Investigation of Phase Structure of Blends of Poly[(*N*-ethylcarbazol-3-yl)methyl methacrylate] and Poly{2-[(3,5-Dinitrobenzoyl)oxy]ethyl methacrylate} Using ^{1}H CRAMPS NMR

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^{1}H CRAMPS NMR techniques are used to study the phase structure of complexed and decomplexed blends of poly[(*N*-ethylcarbazol-3-yl)methyl methacrylate] [poly(NECMM)] and poly{2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate} [poly(DNBEM)] (mole ratio = 1:1). ^{1}H CRAMPS spectra of two-layer, decomplexed, and complexed samples show a line-shape change in the aromatic region which reflects the electron density change due to charge-transfer interaction. ^{1}H spin diffusion experiments are employed to estimate the domain sizes of the complexed sample and the domain sizes and interface size of the decomplexed sample. The complexed sample is mixed at the molecular level. The domain sizes and interface size of the decomplexed sample are too large for these experiments. It is estimated that the decomplexed sample has about 30% of the volume fraction in the interface and that in it poly(NECMM) and poly(DNBEM) are mixed at a molecular level.

Introduction

The macroscopic properties of a solid polymer material depend on its molecular-level structure and dynamics. Many polymer materials are phase-separated, and their phase structure is essential for their use properties. A few NMR techniques can be used to investigate the phase structure of a polymer material, i.e., phase sizes and the presence and thickness of interfaces. Perhaps one of the most promising techniques is based on selective excitation of one of the phases, followed by monitoring the spin diffusion to reequilibrate the system. This technique was initially proposed by Goldman and Shen.[1] The basis for selective excitation is a difference in mobility of the two phases, and hence materials consisting of hard−soft components can be easily analyzed. Spiess et al. developed a pulse sequence named "dipolar filter" and used it to analyze a variety of soft−hard materials.[2,3] Of critical importance in the analysis is the model of spin diffusion, which contains spin diffusion coefficients for each of the phases (and the interface), proton densities, and volume fractions of the corresponding phases.[4] Although there are already a few studies published in the literature, including our own[5,6] the reliability of the data obtained is directly related to the model used for magnetization transfer. Some refinements of the model have already been reported in the literature.[7] A three-phase model (the third being the interface) was translated into a computer program named TREEDIFDISOR and very generously made available to us by Prof. Spiess's group. This program operates based on the same physical principles as the two-phase model, i.e., it assumes three possible domain geometries on the basis of the dimensionality (one-dimensional lamellae, two-dimensional cylinders, and three-dimensional spheres), it takes into account the spin−lattice relaxation using a correction term ($\exp(t_m/T_1)$), and it does not distinguish between main-chain and side-groups motions. The results obtained using TREEDIFDISOR depend on the measurement temperature, since increased motion should change spin diffusion coefficient values, but not on the field strength, since the T_1 effect is eliminated. This reflects the fact that the domains geometry and phase sizes are dependent on temperature but independent on the magnetic field.

This "dipolar filter" pulse sequence can be applied only if one of the components of the material is "soft", i.e., if its mobility is relatively great at the measuring temperature. This condition applies to many polymer materials, but it also excludes a majority of polymer blends, mixtures, and composites, those of the hard−hard type. An alternative method for selective excitation in a multicomponent system may be based on differences in proton chemical shifts. This selective excitation may consist of complete elimination of the magnetization from one region of the spectrum[8] or of creating a maximum polarization gradient between the two components.[9−11] The proton shift selection may work on hard−hard systems, but it is restricted to materials with significant proton shift differences, i.e.,

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containing aromatic or alkoxy groups as opposed to completely aliphatic proton components. This is an even more restrictive condition than the high mobility of one of the phases, since the whole proton shift range is of only 10 ppm. The polarization gradient requires systems with significantly different numbers of protons in them and some proton shift differences, and this is less restrictive than the proton shift selection.

Independent of which of the selection method is employed, the key element in determining phase sizes and interfaces is the model for spin equilibration, and the models currently used still have some limitations: (1) They are usually "symmetric", i.e., considered to work the same independent of which of the phases (continuous or dispersed) is being selected. It has been shown that the sizes of magnetization source and sink play a definite role in the process of magnetization reequilibration.[7] (2) There is a lack of understanding of the magnetization distribution within the interface. (3) Most of the required parameters (especially spin diffusion coefficients) are not available in the literature, and thus one has to use approximations. To contribute to the refinement of the magnetization transfer model, more experimental data on spin diffusion is required. This paper presents an attempt to measure spin diffusion in a "model" polymer blend.

Charge-transfer interacting polymer blends have been the subject of investigation in our laboratory, as well as in other groups. It has been reported that mixing a polymer containing electron-donor structural units with a polymer containing electron-acceptor structural units, one may obtain a molecularly homogeneous blend, judging from its single glass transition temperature (T_g).[12] Such a blend is not thermodynamically stable, however, and the two components phase separate when heated about a decomplexation temperature. Subsequent solid-state NMR studies[13] confirmed that the two components are mixed at the molecular level in the 1:1 blend, judging by the existence of a single spin−lattice relaxation time constant in the rotating frame ($T_{1\rho}$(H)). The actual value of the constant suggests such an intimate mixing that the chains are pulled toward each other, increasing the overall density of the blend. When the 1:1 blend is heated above the decomplexation temperature, phase separation occurs and the two phases exhibit two $T_{1\rho}$(H) values. The lower value corresponds to the $T_{1\rho}$(H) of the homopolymer containing electron-acceptor groups, but the higher value is lower than the $T_{1\rho}$(H) of the homopolymer-containing electron-donor groups. This is believed to be due to the interface formed on phase separation. At the boundary between phases, at room temperature, the electron-donor and electron-acceptor groups will interact to form a mixed interface, containing both types of polymers. This interface will facilitate spin diffusion, thus the phase with the lower spin diffusion rate will be dominated by spin diffusion through the interface. Scheme 1 shows the chemical structure of the two polymers used and a cartoon of the phase structure of the 1:1 blend before and after being heated above the decomplexation temperature (ca. 185 °C).

Experimental Section

Poly{2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate} {poly(DNBEM), polyA} and poly [(*N*-ethylcarbazol-3-yl)methyl methacrylate {poly(NECMM), polyD} were prepared by A. Simmons. A 1:1 mole blend of poly(DNBEM) and poly(NECMM) mixed at the molecular level was obtained by the published method.[13] A decomplexed blend sample was obtained by heating the previous blend at 190 °C in an oven for 10 min. A two-layer sample was obtained by half filling the rotor with poly(DNBEM) powder, and the rest with poly(NECMM), after a Teflon tape was introduced to physically separate the two layers.

^{1}H CRAMPS NMR spectra were acquired on a Bruker ASX-200 spectrometer (200 MHz) equipped with a Bruker CP-MAS probe with 7 mm o.d. To minimize radiofrequency inhomogeneities and to improve magnetic field homogeneity, samples were packed into a spherical arrangement in the rotor using two Teflon spacers. The measurement of $\pi/2$ pulse and the minimization of phase transients were performed by the manufacturer procedure described in "Painless CRAMPS on the MSL" by D. P. Burum. The dead time of the probe was reduced down to 4.3 μs using an overcoupling method.[14] The $\pi/2$ pulse length was 2.0 μs, and the basic cycle time of the MREV multiple-pulse sequence was 51.6 μs.

One of the chemical shift selection methods used by VanderHart and co-workers was employed for the spin diffusion experiment.[9−11] The experimental details to achieve a maximum polarization gradient are given in ref 9. The chemical shift selection by this method should satisfy two conditions: (a) a maximum spin polarization gradient should be introduced between the two components and (b) total integrals of the spin diffusion spectra at various mixing times $I(M_{mt})$ should be less than 2% of the integral of a Boltzmann CRAMPS spectrum $I(M_0)$. The above conditions for the samples were satisfied by creating positive aromatic and alkoxy peaks of poly(NECMM), and negative aromatic and alkoxy peaks of poly(DNBEM). The number of multiple pulse cycles used was 27 (the sinusoidal period = 7.2 ppm). The spinning speed was set to 3 times of the sinusoidal period (2871 Hz). The phase cycling pulse was used to eliminate the addition of the intensity due to proton spin lattice relaxation in the laboratory frame.

Results and Discussion

The T_g's of poly(NECMM) and poly(DNBEM) differ by about 20 °C, which indicates that the motional difference between poly(NECMM) and poly(DNBEM) is not large.[13] The aromatic, alkoxy, and aliphatic peaks of poly(NECMM) and poly(DNBEM) can be resolved using a combined rotation and magic angle spinning multiple pulses (CRAMPS) technique, as shown in Figure 1.

Therefore, a spin diffusion pulse sequence that selects magnetization by exploiting chemical shift differences using the CRAMPS technique can be used in this instance. The use of proton shift selection[4,15] in this case would be complicated by the fact that both poly(NECMM) and poly(DNBEM) contain aromatic, alkoxy, and aliphatic peaks. If ^{13}C detection were used, intra- and intermolecular spin diffusion may occur during the cross-polarization time, but most of the intensity of a nonselected peak grows from intramolecular spin diffusion, which usually occurs very fast, during the cross-polarization time. The low natural abundance of ^{13}C would make the smaller intensity changes due to intermolecular spin diffusion hard to detect. Therefore, a method that does use ^{13}C detection would not be

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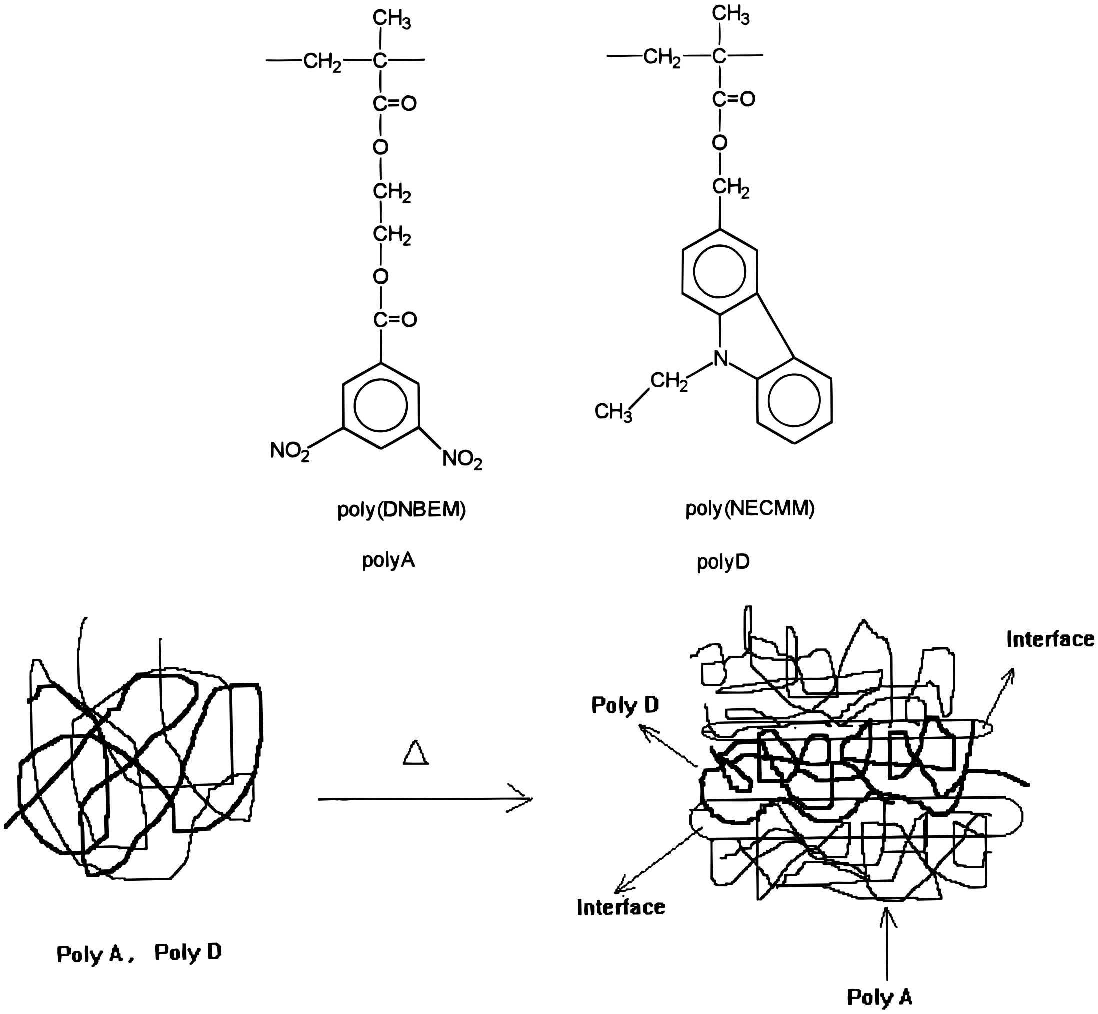
Scheme 1



preferable. The preferred method here is the one reported recently by VanderHart et al., who obtained information about the domain size and morphology of polymer blends whose proton peaks are overlapped, by generating the maximum polarization gradient and ^{1}H detection.[9-11]

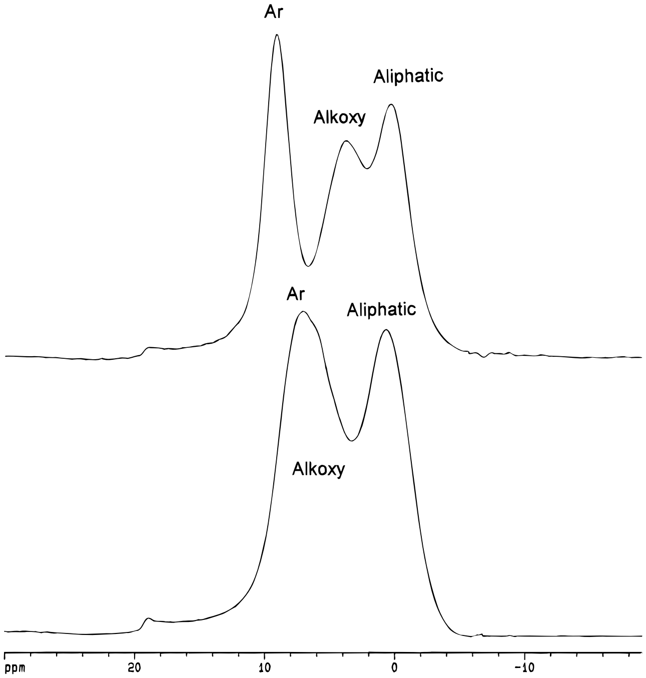


Figure 1. ^{1}H CRAMPS spectra of poly(NECMM) (a) and poly(DNBEM) (b).

^{1}H CRAMPS spectra of poly(NECMM) and poly(DNBEM) are shown in Figure 1. The chemical shift of poly(dimethylsiloxane) (PDMS) was used as an internal reference (0.09 ppm) only in the samples where chemical shifts were determined. The assignment of the spectra is on the figure. While both spectra cover most of the available proton range for both polymers, there are some differences. Poly(DNBEM) has two nitro groups in the aromatic ring, thus its aromatic protons resonate at lower field than the aromatic protons of poly(NECMM). The alkoxy protons, on the other hand, are bonded to an aromatic ring in poly(NECMM), which shifts their resonance downfield in comparison with the alkoxy protons of poly(DNBEM). The chemical shift difference between the aromatic peaks of poly(NECMM) and poly(DNBEM) is 2.0 ppm, while the difference between the alkoxy peaks of poly(NECMM) and poly(DNBEM) is 2.1 ppm. The maximum polarization between poly(NECMM) and poly(DNBEM) can be obtained by making the aromatic and alkoxy peaks of poly(DNBEM) negative, and the aromatic, alkoxy, and aliphatic peaks of poly(NECMM) positive. The pulse sequence used to study the spin diffusion shows that the line shape is determined by the length of multiple pulse irradiation (sinusoidal period). The adjustment of the length of the multiple pulse generates the

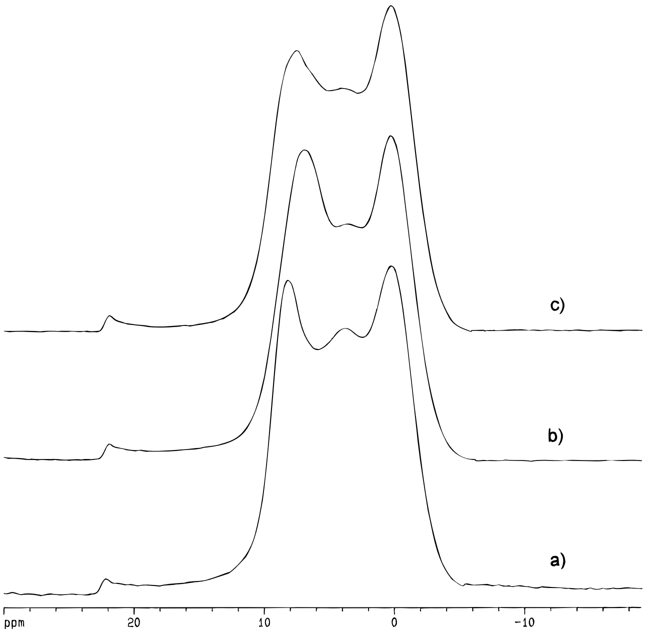


Figure 2. ^{1}H CRAMPS spectra of two-layer (a), complexed (b), and decomplexed (c) samples.

maximum polarization between poly(NECMM) and poly(DNBEM). The parameters used are given in the Experimental Section.

Figure 2 shows the ^{1}H CRAMPS spectra of three samples. The two-layer sample has poly(NECMM) on the top and poly(DNBEM) on the bottom layer in a rotor divided by a Teflon tape. Therefore, because of the physical barrier between poly(NECMM) and poly(DNBEM), the charge transfer interaction between the two components must be negligible. The chemical shifts of each peak in the three samples do not change significantly, although the aromatic protons of polyA, which presumably resonate at the lowest field, seem to be shifted upfield when there is some charge-transfer (CT) interaction present in the interface (Figure 2c, decomplexed blend) and even more when the two polymers interact throughout their bulk (Figure 2b, blend obtained by coprecipitation). This kind of upfield shift upon complexation has been previously reported for protons in solution[16] and for carbons in the solid state.[17,18] More noticeable, however, are the line shapes and line widths of the three samples, which are different, especially in the aromatic regions. The CT interaction between NECMM and DNBEM changes the electron densities of the aromatic rings and the different electron densities produce different ^{1}H line shapes. It is clear from Figure 2 that the CT interactions are different in these three samples.

The integrated intensities [$I(M_{\mathrm{mt}})$] of the raw spin diffusion spectra were about 1% of $I(M_0)$. All spectra were subtracted by an M_0 line shape which was multiplied by $I(M_{\mathrm{mt}})/I(M_0)$ using a software tool in Bruker UXNMR. This procedure is necessary in order to compensate for minor spectrometer instabilities, as described in the literature.[11] The integrated intensities of the spin diffusion spectra are made to be zero. Spin diffusion was measured using peak amplitudes, i.e., the height between the negative peak at 9 ppm and the positive peak at 6 ppm. Figures 3 and 4 show the ^{1}H spin diffusion spectra of the two-layer sample and of the complexed blend obtained at various mixing times after the above manipulation. The two-layer sample experiences only intramolecular spin diffusion, and it reaches an equilibrium within a few milliseconds. Therefore, the negative and positive peaks in Figure 3d are a consequence of the polarization gradient between poly(NECMM) and poly(DNBEM). The amplitudes of

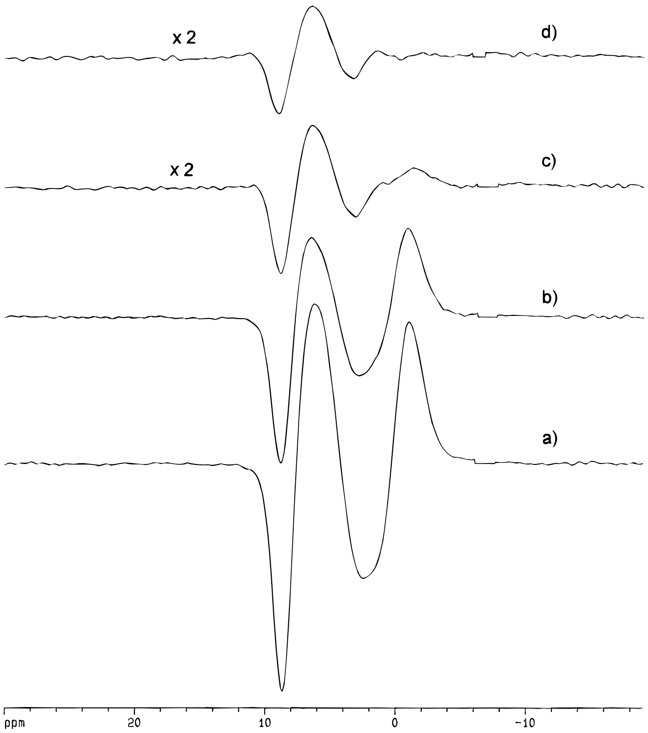


Figure 3. ^{1}H CRAMPS spectra of the two-layered sample obtained with the polarization gradient pulse sequence at various mixing times: (a) 1 μs; (b) 100 μs; (c) 1 ms; (d) 10 ms. See text for details.

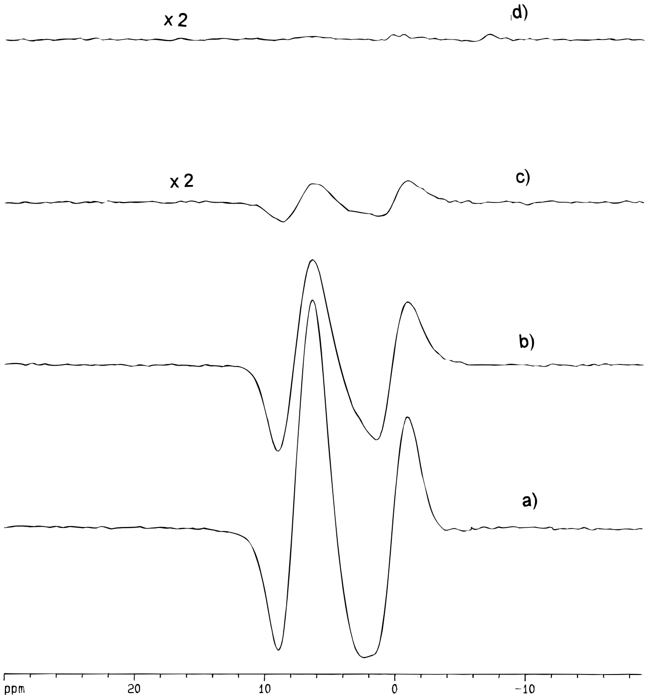


Figure 4. ^{1}H CRAMPS spectra of the complexed sample obtained with the polarization gradient pulse sequence at various mixing times: (a) 1 μs; (b) 100 μs; (c) 1 ms; (d) 10 ms.

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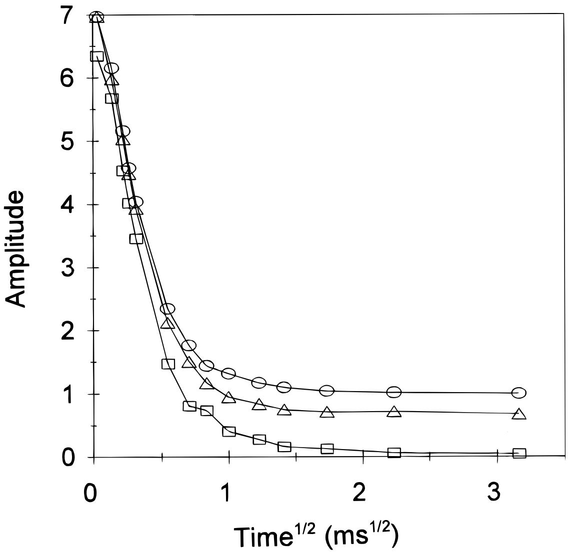

Figure 5. Plot of the polarization gradient signal amplitudes for the three samples vs the square root of mixing time; two-layer (open circle), complexed (open square), and decomplexed (open triangle). The amplitude is measured as the height between the negative signal at 9 ppm and the positive signal at 6 ppm and is given in arbitrary units.

the spin diffusion spectra of poly(NECMM) and poly(DNBEM) become zero when each reaches an equilibrium through intermolecular spin diffusion. Zero amplitudes in Figure 4d indicate that both intra- and intermolecular spin diffusion is finished within about 10 ms of mixing time.

The plot of amplitudes of the signals of the three samples as a function of mixing time is shown in Figure 5. All amplitudes are corrected by the factor $\exp[t_m/T_1(H)]$, where t_m is the mixing time,[19] and normalized to the amplitude of the two-layer sample at 10 ms mixing time, which was arbitrarily considered to be 1. The $T_1(H)$ values of the two homopolymers were measured to be 380 ms, and this value was used for all samples. The amplitude of the complexed blend is almost 0 at 10 ms, which means that the spins of poly(NECMM) and poly(DNBEM) reach the equilibrium within this time. The amplitude of the two-layer sample decreases fast initially, due to intramolecular spin diffusion, and then plateaus at an amplitude of 1 (arbitrary units). Hence, intermolecular spin diffusion is present in the decomplexed blend, since its plateau amplitude is less than 1. The decomplexed blend displays a plateau at about 0.7 (a further decrease of the amplitude is not evident until about 300 ms mixing time, which is not shown here). This means that 30% of the possible intermolecular spin diffusion is complete.

The amplitude decrease of the complexed and decomplexed blends signals is due to the intra- and intermolecular spin diffusion. The domain size reflected by the intermolecular spin diffusion can be obtained from a separation of intra- and intermolecular spin diffusion curves, based on the spin diffusion plot of the two-layer sample, which has only intramolecular spin diffusion. The TREEDIFDISOR program can be used to separate the intra- and intermolecular spin diffusion curves. If either the spin diffusion coefficients or the domain sizes are known, the spin diffusion curve can be fitted using the TREEDIFDISOR program, by varying the spin diffusion coefficients (or the domain size). A maximum proton distance between the aromatic and alkoxy groups of poly(NECMM) (about 0.8 nm) was roughly calculated using a molecular modeling program (PCMOD). The spin diffusion rates within NECMM and DNBEM molecules were assumed to be the same, and the TREEDIFDISOR program was used to fit the amplitude decrease of the two-layer sample with different spin diffusion coefficients. The data are well fitted using a spin diffusion coefficient of 0.40 nm^2/ms. The result is shown in Figure 6.

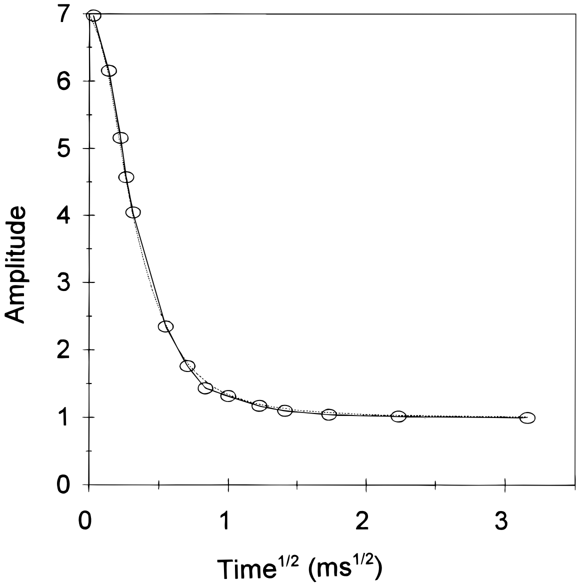

Figure 6. Plot of the polarization gradient signal amplitude of the two-layer sample fitted by TREEDIFDISOR program. The fit is indicated by a dotted line. It is assumed that the dimensionality is one. See text for details.

Since the two-layer sample has only intramolecular spin diffusion, the result of the curve fitting in Figure 6 can be used to measure the domain size of the complexed and decomplexed blends. The amplitude changes of the complexed and decomplexed blends in Figure 5 result from intra- and intermolecular spin diffusions. The spin diffusion curves of these samples can be fitted by the sum of the known intramolecular spin diffusion curve (two-layered sample) and the intermolecular spin diffusion curve with various domain sizes. Figure 5 suggests that the ratio of the amplitude decrease of the intra- and intermolecular spin diffusions of the complexed sample is about 6:1, since the initial polarization gradient is 7 (arbitrary units) and the residual polarization gradient signal after all intramolecular spin diffusion has taken place is 1. The spin diffusion curve of the complexed sample was fitted by the sum of the $^6/_7$ of the simulated intramolecular spin diffusion curve (from Figure 6) and $^1/_7$ of a simulated intermolecular spin diffusion curve using various domain sizes. The amplitude decrease of the intermolecular spin diffusion is about $^1/_6$ of the intramolecular spin diffusion, and the equilibrium time of the intermolecular spin diffusion is not very different from that of the intramolecular spin diffusion. Thus, it is difficult to separate the two. A domain size of 1.2 nm gave a good fitting, and the fitting becomes worse when the domain size is increased to 2 nm (see Figure 7). Thus,

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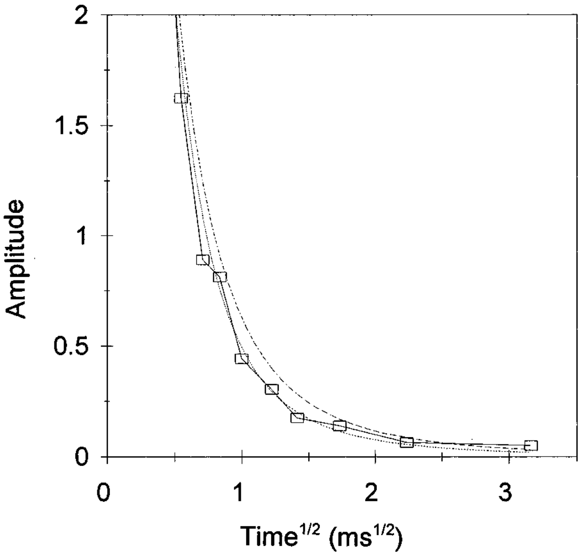

Figure 7. Plot of fitting the polarization gradient signal amplitude for the complexed sample. It is assumed that the dimensionality is one. The fitted lines are the summation of $^6/_7$ of the sample having a domain size of 0.8 nm and $^1/_7$ of the sample having domain sizes of 1.2 nm (dotted line) and 2.0 nm (broken dashed line).

the domain size obtained for the intermolecular spin diffusion (or the phase sizes in the complexed blend) should be between 1.2 nm and 2.0 nm. The maximum distances between protons in the structural unit of poly(NECMM) and poly(DNBEM) calculated using PCMOD are about 1.3 nm. Therefore, it can be concluded that poly(NECMM) and poly(DNBEM) in the complexed blend are mixed at a molecular level.

The spin diffusion curve of the decomplexed blend in Figure 5 does not go down to 0 but displays a plateau at about 0.7. Since the amplitude change between 0 and 1 results from intermolecular spin diffusion between poly(NECMM) and poly(DNBEM), the amplitude between 0 and 1 can be used to estimate the amount of intermolecular spin diffusion. Some 30% of the decomplexed blend reaches equilibrium between poly(NECMM) and poly(DNBEM) within 10 ms. The equilibrium time is almost the same as that of the complexed blend. Thus, 30% of the decomplexed blend must be mixed at molecular level.

At this stage, one must consider the intensity contribution from $T_1(H)$, which is not negligible during longer mixing times [compared to $T_1(H)$]. A phase cycling pulse was experimentally used to eliminate the added intensity from $T_1(H)$. Since the phase cycling pulse produces a decay of the overall intensity, the length of the mixing time is experimentally limited. If the domain sizes are relatively large, the decrease in the polarization gradient amplitude may take place over a longer time than that allowed by the $T_1(H)$ limitation. A simulated spin diffusion curve has shown that if the domain size is larger than 200 nm in one-dimensional phase structures (spin diffusion coefficient = 0.6 nm^2/ms), the amount of spin diffusion, measured there by the growth of the suppressed signal, is small.[8] Therefore, experimentally, the slow intensity changes due to spin diffusion and the changes due to $T_1(H)$ relaxation make it difficult to observe spin diffusion in larger domain sizes. The plateau of the decomplexed blend suggests that the domain size of the other 70% of the sample is probably greater than 200 nm and cannot be measured.

The decomplexed sample shows two intermolecular spin diffusion processes, one fast in about 30% of the sample and the other slow in the remaining 70% of the sample. The slow process is not shown in the figures presented here, but it does take place at mixing times of about 300 ms and higher. Obviously, at such long mixing times, the spin–lattice relaxation process begins to interfere significantly with the spin diffusion, and the spin diffusion cannot be properly analyzed. The weight ratio between poly(DNBEM) and poly(NECMM) is 52:48, and the phase structure of this sample is assumed to be one-dimensional based on the almost equal volumes of the two components. Thus, the decomplexed blend is probably composed of successive layers of polyD, interface (having mixed polyD and polyA) and polyA. The fast intermolecular spin diffusion rate can be assigned to the interfacial area and suggests that polyD and polyA are mixed there at the molecular level. The question now is what is the size of the interfacial area? The volume ratio between the interface and the separated phases should be about 3:7. If the size of the interface were of the order of 1 or 2 nm, the size of the other phases should also be just a few nanometers and the magnetization would reach equilibrium within 10 ms. However, the domain sizes of the decomplexed blend of poly(NECMM) and poly(DNBEM) should be larger than 200 nm, because the polarization gradient amplitude had the plateau at 0.7 and did not decrease more within the $T_1(H)$ measurement time. Since the estimated domain size of poly(DNBEM) and poly(NECMM) is larger than 200 nm, the interfacial size should be about 86 nm in thickness. This is a huge number and is not within the range of what one normally estimates for an interface. A possible explanation is related to the “special” nature of this blend. It is known that polyA and polyD can be mixed at the molecular level even in the solid state, by grinding the powders together. Decomplexed samples are also known to re-form the complexed blend if left for a long time at room temperature. This recomplexation process may be accelerated by spinning in the NMR spectrometer, due to relatively high pressures generated there. It is known that grinding the two polymer powders together produces enough pressure to generate complexation[12]. High-speed spinning in the rotor should produce a much higher pressure, probably favoring re-complexation. If this hypothesis is correct, then the “interface” is actually a third phase present in this system, and its size may slowly grow until it becomes the dominant phase.

These findings correlate well with the previous analysis of glass transition temperatures and proton spin–lattice relaxation time constants in the rotating frame.[13] Although the “interface” (or the “third, mixed phase”) appears to be large in the sample analyzed here, it is still much smaller than the polyD and polyA “pure” phases, and does not exhibit an intermediate Tg or $T_{1\rho}(H)$, as the complexed polyD–polyA blend does.[13] One should remember, though, that “annealing” at room temperature for months, as well as spinning in the rotor may cause re-complexation in a phase separated blend to some extent.

Conclusions

A ^{1}H CRAMPS experiment was used to study polymer blends of poly(DNBEM) and poly(NECMM). Poly(DNBEM) and poly(NECMM) are mixed at a molecular level in the complexed blend. The estimated intramolecular spin diffusion coefficient in each polymer is 0.40 nm^2 /ms. The decomplexed blend is phase-separated, with phase sizes exceeding 200 nm in length and has an "interface" volume which is some 30% of the total sample volume. The actual thickness of the interface cannot be measured, but it is estimated to be of at least 86 nm. Poly(DNBEM) and poly(NECMM) are mixed at the molecular level in the interfacial area.

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