Diffusive Mixing of Polymers Investigated by Raman Microspectroscopy and Microrheology

A. Jonás,† A. C. de Luca,‡§ G. Peseč,‡§ G. Rusciano,‡§ A. Sasso,‡§ S. Caserta,† S. Guido,‡§# and G. Marrucci‡

†Institute of Scientific Instruments of the ASCR, v.v.i., Academy of Sciences of the Czech Republic, Kralovopolska 147, CZ-612 64 Brno, Czech Republic, ‡Dipartimento di Scienze Fisiche, Università di Napoli Federico II, Via Cinthia, I-80126, Naples, Italy, §Consorzio Nazionale interuniversitario per le Scienze Fisiche della Materia (CNISM), UdR Naples, Italy, ‡Dipartimento di Ingegneria Chimica, Università di Napoli Federico II, P.le Tecchio, 80, I-80125, Naples, Italy, and #CEINGE—Advanced Biotechnologies, Via Sergio Pansini, 5, 80131 Naples, Italy

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Diffusive mixing in a model polymer blend of limited miscibility (i.e., the pair polydimethylsiloxane/polyisobutene) is investigated. The diffusion process is followed in the actual droplet-based microstructure of the polymer blend, as opposed to the ideal planar geometry used in previous studies (Brochard et al. Macromolecules 2003, 16, 1638; Composto et al. Nature 1987, 328, 234). In our experiments we combine Raman microspectroscopy and video particle-tracking microrheology. The first technique allows us to monitor local concentration of the two polymers with high spatial resolution both inside and outside a micrometer-size droplet of the dispersed phase. In addition, microrheology enables to follow how the local viscosity inside the droplet changes during the diffusion. The polymer viscosity inside the droplet is determined by video tracking the Brownian motion of a polystyrene bead microinjected into the droplet. The microspectroscopic and microrheological data are combined to estimate the concentration dependence of the monomer friction factor of the two species, which is a key parameter to calculate the interdiffusion coefficient $D$. Numerical calculations based on such concentration-dependent interdiffusion coefficient $D$ and several alternative models of the polymer diffusion are compared to the experimental concentration profiles. A satisfactory agreement is found for the so-called "slow theory" (Brochard et al.). A phenomenological model improving the agreement of the model with the experimental data is also presented.

Introduction

Blending of two or more polymers with different physical and chemical properties is a common technological route used for obtaining target compounds with specifically tuned material properties. Since the miscibility of different polymers is limited, polymer blending typically leads to a phase-separated mixture with micrometer-sized droplets of one polymer dispersed in the continuous matrix of the other one. The distribution of sizes and shapes of the dispersed phase droplets has then a significant impact on the properties of the final blending product. The distribution of droplet size and shape is mainly determined by the blend preparation procedure and by the viscoelastic and interfacial properties of the mixed compounds that are significantly influenced by molecular diffusion between the two phases. The ability to follow the dynamics of this diffusion on the relevant time and length scales given by the matrix viscosity, molecular weight of the polymers, droplet size, and mean distance between the droplets provides a unique insight into molecular scale processes that can be further utilized for optimizing polymer blending operations.

There are a number of experimental techniques available for studying the process of diffusion in polymer blends (see also review1), such as attenuated total reflection FT infrared spectroscopy, nuclear reaction analysis, Rutherford backscattering spectrometry, and electron microscopy. While these are quite powerful experimental tools allowing in some cases subnanometer resolution, they are best suited to a planar film geometry and often require some labeling with exogenous markers, which can affect the phase behavior of the polymer blend. Thus, alternative methods are needed to investigate noninvasively the dynamics of the diffusion process in the actual microstructure of polymer blends, such as a dispersed phase formed by micrometer-sized droplets in a continuous matrix.

In this work, we study the dynamics of molecular diffusion between a micrometer-sized droplet of the dispersed polymer phase and the host polymer matrix with the use of Raman microspectroscopy and video particle-tracking microrheology. These techniques allow us to determine with high spatial resolution chemical and viscoelastic properties of complex systems such as the considered droplet-based blend microstructure. In particular, Raman microspectroscopy has been gaining increasing attention as it allows selective, external label-free analysis of the molecular composition of micrometer-sized samples based on the identification of characteristic peaks in the Raman scattering spectrum that represents the molecular bonds vibrations (molecular fingerprinting). The ratio of concentrations of the individual molecules constituting the sample can be then determined from the relative intensity of their characteristic spectral peaks.2 Raman scattering spectra can be typically obtained on the time scales from seconds to tens of seconds depending on the

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concentration of the target substance and the excitation light intensity. Spatial resolution of the Raman microspectroscopy lies in the submicrometer range in the lateral direction and the micrometer range in the axial direction. Therefore, it is possible to obtain time-resolved three-dimensional concentration maps of the studied sample constituents with high spatial resolution.

Raman spectroscopic experiments have been further complemented by independent microrheological measurements inside the dispersed phase microdroplets. These measurements allow one to determine local sample viscosity from the statistical analysis of the thermal motion of a small probe particle seeded inside the droplet. The viscosity changes can be related to the polymer mixing due to diffusion, and thus, the microrheological data provide an independent way to follow the diffusion dynamics. In particular, local blend viscosity can be used to estimate the monomer friction factor of the polymer species, which is a key parameter controlling the rate of the diffusion process.

From a theoretical point of view, as recognized by de Gennes, the interdiffusion (mutual diffusion) of chemically different polymers is dominated by the strength of segment–segment interactions represented by the Flory–Huggins interaction parameter \( \chi \). This is due to the negligible contribution of the combinatorial entropy of mixing going as \( 1/N \), where \( N \) is the degree of polymerization. On the basis of this thermodynamic approach, the interdiffusion coefficient \( D \) characterizing the dynamics of the polymer mixing is

\[
D = \left( \frac{\phi_A}{N_A} + \frac{\phi_B}{N_B} + 2\phi_A\phi_B \right) D_T \tag{1}
\]

where \( \phi_A, \phi_B, N_A, \) and \( N_B \) are the volume fraction and the degree of polymerization of the two components \( A \) and \( B \), respectively. The coefficient \( D_T \) can be expressed as a function of the tracer diffusion coefficients \( D_A \) and \( D_B \), which refer to the diffusion of labeled chains of \( A \) or \( B \) at dilute concentration in a polymer blend of the two components. In turn, the tracer diffusion coefficient is related to the monomer friction factor \( \zeta \) by the equation

\[
D_T = \frac{kT}{\zeta} \tag{2}
\]

Two alternative theoretical approaches have been adopted in the literature to model \( D_T \). In the so-called “slow theory”, developed by Brochard et al. and leading to the expression

\[
1 \frac{1}{D_T} = \frac{1}{D_A^s N_A} + \frac{1}{D_B^s N_B} \tag{2}
\]

the interdiffusion coefficient \( D \) is dominated by the diffusion of the slower moving component. On the other hand, the “fast theory” developed by Kramer et al., leading to the expression

\[
D_T = \phi_B D_A^s N_A + \phi_A D_B^s N_B \tag{3}
\]


**Experimental Section**

**Materials.** Our model experimental system consists of blends of polyisobutene (PB, from BP Chemicals) and polydimethylsiloxane (PDMS, from Rhone-Poulenc), which is a pair of limited-miscibility Newtonian fluids widely used in the literature. Both PB and PDMS are transparent, but the refractive index of PB (1.50) is higher than the PDMS refractive index (1.40) which facilitates the bright field microscopy observation of the droplet formation and size evolution. It is known from previous studies that when a high-viscosity (around 10^5 Pa·s) PB droplet is immersed into a high-viscosity PDMS matrix (a system which is considered immiscible for practical purposes), droplet shrinkage takes place with time, paralleled by progressive increase of interfacial tension and droplet viscosity. Such a phenomenon has been attributed to selective migration of lower molecular weight chains of PB into the PDMS continuous phase. When the phases are reversed (i.e., PDMS droplet is suspended in PB matrix), no significant changes of droplet size, interfacial tension, and viscosity are observed, which has been attributed to the lower solubility of PDMS in PB.

In this work, we focus on the experimental geometry of PDMS droplets suspended within the quasi-infinite PB matrix and study both the diffusion of PB into the droplet and PDMS out of the droplet (see Figure 1 for the illustration of the experimental geometry). The viscosity of the samples used in this work is 11 Pa·s for PB and 23.6 mPa·s for PDMS at room temperature. The former value has been measured by a rotational rheometer and the latter value by a glass capillary viscometer. Both polymers are Newtonian in a wide range of shear rates. On the basis of the
viscosity measurements and data from the manufacturers, for PDMS the average molecular weight \( M_w \) is 4500, the polydispersity \( M_w/M_n \) = 1.8, glass transition temperature \( T_g \) = 150 K; for PB \( M_w \) = 430 with \( M_w/M_n \) = 1.7 and \( T_g \) = 200 K. The molecular weight of each polymer is well below the entanglement molecular weight fraction of the diffusing matrix polymer (thickness \( \sim 50 \mu \text{m} \) and the spectra were recorded using an imaging spectrograph critical value, which is ca. 10 000 for PDMS and ca. 6000 for PB. Some relevant molecular properties of the two polymers are shown in Table 1.

The samples were prepared as follows. First, a thin layer of the matrix polymer (thickness \( \sim 100 \mu \text{m} \)) was deposited on a coverslip and let to relax. Subsequently, spherical PDMS droplets of controlled size (typically 20 \( \mu \text{m} \) in diameter) were created within the matrix by using PDMS microinjection from a glass capillary. The spacing between the individual droplets and the distance of the droplet from the sample chamber boundary were sufficiently large (typically several droplet diameters) to avoid mutual influence of the droplets upon each other (e.g., faster depletion of the small molecular weight fraction of the diffusing matrix polymer within the gap between the droplets) and keep the condition of quasi-infinite extent of the matrix.

Raman Microscopy and Video-Tracking Micro-rheology. The Raman scattering spectra from the samples were acquired using a home-built experimental setup described previously. In brief, the inverted Raman microscope consisted of an excitation laser (wavelength 532 nm, power at the specimen \( \sim 20 \text{ mW} \)) that was focused on the specimen with an oil-immersion objective lens (Olympus, 100×, NA 1.40). The specimen was mounted on a translation stage that allowed precise positioning of the target polymer droplet with respect to the Raman beam focus. The scattered light was collected with the same objective, spatially filtered using a 1:1 telescope with a 50 \( \mu \text{m} \) pinhole placed in the common focus of the telescope lenses (confocal detection), and the spectra were recorded using an imaging spectrograph (Triax 180, Jobin Yvon) with input slit opened up to 50 \( \mu \text{m} \) equipped with a thermoelectrically cooled CCD camera (Pixis 1024, Princeton Instruments).

The acquired spectra were analyzed using Origin software to determine the relative concentrations of PB and PDMS at a given spatial location within or outside the droplet. To this end one peak was chosen for each polymer which did not show overlapping with the other polymer (see ref 16 for details). These two peaks were fitted by a sum of Lorentzian curves whose amplitudes, widths, and peak positions were the free fit parameters. Subsequently, the areas under the characteristic spectral peaks of both molecules were calculated and divided by the areas of corresponding spectral peaks acquired with pure substances to yield relative molecular concentration at the Raman beam focus (see Experimental Section). In parallel with the Raman spectra acquisition, we recorded the images of the PDMS droplet with a CCD camera connected to a frame grabber in order to evaluate the changes of the size of the droplet with time. For microrheological measurements carried out on a different experimental setup, the PDMS droplets were seeded with tracer polystyrene particles of 2 \( \mu \text{m} \) diameter whose thermal motion was monitored using a standard CCD camera (frame rate 25 fps) and Particle Tracker plugin of ImageJ software. The local viscosity in the tracer particle vicinity was then determined from the analysis of the mean-square displacement of the particle as a function of time and normalized relative to the bulk viscosity of pure PDMS obtained from calibration measurement.

Numerical Calculations. The time evolutions of the PDMS concentration profiles inside and outside the droplet were calculated using the FPE approach. Because of the spherical symmetry of the problem, the calculations were performed in a unidimensional domain about 5 times the initial drop radius \( R_0 \) oriented along the droplet radial direction, imposing symmetrical boundary condition for \( r = 0 \mu \text{m} \) and constant concentration boundary condition for \( r = R_0 \). It is worth mentioning that in general \( R = 5R_0 \) cannot be considered far enough for the Dirichlet boundary condition to be valid; however, it can be accepted in our case since the analysis is extended only to short times where the penetration of PDMS in the \( r \)-direction is smaller than 2\( R_0 \).

The initial conditions for relative PDMS concentration \( \Phi_A \) were \( \Phi_A = 1 \) for \( r < R_0 \), \( \Phi_A = 0 \) for \( r > R_0 \). The initial concentration change between the inner and outer region of the droplet was not stepwise, but the concentration gradient was smoothed out by a linear ramp along 1 \( \mu \text{m} \) distance crossing \( R_0 \) to avoid numerical error due to infinite concentration gradients and take care of the drop interface. Concentration-dependent diffusion coefficients (eqs 2 and 3) were used according to the models presented in the Introduction and Data fitting was performed by minimizing the overall difference between a model and experimental results at all positions and times. The residual error was taken as an estimate of model performance in describing the observed experimental trends.

Results and Discussion

In this paper, we extend the experimental investigation of the diffusive polymer mixing to measuring the entire concentration profile both inside and outside the droplet as a function of time which distinguishes this study from the previous work. Furthermore, fluids of lower viscosity are used in order to investigate the diffusion dynamics on a more extended time scale. We also fit our experimental data to different models of diffusion from the literature to obtain a concentration-dependent diffusion coefficient rather than using simple Fickian diffusion to calculate a time-dependent diffusion coefficient.

Local polymer concentration in the blend was determined by following two different measuring protocols. In the first one, time series of the Raman spectra at a fixed location at the droplet center was acquired. In the second protocol, spatial profiles of the
Raman spectra in the droplet equatorial plane were recorded along the radial axis from the droplet center outward at several successive times. The acquisition time of such spatial profiles (around 20 s integration time for each Raman spectrum) was negligible on the time scale of the diffusion experiment. All the series of the Raman spectra were processed as described in the Experimental Section in order to calculate the temporal and/or spatial profiles of the polymer concentrations. In particular, the PDMS and PB concentrations ($\Phi_A$ and $\Phi_B$, respectively) were estimated by fitting a sum of Lorentzian curves to two spectral lines that belong to the respective Raman spectra of the two polymers and display a minimal spectral overlapping. Once the best fit was achieved, the relative concentrations of the two polymers were evaluated by dividing the areas under the PB and PDMS peaks of the mixture Raman spectrum by the corresponding values determined from pure PB and PDMS samples. The main uncertainty of $\Phi_A$ and $\Phi_B$ derived from the fit procedure. Details of the Raman spectra of pure substances (PB and PDMS) and the spectral peaks used to characterize the concentration of both molecules in the blend were given in a previous paper.\textsuperscript{18}

Typical data on the time evolution of the PB and PDMS relative concentrations at the droplet center are shown in Figure 2 for a droplet of initial radius $R_0 = 9.2 \mu m$ (the error bars are of the same order of magnitude as the data point sizes).

Because of the PDMS diffusion outside the droplet, PDMS concentration decreases with time, while the opposite trend is found for PB which diffuses into the droplet from the continuous phase. It can be noticed that the two relative concentrations sum up to 1 within experimental error, as expected.

The diffusion process is associated with a significant droplet shrinkage ($\sim$20% diameter reduction in 2 h), as shown in Figure 3.

where the droplet diameter is plotted vs time. The droplet diameter is evaluated by analyzing the bright-field images of the droplet. In particular, the droplet perimeter is defined as the location of the maximal gradient of the image intensity (maximal image contrast). Since the image contrast depends on the gradient of the index of refraction which in turn is given by the local composition of the polymer mixture, evaluation of the droplet size provides additional information on the progress of diffusion independent from the Raman concentration measurements.

The continuous line is a simple exponential fit to the experimental data as a guide to the eye. The observed trend is at variance with the behavior found in high-viscosity PDMS/PB blends, where PDMS droplet size remains essentially constant with time.\textsuperscript{11,18}

Such apparent lack of droplet shrinkage can be explained by the significantly lower mobility and miscibility of higher $M_w$ PDMS used in previous experiments. In any case, an isolated PDMS droplet will eventually tend to dissolve in a much larger quantity of PB in order to reach phase equilibrium, even though the diffusion process could have kinetics that is much slower than the time scale of our experiments (which last a few hours).

Representative data on the spatial concentration profiles inside a PDMS droplet at several time points are shown in Figure 4, where the PB weight fraction $\Phi_B$ at each time is plotted as a function of the distance from the initial droplet surface location (distance is measured inward). Measurement range: 0.1 $\mu m$ (droplet surface) to 11 $\mu m$ (droplet center).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Dynamics of PB diffusion into a PDMS droplet. Concentration of PDMS ($\Phi_A$), PB ($\Phi_B$), and total concentration ($\Phi_A + \Phi_B$) are plotted as functions of time at the droplet center. Initial droplet radius $R_0 = 9.2 \mu m$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{PDMS droplet diameter as a function of time. Experimental data are fitted with an exponential (solid line) to estimate the characteristic time of the droplet radius evolution.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Time evolution of the spatial profile of PB concentration $\Phi_B$ inside a PDMS droplet. Concentration of PB inside a PDMS droplet at different times, reported as $\Phi_B$, is plotted as a function of time. The PB weight fraction $\Phi_B$ at each time is plotted as a function of the distance from the initial droplet surface location (distance is measured inward). Measurement range: 0.1 $\mu m$ (droplet surface) to 11 $\mu m$ (droplet center).}
\end{figure}
function of the radial distance, starting 0.1 μm away from the initial droplet surface and going up to the droplet center.

At short times PB concentration within the droplet varies significantly between the droplet surface and center; however, it tends to level out after about 2 h. One of the most interesting features in Figure 4 is that the PB concentration at the droplet interface remains at a constant value of ~0.4, which is almost uniformly reached inside the droplet at the end of the experiment. Thus, phase equilibrium is established quickly and then maintained at the interface, as usually postulated in the boundary conditions of transport phenomena. However, this is not a trivial result in our case of polydisperse diffusing polymers, and it could be attributed to the fact that the lower M_w chains are dominant at the interface where they act as a compatibilizer between the two polymers.11,12 The rather high values of PB concentration inside the PDMS droplet at the end of the experiment show that the two polymers used in this work are quite compatible. This finding is at variance with the phase behavior of a PB/PDMS blend with the PDMS concentration outside the droplet is a decreasing function of the radial distance, starting 0.1 μm away from the initial droplet surface and going up to the droplet center.

Continuous lines were obtained by fitting the classical Fick’s diffusion equation to the data at each time point19 and are shown here as a guide to the eye. The diffusion coefficient calculated by data fitting at successive time points is a decreasing function of time (not shown here for the sake of brevity), rather than being constant as assumed in Fick’s theory. A more rigorous approach for data interpretation will be shown later on.

PDMS concentration outside the droplet is a decreasing function of the distance from the droplet at any time, and the profiles tend to penetrate deeper in the continuous phase at increasing time. This qualitative trend is expected for a diffusion process from a droplet.18

To investigate further the apparent decrease of diffusion coefficient with time, time-lapse microrheological measurements of the polymer blend viscosity were also performed by tracking the Brownian motion of microspheres of 2 μm radius seeded into the droplets and localized close to the droplet center. The local viscosity was then determined from the time dependence of the mean-square displacement (MSD) of the tracer particle.20 A typical image of the droplet with a polystyrene bead inside is reported in Figure 6a along with the measured bead trajectory. The drop radius at t = 0 is 22.5 μm.

Figure 6b shows the behavior of the tracer particle MSDs at different times after the droplet formation. Every single curve is an average over five repeated measurements, each of them obtained from a 30 s movie. After every measurement the tracer particle was repositioned close to the drop center with an optical trap. We neglect the variations of the viscosity inside the droplet during the five repeated measurements with respect to the variations measured at the different successive times reported in Figure 6b. It can be seen that the first few curves of Figure 6b show evidently a parabolic behavior. This effect is caused by a small residual drift of the whole droplet, and it becomes negligible for the later measurements. In order to properly take into account any residual drift, the experimental curves were fitted with the following equation

\[ \langle r^2 \rangle(t) = 4Dt + v^2t^2 \]

where D is the Stokes–Einstein diffusion coefficient, \( D = \frac{k_BT}{6\pi\eta_a} \), and v is the residual drift velocity. D and v are regarded as free fit parameters. From the fitted diffusion coefficient D, the value of the droplet viscosity is straightforwardly computed provided the bead diameter 2a and the sample temperature T are known.

The measured blend viscosity inside the PDMS droplets, which is plotted in Figure 7a, shows a significant increase with time.

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This is consistent with the increasing concentration of the higher viscosity PB inside the PDMS droplet as determined from the Raman spectroscopic measurements presented in Figure 2. The two sets of data, i.e., concentration vs time and viscosity vs time, can indeed be combined into a single diagram, provided that some rescaling is applied due to the different radii of the droplets of Figure 2 (16 μm) and Figure 7a (22.5 μm). This was done by exploiting droplet diameter vs time for the 16 μm droplet to estimate the dependence of concentration on diameter reduction by data fitting with a power law expression (not shown for the sake of brevity). The so-obtained data fitting expression was used to calculate concentration as a function of time for the 22.5 μm droplet, being diameter reduction vs time available for this droplet, too. In Figure 7b the measured blend viscosity is plotted as a function of the PDMS concentration rescaled as described above.

The continuous line in Figure 7b is a fit to the viscosity data obtained from the log-mixing rule \(\log \eta = \phi_A \log \eta_A + \phi_B \log \eta_B\), which provides a simple, though rather approximate description of the experimental results. This fit is used in the numerical calculations presented below.

As the diffusion coefficient is now concentration-dependent, a simple Fick model of diffusion no longer holds and a different approach to model the diffusion process is needed, as outlined in the Introduction. In order to model the polymer diffusion process, the material balance equation

\[
\frac{\partial \phi_A}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi_A}{\partial r} \right)
\]

was numerically solved with the concentration-dependent \(D\) of eq 1 and both the \(D_T\) coefficients based on the “fast” and “slow” theories (see eqs 2 and 3). To calculate \(D_T\), tracer diffusion coefficients \(D^* = kT/\zeta\) of both polymers linked to their monomer friction factors \(\zeta\) have to be known. Since the molecular weight of both used polymers was below the entanglement threshold \(M_e\) (see Table 1), the values of \(\zeta\) were calculated according to the Rouse expression \(\zeta = 6\eta M/\rho N_A \langle R_0^2 \rangle\), where \(\eta\) is the concentration-dependent blend viscosity given by the experimentally determined log-mixing rule (see Figure 7b), \(M\) is the polymer molecular weight, \(\rho\) is the polymer density, \(N_A\) is the Avogadro number, and \(\langle R_0^2 \rangle\) is the mean-square end-to-end distance (values can be found in Table 1). The models were fit to the experimental data through an iterative procedure by using the interaction parameter \(\chi\) as the only adjustable parameter. (As described in the Numerical Calculations section, the fitting was done by finding the value of \(\chi\) minimizing the mean-square difference between experiments and calculations at all experimental times.)

In Figure 8, the results of the numerical calculations of the “slow theory” by Brochard et al. (eq 2) are compared to the experimental data on PDMS concentration. (A value of \(\chi = 9.6 \times 10^{-5}\) was obtained from the fitting procedure with a residual error of 0.24.) Both the concentrations inside and outside the droplets are plotted in the same graph as a function of the radial distance from the droplet center and parametric in time. In Figure 8a, it can be noticed that the numerical results increasingly deviate from the experimental data at longer times. In Figure 8b, the same numerical and experimental results are plotted as a function of the
The functional form of eq 5 is proposed since it responds to the polymerization (see eq 1). These terms were dominant due to the friction factor according to the Rouse model. In turn, these friction factor effects which are not accounted for in any of the tested models. The selective migration of polymer chains based on molecular weight (the shorter chains moving faster than the longer ones) can indeed generate a complex dependence of the diffusion coefficient on polymer concentration. Nevertheless, Brochard and Fick models provide a quite satisfactory agreement with experimental data at short times, while phenomenological eq 5 allows a good data representation at more extended times.

Conclusions

In conclusion, we have investigated experimentally the dynamics of molecular diffusion in a partially miscible polymer blend formed by microdroplets of one polymer dispersed in a continuous matrix of another polymer. With the use of Raman microspectroscopy and microrheology, we were able to monitor the temporal changes of the host polymer concentration inside the dispersed polymer droplets and correlate them with the changes of the local viscosity within the droplet. To our knowledge, these are the first experimental data on polymer inter-diffusion inside a droplet, since in previously published work only planar geometries were investigated. Local viscosity measurements have been exploited to estimate the blend viscosity as a function of concentration and, subsequently, the monomer friction factor according to the Rouse model. In turn, these results were used to fit models available from the literature to the experimental values of the spatial profiles of polymer concentration. A satisfactory representation of the experimental data was obtained by the “slow theory” developed by Brochard et al. The agreement between experiments and modeling was improved by using a phenomenological approach based on different scaling of the diffusion coefficient with the dispersed phase.
and matrix polymer concentrations. The remaining residual discrepancy can be attributed to the effects of polydispersity, which are not accounted for in the models considered in this work. Overall, this analysis provides a consistent picture of polymer interdiffusion in a geometry relevant to actual polymer blends, which are usually made of dispersed-phase droplets in a continuous matrix. Thus, our results furnish new insight into the basic physical mechanisms governing the formation of partially miscible polymer blends and the dynamics of their temporal evolution and stability.

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