of substance passing through the original interface scales with time as  $t^{1/2}$ , with a slope proportional to  $D$ ; this relationship holds for constant or concentration-dependent  $D$ .<sup>18</sup> For the latter case, if a diffusion front develops, its advancing kinetics is also predicted to scale as  $t^{1/2}$ . Boundary conditions, source dimensions (limited or unlimited supply), and polydispersity in molecular weights may affect, to different extents, the apparent scaling laws for diffusion kinetics. In systems described by a single concentration-independent  $D$ , diffusion kinetics always scales as  $t^{1/2}$ , independently of the type of supply. In systems represented through concentration-dependent  $D$ , i.e., interdiffusion, the condition of limited supply (or finite source) may produce departures from the  $t^{1/2}$  scaling. In the polymer couple, the constraint of mass conservation forces the concentration throughout the thinner layer to progressively decrease, thus changing local values of  $D$  and the slope of the Fickian plot.<sup>19</sup> A similar case is found in systems with polydispersity in molecular weights. At early stages, diffusion is dominated by the lower molecular weight species, ascribed to higher  $D$  values, while at longer diffusion times, center-of-mass transport of the higher molecular species prevails. Diffusion in polymer latex films exemplifies well this kind of behavior: the plots of mass fraction of diffused polymer as a function of  $t^{1/2}$  usually show a downward curvature that reflects the decrease of  $D$  as the extent of diffusion increases.<sup>20</sup>

Several diffusion regimes have been described for diffusion of small molecules in glassy polymers, many of them Fickian, for which the above-mentioned scaling laws hold. Under certain conditions of penetrant activity and temperature, some systems manifest case II behavior.<sup>3</sup> In a typical experiment, a piece of glassy polymer is put in contact with an infinite source of gas or liquid penetrant. Over the induction period, penetration is essentially Fickian, described by a constant  $D$ .<sup>1</sup> Once conditions for control by case II are established, further transport of small penetrants in the glassy matrix occurs through a self-similar propagating front, with the Fickian precursor ahead.<sup>4</sup> The front is preceded by a plasticized layer with a nearly constant concentration of penetrant, which is continuously supplied by the infinite source. The resulting penetrant concentration profile is highly asymmetric due to the dramatic changes in molecular mobility experienced by the penetrant along its diffusion path. The advancing front kinetics has been modeled by a coupled



**Figure 1.** Schematic of the experimental setup used for optical sectioning by confocal Raman with (A) immersion optics and (B) dry optics.

**Table 1. Characteristics of the Samples Used for Diffusion Experiments**

system	low- $T_g$ layer		high- $T_g$ layer	
	$\Phi^{PS}$	$T_g$ [°C]	$\Phi^{PS}$	$T_g$ [°C]
1-PS0.7/g-PPO	0.7	25	0.05	200
1-PS1.5/g-PPO	0.9	51	0.1	182
1-PS3.9/g-PPO	0.9	80	0.1	185

nonlinear system of mass and momentum balance equations; a summary of the most relevant approaches can be found in ref 4. Under the assumption of constant (equilibrium) concentration of penetrant in the plasticized layer, the front is predicted to advance at constant velocity. A quantitative description of the effect of penetrant concentration in the plasticized layer on front velocity was first made by Hui<sup>1</sup> and has been recently revisited by Argon.<sup>4</sup> It is predicted that front velocities increase sharply with concentration of small molecules in the plasticized layer, particularly in the concentration range slightly above the critical value necessary for case II initiation. On the basis of those predictions, we anticipate that the type of supply ought to affect the apparent diffusion front kinetics: in experiments under limited liquid supply, as concentration of small molecules in the plasticized layer decreases, a downward deviation from the characteristic linear time scaling should be expected.

### Experimental Section

**Materials Characterization.** Polystyrene (PS) samples were purchased from Polymer Source (Dorval, Canada), as materials with narrow molecular weight distributions ( $M_w/M_n < 1.1$ ). Three PS samples having different molecular weights were employed, referred to here as PS0.7 ( $M_w = 740$  g/mol,  $T_g = -5$  °C), PS1.5 ( $M_w = 1460$  g/mol,  $T_g = 45$  °C), and PS3.9 ( $M_w = 3900$  g/mol,  $T_g = 77$  °C). The poly(phenylene oxide) (PPO) sample ( $M_n = 31\ 000$  g/mol,  $M_w/M_n = 2.0$ ,  $T_g = 212$  °C) was purchased from Aldrich. The oil used as immersion fluid (B446082), with refractive index = 1.5, was purchased from Merck. Glass transition temperatures for pure polymers and their blends were measured by differential scanning calorimetry (DSC), with a Perkin-Elmer Pyris II DSC instrument. Samples were cooled and heated from  $-70$  °C at rates of  $10$  °C/min under a  $N_2$  atmosphere.  $T_g$ s were determined as the onset of the transition.

**Sample Preparation for Diffusion Experiments.** Details about samples for diffusion experiments can be found in Table 1. Cylindrical specimens (6.5 mm diameter) were prepared via sequential molding in a two-step process, carried out in a mold that operates under vacuum to avoid sample degradation. First, a thin film of the high- $T_g$  PPO-PS blend, about  $200$   $\mu$ m thick, was molded at  $40$  °C above its  $T_g$ . Next, an aluminum guard ring (see Figure 1) was placed and secured on top of that film, at room temperature. Finally, a thick layer of the low- $T_g$  PPO-PS blend was vacuum-molded on top of the high- $T_g$  blend layer, in the cavity formed by the aluminum guard ring. The temperature of the second

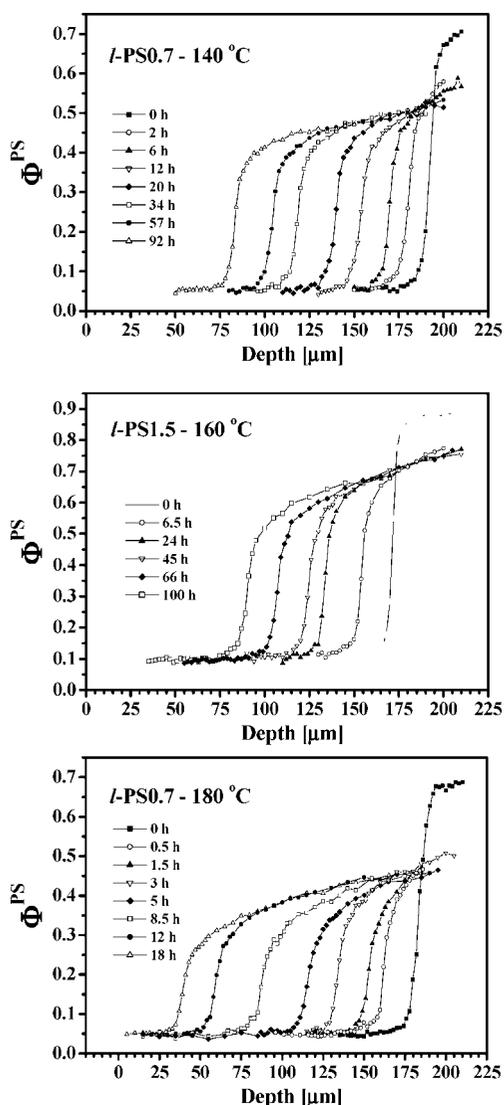
molding step was set to about  $30$  °C above the respective blend  $T_g$ , to minimize diffusion between layers at this stage. To fulfill the condition of unlimited liquid supply, the liquid layer was about 5 times thicker than the glassy layer. These samples were annealed in a temperature-controlled oven ( $\pm 0.5$  °C) under a dry nitrogen atmosphere for a period of time. They were then removed from the oven and quickly cooled to room temperature, which virtually stops interphase evolution, to be microscopically characterized.

**Confocal Raman Microspectroscopy.** Local Raman spectra were measured at room temperature on a microspectrometer DILOR LabRam Confocal, equipped with a 16 mW He-Ne laser beam (632.8 nm wavelength). The pinhole opening ( $h$ ) was set at  $200$   $\mu$ m ( $h$  maximum is  $1000$   $\mu$ m). In the excitation and collection path, an immersion Olympus x100 (numerical aperture,  $NA = 1.39$ ) was the microscope objective primarily used. Some measurements were also carried out with a dry Olympus x100 ( $NA = 0.9$ ) objective. A slit opening of  $500$   $\mu$ m and a holographic grating of 1800 lines/mm were used to acquire Raman spectra in the shifts range between  $500$  and  $1500$   $cm^{-1}$ , with a spectral resolution of about  $4$   $cm^{-1}$ . The acquisition time for each spectrum varied between 2 and 5, and four spectra were accumulated for each data point.

Figure 1 shows two configurations for depth profiling by confocal Raman. Figure 1B shows that used in a major part of our previous work, which employs dry objectives. This configuration has the advantage of being noninvasive; i.e., the sample is scanned without contact, but at the cost of sacrificing spatial resolution.<sup>11,21</sup> With dry objectives, laser refraction at the air/sample interface distorts significantly the size of the laser spot, originally limited by diffraction, with the consequent worsening in depth discrimination.<sup>22-24</sup> At nominal focusing depths of  $50$   $\mu$ m, predicted values of depth resolution are in the range  $20-30$   $\mu$ m,<sup>24</sup> i.e., 1 order of magnitude larger than those predicted by diffraction theory. This deterioration in depth resolution is not steady and becomes more severe as one focuses deeper below the sample surface.<sup>22</sup> Another undesirable effect is that the depth scale is artificially compressed, making sample features to appear artificially closer to the microscope objective. Although this distortion can be corrected by rescaling the depth scale with a factor obtained from calculations based on geometric optics,<sup>22</sup> the broadening of sharp sample features due to the enlargement of the laser focal volume remains in the measurements.<sup>25</sup>

The configuration used in the present work overcomes those limitations by using immersion optics (Figure 1A). A coupling fluid between objective and sample that matches the sample refractive index is used to minimize laser deviation at the sample surface. In this way, the refraction influence is substantially reduced and depth resolution within the diffraction limits recovered. In order to adapt to operation with immersion optics, the glassy-liquid polymer interphase is now approached through the high- $T_g$  solid layer, with the coupling oil on the external part of this layer, as shown in Figure 1A. Although PPO resisted well direct contact with the oil used here, we have proposed the use of a thin protective coating which can be reversibly applied onto the sample surface avoiding direct oil/sample contact and potential sample damage; details can be found elsewhere.<sup>26</sup> Notice that the initial thickness of the glassy layer was kept just below the working distance of the objective ( $210$   $\mu$ m), which allows us to see the original position of the glassy-liquid polymer interface and, at the same time, a wide span of depths to monitor interphase evolution inside the solid film. Overall, the method is expected to yield consistent depth resolution close to the diffraction limit and to completely suppress distortions of the depth scale.

For optical sectioning, diffusion specimens were mounted on a microscope stage with controlled vertical displacement ( $z$ -axis) coupled to the Raman spectrometer. A drop of coupling oil was placed between the glassy layer and the microscope objective just before confocal Raman profiling were carried out. The oil was exhaustively removed with tissue paper before sample annealing. Optical sections were obtained at various distances from the glassy layer surface by moving the focal plane along the  $z$ -direction (see Figure 1), resulting in a series of Raman spectra as a function of

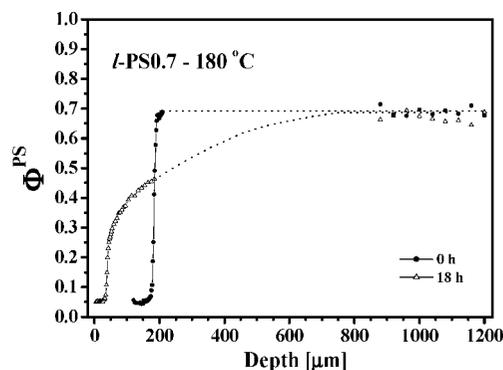


**Figure 2.** Typical PS concentration profiles obtained by confocal Raman depth profiling at l-PS/g-PPO interphases. Annealing times and temperatures and the type of PS sample are specified in the legends.

depth. The methodology used to obtain local concentration from the local Raman spectra has been described previously.<sup>27</sup> It takes about 20 min to acquire the whole concentration profile. The operative depth resolution in the instrumental conditions of the present work ( $\lambda = 632.8$  nm, NA = 1.39,  $h = 200$   $\mu\text{m}$ ) was obtained by scanning in  $z$ -direction the intensity of the  $520$   $\text{cm}^{-1}$  band of a silicon wafer immersed in the coupling oil. Silicon acts as a layer of infinitesimal thickness, providing the point-by-point depth response of the instrument. The full width at half-maximum from the bell shaped curve (nominal depth resolution) that was obtained was  $3.2$   $\mu\text{m}$ .

## Results

Figure 2A–C shows representative liquid PS concentration profiles for diffusion experiments conducted at temperatures well below the  $T_g$  of the corresponding glassy matrices. Figure 2A shows the volume fraction of PS ( $\Phi_{\text{PS}}$ ) for the l-PS0.7/g-PPO interphase, which was annealed at  $140$   $^{\circ}\text{C}$  ( $60$   $^{\circ}\text{C}$  below the matrix  $T_g$ ), for several time lengths. Figure 2B,C shows the same information for the l-PS1.5/g-PPO and l-PS0.7/g-PPO interphases, held at  $160$  and  $180$   $^{\circ}\text{C}$ , respectively, about  $20$   $^{\circ}\text{C}$  below the corresponding matrix  $T_g$ . To obtain these concentration profiles, “optical sectioning” by confocal Raman was started at the rich-PPO/coupling oil interface, the zero in the depth scale

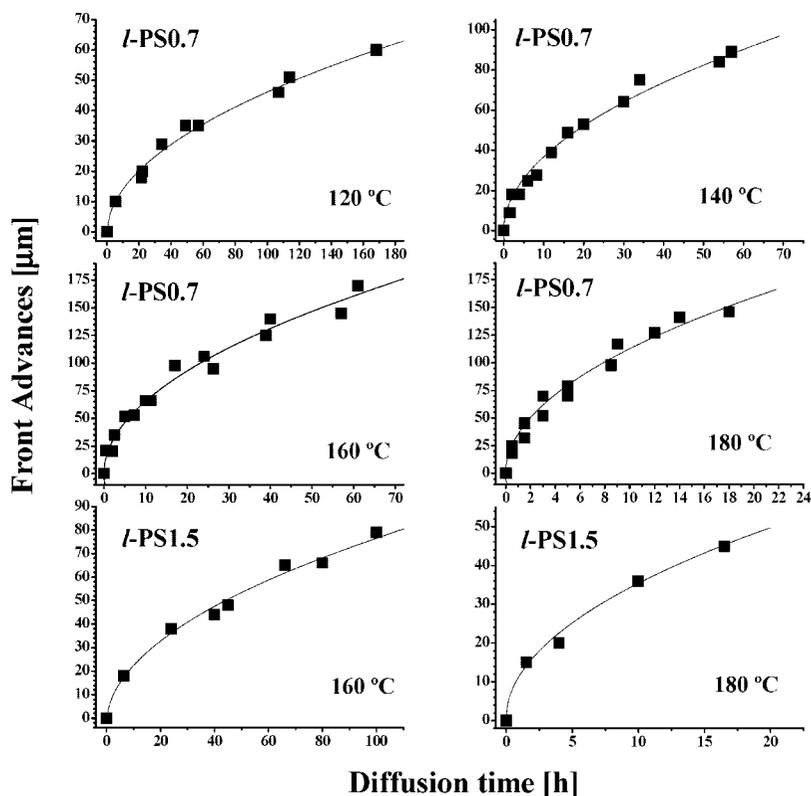


**Figure 3.** Complete PS profile showing the range of depths covered by confocal Raman measurements. Dotted lines were drawn as a guide to the eye.

axis, and then repeated at deeper positions along the PPO diffusion path.

Overall, the profiles shown in Figure 2 look sharper and better defined than those reported in earlier work, which reflects the substantial improvement in depth resolution obtained by working within the diffraction limit instead of limited by refraction.<sup>28</sup> Originally, the boundary between polymer layers was located at about  $200$   $\mu\text{m}$  on the depth scale, dividing glassy ( $0$ – $200$   $\mu\text{m}$ ) and liquid ( $200$ – $1200$   $\mu\text{m}$ ) regions. As time increased, PS advanced toward the PPO-rich side in the form of sharp diffusion fronts. Behind the fronts, the profiles are fairly flat, with subtle differences depending on PS molecular weight and temperature. Notice that the experiment captures the profile region within the working distance of the microscope objective ( $210$   $\mu\text{m}$ ) and that a major part of the liquid layer is beyond the observational window. The original thickness of this layer was set to about  $1000$   $\mu\text{m}$  to satisfy the condition of infinite liquid supply, i.e., l-PS diffusion from a source of invariant properties. This condition was verified by placing the composite specimen upside-down on the microscope stage and using a “dry” objective to examine changes from the outside of the PS-rich layer. An example of this type of data is given in Figure 3, which shows experimental information obtained with both types of objectives. Data correspond to the l-PS0.7/g-PPO system, before and after being annealed for  $18$  h at  $180$   $^{\circ}\text{C}$ . Data in the range of depths between  $0$  and  $200$   $\mu\text{m}$  are the same that those shown in Figure 2C, while data in the range  $850$ – $1200$   $\mu\text{m}$  were obtained with a dry objective. We see that PS concentration on the right border of the polymer couple did not deplete with diffusion time, remaining essentially constant. This verifies that the liquid is supplied from a plasticized layer that remains invariant in concentration, which is different from previous studies on this system, where polymer liquid concentration in the plasticized layer was found to considerably decrease in the course of the diffusion process.<sup>12,19</sup>

Figures 4 and 5 present a series of plots that characterize the interphase kinetics in the PS/PPO polymer pair. We mainly focus on the time evolution of front positions, a direct way of revealing the type of scaling for the diffusion controlling step. With a depth resolution of about  $3$   $\mu\text{m}$ , invariant with focusing depth, the localization of the diffusion front is now straightforward and precise. Indirect calculations employed in previous work, arising from the lower depth resolution of the focusing mode employed, were not needed.<sup>28</sup> The position of the diffusion front was calculated as the maximum of the derivative curve of the PS concentration profile. In Figure 4, the aim is to explore the advancing diffusion front positions in the context of the case II diffusion theory, showing the successive front positions as a function of annealing time. Figure 5 shows the same plot in



**Figure 4.** Kinetics of the advancing diffusion front as a function of the elapsed diffusion time for several diffusion temperatures for two of the PS samples (*l*-PS0.7 and *l*-PS1.5).

413 the Fickian fashion as a function of the square root of the  
414 elapsed diffusion time.

#### 415 Discussion

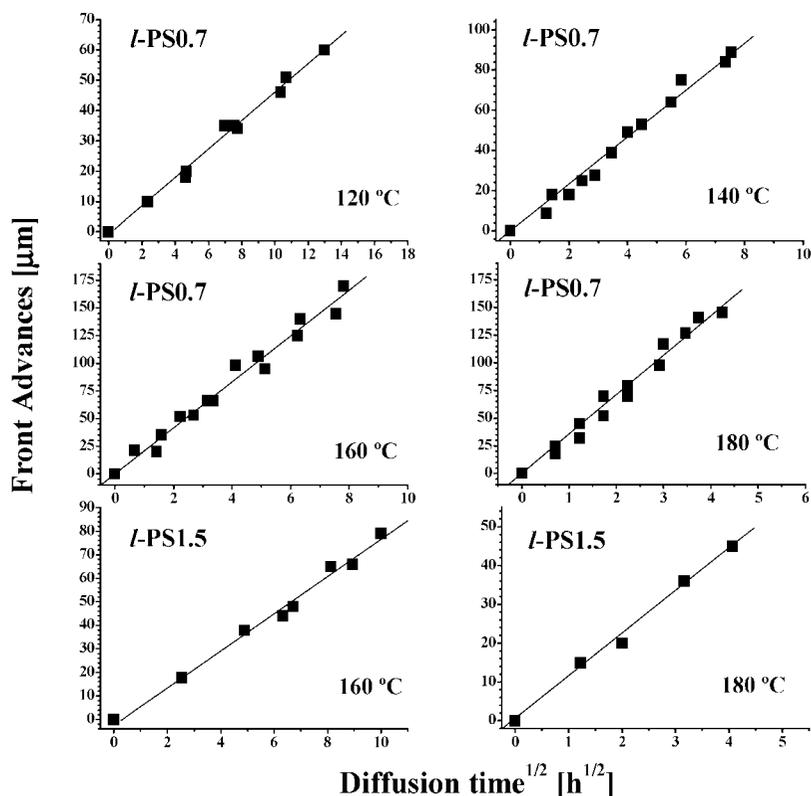
416 **Analysis of Diffusion Kinetics.** We begin by examining  
417 details of the shape of the liquid diffusion profiles. Overall, they  
418 show a marked asymmetry, ascribed to the dramatic changes  
419 in molecular mobility experienced by the PS chains in the  
420 pathway from the liquid to the glassy side. As a common feature  
421 for all the experiments, the profile in the liquid-glassy transition  
422 region drops off sharply, in a form of diffusion front. The steep  
423 front is a result of the beginning of the high- $T_g$  region (low PS  
424 content), where molecular mobility decreases dramatically. On  
425 the scale of the spatial discrimination of our experimental  
426 technique, the diffusion fronts are sharp, with no leading tails:  
427 the rounding observed at the profiles' edges entering to the  
428 glassy layer has a width on the order of the depth resolution of  
429 the technique.

430 Throughout the liquid layer (high PS content region), which  
431 is highly plasticized at the temperature of the experiment, the  
432 volume fraction of PS is fairly constant, indicating that, once  
433 incorporated to this layer, distribution of PPO molecules is rapid.  
434 Depending on PS molecular weight and temperature, we observe  
435 differences in the local slope of the liquid profiles and a shifting  
436 in the PS volume fraction where profiles crossover (see Figure 2).  
437 As this region is in the liquid state at the temperature of the  
438 experiment, these differences can be explained in terms of  
439 the particular  $T_g$  of each PS sample, which at the end affects  
440 the composition dependence of chain diffusivity.

441 In the context of the diffusion mechanisms under discussion,  
442 the presence of sharp diffusion fronts followed by a highly  
443 plasticized region with nearly constant liquid concentration  
444 appears at first sight compatible with both Fickian and case II  
445 mechanisms. Both Fickian diffusion models with variable  
446 (locally adjusted)  $D$  values and classic case II treatments give  
447 rise to liquid profiles with the above-mentioned characteristics.

448 There is, however, a typical case II feature apparently absent:  
449 the Fickian concentration tails preceding the advancing front.  
450 Fickian tails develop over the so-called induction period and  
451 persist as precursors of the advancing case II front. They form  
452 by random movements of the small molecules through interstitial  
453 sites in the glassy polymer (free volume) and play an important  
454 role in plasticizing the glassy matrix, additionally reducing its  
455 yield stress and thus favoring case II initiation. Typically,  
456 Fickian tails extend over ranges of several hundreds of  
457 nanometers<sup>2b</sup> and one may argue that, if present, they are  
458 overlooked by CRM. It will be shortly shown that, when the  
459 interphase is examined at higher spatial resolution, concentration  
460 tails are truly absent in this type of system. We have advanced  
461 some reasons for this apparent common pattern: the probability  
462 that local fluctuations in density produce a hole of sufficient  
463 size for a large-sized molecule to move in the glassy matrix is  
464 very small.<sup>19</sup>

465 Solid evidence to discern the nature of the rate-controlling  
466 step for liquid transport can be obtained from the analysis of  
467 the time scaling laws for the diffusion front propagation revealed  
468 by Figures 4 and 5. Figure 4 shows that for all our experiments  
469 the displacements of the PS diffusion fronts that advance into  
470 the glassy matrix are markedly nonlinear with time. At this point,  
471 we should consider that the experimental setup guarantees  
472 diffusion under almost constant liquid supply over the complete  
473 process and that this condition necessarily leads to the observa-  
474 tion of linear diffusion kinetics in case II conditions. Thus, the  
475 marked departure from a linear front advance-time relationship  
476 definitively rules out the occurrence of case II in our experi-  
477 ments. On the contrary, the very close scaling of front advances  
478 with  $t^{1/2}$  observed in Figure 5 strongly suggests that the transport  
479 of PPO toward the PS layer is Fickian in all of the cases. The  
480 obedience to a  $t^{1/2}$  scaling law is remarkable given the large  
481 amount of experimental data collected, which includes several  
482 PS samples with molecular weights in the lower end, and wide  
483 ranges of annealing time and temperatures. Notice the absence



**Figure 5.** Advancing diffusion front kinetics plotted in Fickian fashion for several diffusion temperatures and two of the PS samples studied.

484 of departures from linearity typically observed in previous  
485 experiments carried out under conditions of limited liquid  
486 supply.<sup>19</sup>

487 **Comparison with Other Diffusion Experiments in the**  
488 **l-PS/g-PPO System.** The first experiments on the l-PS/g-PPO  
489 system were reported by Composto et al.<sup>6</sup> They studied the  
490 diffusion of PS ( $M_w = 390$  kg/mol) into a pure PPO matrix  
491 ( $M_w = 35$  kg/mol) at temperatures between 6 and 39 °C below  
492 the PPO  $T_g$ , using Rutherford backscattering spectrometry  
493 (RBS). Diffusion was promoted through a planar interface  
494 between a 2  $\mu\text{m}$  thick PS layer with a 1  $\mu\text{m}$  thick layer of pure  
495 PPO on top. The authors reported PPO profiles with a marked  
496 asymmetry, complementary to those reported here for the PS  
497 species: a steep slope or diffusion front at high PPO volume  
498 fractions, followed by a rather flat region at higher depths, where  
499 PPO concentration is much lower and almost uniform. The  
500 diffusion fronts were sharp, with no indication of preceding  
501 concentration tails. This point is relevant, as discussed earlier,  
502 given the excellent depth resolution of the technique employed,  
503 which is able to resolve diffusion distances below 30 nm. The  
504 authors observed that the displacement of the interface followed  
505 a  $t^{1/2}$  scaling law. A close inspection of the data (Figure 8, ref  
506 6) reveals that the plots are not strictly linear and show the same  
507 type of downward curvature observed in limited liquid supply  
508 experiments.<sup>19</sup> The Matano–Boltzmann analysis applied to the  
509 data showed that the diffusion coefficients extracted from  
510 concentration profiles were in good agreement with those  
511 predicted by diffusion theories for polymer dynamics in the melt  
512 state. Overall, these results appear fully compatible with the  
513 Fickian case, showing no evidence of case II.

514 In contradiction with these observations, Lin and co-workers  
515 recently claimed evidence of case II in a new set of diffusion  
516 experiments monitored by secondary ion mass spectroscopy  
517 (SIMS). The molecular weight of the PPO sample used was  
518  $M_w = 244$  kg/mol ( $M_w/M_n = 3$ ); the PS samples, nearly  
519 monodisperse, had molecular weights ranging from 9 up to 2000

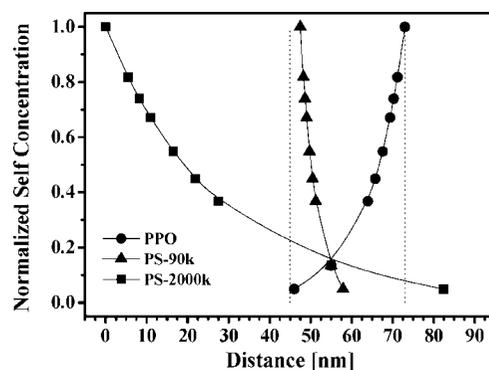
kg/mol. Diffusion samples consisted of a flat 0.5  $\mu\text{m}$  thick PS 520  
521 layer deposited on top of a 0.5  $\mu\text{m}$  thick PPO layer, which were  
522 subsequently annealed at temperatures well below the PPO  $T_g$ .  
523 Via SIMS, the authors were able to probe the l-PS/g-PPO  
524 interphase with a spatial (depth) resolution of 10 nm. The PPO  
525 concentration profiles reported were not symmetric, showing  
526 similar features to those reported here and previously by  
527 Composto. Confirming what appears as a common feature in  
528 these systems, the diffusion fronts reported look remarkably  
529 steep at a resolution of 10 nm, with no discernible tails in front.  
530 As the thickness of both PS and PPO layers were comparable,  
531 marked effects of the limited PS supply were observed. For  
532 instance, the average  $\Phi^{\text{PS}}$  throughout the liquid layer decreases  
533 from 1 to 0.7 in the course of the experiment (see Figure 2, ref  
534 12). Although the PPO concentration profiles shown are  
535 remarkably clear, reported data on diffusion kinetics were  
536 relatively scarce, with at most four experimental data (front  
537 advances) in each example shown (only two). The analysis of  
538 the diffusion kinetics is not conclusive: while some of the data  
539 show an apparently linear tendency, others show a clear Fickian  
540 dependence.

541 Using the argument of the marked asymmetry of the liquid  
542 concentration profile, Lin claims that the liquid–glassy polymer  
543 interphase evolves via a case II mechanism. To explain such  
544 evolution, the authors envision the existence of an “intermixing  
545 layer”, whose width is determined by two arbitrarily positioned  
546 planes (see Figure 5, ref 12). One of those planes limits the  
547 pure glassy PPO layer; the second one is positioned where  
548 the PPO–PS interphase becomes liquid during the annealing  
549 that promotes diffusion. The authors determined the position  
550 of the second plane by calculating local  $T_g$  values from the  
551 measured PPO concentration profile via Flory–Fox equation.  
552 In other words, the intermixing layer corresponds to the region  
553 where the PPO–PS interphase remains glassy during the  
554 annealing process that promotes diffusion. Values of the  
555 intermixing layer thicknesses reported are in the range between

556 27 and 34 nm and change very little with PS molecular weight,  
 557 despite the wide range covered (9200 and 2000 kg/mol). The  
 558 authors propose that diffusion proceeds via case II diffusion in  
 559 the intermixing layer but in normal Fickian fashion at the liquid  
 560 side of the interphase.

561 **Molecular Transport at the Liquid/Glassy Polymer**  
 562 **Boundary.** Our results on the l-PS/g-PPO diffusion indicate  
 563 that the kinetics of liquid fronts advances in conditions of  
 564 unlimited supply are clearly Fickian. Before proposing a  
 565 mechanism that explains the observed behavior at the molecular  
 566 level, we would like to offer a different interpretation of the  
 567 valuable experimental data on the l-PS/g-PPO published by Lin.  
 568 Our first point of disagreement is that the asymmetry of the  
 569 liquid profiles is not itself a conclusive proof for case II, an  
 570 argument used by many authors, including Lin. Unfortunately,  
 571 the results on diffusion kinetics reported by Lin are not so  
 572 extensive to discern between linear and square root time  
 573 dependences due to the relatively narrow range of diffusion  
 574 times studied. Besides, diffusion experiments were conducted  
 575 in conditions of limited liquid supply and under continuous  
 576 depletion of liquid PS concentration in the plasticized layer; in  
 577 this configuration, scaling laws for diffusion kinetics have to  
 578 be interpreted with caution, as discussed earlier. Therefore, from  
 579 the point of view of the analysis of diffusion kinetics, we believe  
 580 that there are no solid proofs for case II in Lin's results.

581 We share with the authors the idea of existence of an  
 582 "intermixing layer", a region where those mass transport steps  
 583 which are crucial to explain the overall diffusion kinetics take  
 584 place. We disagree, however, on how this region is calculated  
 585 and interpreted. On one hand, the assignment of local  $T_g$  values  
 586 by calculation from a standard Flory-Fox equation may not  
 587 be readily applicable to the PPO-PS interphase, as this equation  
 588 is only valid for mixtures that can be considered homogeneous  
 589 over length scales much larger than the average end-to-end  
 590 distances for the polymer chains present. Considering that the  
 591 average end-to-end distance for the PPO used is about 36 nm  
 592 (see below), similar to the reported values for the intermixing  
 593 layer thickness (about 30 nm), we see that the requisite is not  
 594 fulfilled. On the other hand, Lin uses these local  $T_g$  values to  
 595 somewhat define a limit for chain segment mobility that give  
 596 rise to diffusion or not. The situation may not be so simple if  
 597 self-concentration effects are considered, an idea proposed by  
 598 Lodge and McLeish.<sup>29</sup> The Lodge-McLeish model predicts  
 599 that, in homogeneous mixtures between polymers with widely  
 600 different  $T_g$ , each component "feels" in the blend an environment  
 601 enriched in itself, compared with the average blend composition.  
 602 While the component with lower  $T_g$  can have a significant  
 603 segmental mobility at temperatures quite lower than that  
 604 predicted by Flory-Fox, the higher  $T_g$  component is character-  
 605 ized by the opposite. This conception has been shown to describe  
 606 very well several aspects of the behavior of miscible blends,  
 607 yielding a more accurate description of polymer dynamics at  
 608 the monomeric level.<sup>30</sup> We found that by using the Lodge-  
 609 McLeish model instead of the simple Fox-Flory equation the  
 610 thickness values predicted for the intermixing layer were about  
 611 12-14 nm smaller (about 30-40%) than those reported in  
 612 Figure 7 of ref 12. Again, the Lodge-McLeish approach applies  
 613 to mixtures that are homogeneous for length scales much larger  
 614 than the average end-to-end distances: for the large PS  
 615 concentration gradients existing at the intermixing layer the  
 616 differences with the Fox-Flory approach can be even more  
 617 pronounced. Lin's too simple interpretation of  $T_g$  at short  
 618 length scales may also have led to the author to claim the  
 619 phenomenon of *glassy-glassy* polymer diffusion (Figure 10, ref 12),  
 620 entirely based on calculating local  $T_g$ s from the simple Fox-  
 621 Flory approach.



622 **Figure 6.** Normalized self-concentration profile for PS and PPO  
 623 molecules, as calculated from their Gaussian autocorrelation functions.

624 It is useful to put values of intermixing layer thicknesses in  
 625 context by comparing them with statistical parameters for the  
 626 polymer molecules employed by Lin. For instance, the unper-  
 627 turbed end-to-end distance for PPO of  $M_w = 200$  kg/mol is  
 628 estimated to be at least 36 nm;<sup>31</sup> for PS samples of  $M_w = 90$   
 629 kg/mol and  $M_w = 2000$  kg/mol, referred to as PS-90K and PS-  
 630 2000K, we calculated distances of 15 and 110 nm, respec-  
 631 tively.<sup>32</sup> Figure 6 shows a sketch with normalized self-  
 632 concentration profiles for individual chains of these three  
 633 polymers, calculated from Gaussian autocorrelation functions.<sup>32</sup>  
 634 For the depicted PPO concentration profiles the  $T_g$  of the pure  
 635 liquid PS phase would be about 100 °C. The dotted vertical  
 636 lines limit the thickness of the intermixing layer, calculated by  
 637 averaging values of Lin's calculation and our estimation using  
 638 the Lodge-McLeish model, and have been arbitrarily placed  
 639 next to the PPO center of mass. The PS-2000K concentration  
 640 is assumed to be essentially zero at the pure PPO glassy  
 641 intermixing layer limit, as shown by Lin's experimental data.  
 642 The position for the normalized PS-90K self-concentration  
 643 profile was arbitrarily chosen with the center of mass of the  
 644 molecule next to the intermixing layer of the liquid-glassy  
 645 boundary.

646 As shown in this quantitative scale, the *whole* PPO concen-  
 647 tration gradient, as measured in Lin experiments, develops over  
 648 a length comparable with the end-to-end distance for an average  
 649 PPO molecule. The dimensions of this region do not appear to  
 650 be related with the end-to-end distance of the PS molecules,  
 651 widely different for the set of liquid PS counterparts employed.  
 652 These observations suggest that the dimension of the liquid-  
 653 glassy boundary, from which originates the PPO molecules that  
 654 diffuse toward the liquid side, is most likely controlled by the  
 655 PPO end-to-end distance. The experimental work needed to  
 656 confirm this idea requires looking for changes in the thickness  
 657 of the intermixing layer in diffusion experiments with several  
 658 PPO molecular weights and a given PS sample.

659 Lin's observation of the liquid-glassy boundary at length  
 660 scales comparable with single chain dimensions gives us a  
 661 deeper insight into the transport process at the molecular level.  
 662 On the basis of Lin's results and our previous analysis, we now  
 663 understand that PPO transport from the glassy side occurs as a  
 664 sequence of events that start when *sections* of the PS molecules  
 665 plasticize first the PPO molecules at the PPO-PS interface,  
 666 almost one PPO molecule at a time, by short-range Rouse-like  
 667 movements. These short scale displacements occur over length  
 668 scales much smaller than the PPO end-to-end distance and do  
 669 not involve center-of-mass displacements of PS chains. We  
 670 believe that this process is favored by the experimental evidence  
 671 that shows that, in the PS-PPO mixture, PS molecular segments  
 672 may display short-range movements at temperatures quite lower  
 673 than the PPO molecules.<sup>29</sup> Once plasticized, the PPO molecules

672 can diffuse in the liquid state toward the PS-rich liquid layer  
673 by a regular Fickean mechanism. The lack of support for a  
674 molecular mechanism initiated by Fickean penetration of the  
675 liquid followed by deformation of the glassy matrix, i.e., case  
676 II, arises from the complete absence of center-of-mass displace-  
677 ments observed for the PS chains toward the glassy side. As  
678 we proposed in our original work, we believe that these ideas  
679 are general and not particular to this polymer pair.

## 680 Conclusions

681 We have shown that the transport mechanism of I-PS into  
682 g-PPO when the PS source was unlimited was clearly Fickean.  
683 In a setting of unlimited supply of the liquid polymer, diffusion  
684 kinetics should be strictly linear if case II was operative; on  
685 the contrary, no manifestations of this diffusion mechanism were  
686 found. This behavior, documented in extensive ranges of  
687 annealing times and temperatures, refutes earlier reports on case  
688 II occurrence in this system. The mechanism of interphase  
689 evolution proposed embraces not only our experiments, carried  
690 out at microscopic level, but also previous observations of  
691 interphase evolution at level of single chain dimensions.

692 Although highly asymmetric liquid concentration profiles are  
693 commonly observed in diffusion experiments that involve a  
694 polymer matrix that remains glassy at the temperature of the  
695 experiment, we emphasize here that these are not *sufficient*  
696 conditions for case II occurrence. The fundamentals established  
697 by Thomas and Windle for case II diffusion define some  
698 essential conditions that should not be overlooked. We have  
699 discussed that the observation of strictly linear kinetics in case  
700 II diffusion is bounded to the condition of unlimited liquid  
701 supply. A close inspection of most of the liquid/glassy polymer  
702 diffusion experiments shows that this condition is frequently  
703 not met. A mechanism controlled by mechanical deformation  
704 of the solid matrix requires that penetrants generate high levels  
705 of osmotic suction, comparable to the yield stress of the solid  
706 matrix. This is definitively not the case for large liquid polymers  
707 employed in most of the previous studies, which generate  
708 osmotic suction levels orders of magnitude lower than those  
709 associated with small sized penetrants, such as, for instance,  
710 the methanol molecule utilized by Thomas and Windle in their  
711 studies of case II diffusion on poly(methyl methacrylate).<sup>28</sup>  
712 Finally, the response of case II to temperature and to the  
713 previous thermal history of the solid matrix is distinctive and  
714 markedly different to the Fickean case.<sup>3</sup> All these manifestations,  
715 and not only the phenomenology reflected in the shape of the  
716 diffusion profiles, have to be properly analyzed when diffusion  
717 mechanisms are investigated.

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