^{13}C-Detected ^{1}H Spin Diffusion and ^{1}H Relaxation Study of Multicomponent Polymer Blends

Naira M. da Silva,[†,‡] **Maria Inês B. Tavares,**[‡] **and E. O. Stejskal**[*,†]

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695, and Instituto de Macromoléculas Prof. Eloisa Mano, Universidade Federal do Rio de Janeiro, RJ Brazil

Received May 20, 1998

ABSTRACT: The miscibility of two macroscopic phase separated polymers, a propylene−ethylene−diene terpolymer and an atactic polypropylene, has been investigated by a combination of several solid-state NMR techniques. Carbon-detected proton $T_{1\rho}$ and carbon-detected proton T_1 in systems conditioned by two-dimensional heteronuclear wide-line separation (WISE) were used. Both techniques are sensitive to spin diffusion between phases, with WISE being suited to making it stand apart from the basic relaxation process. These two techniques yield similar but different assessments of the presence and amount of phase separation present. This is not surprising considering that they involve different relaxation time scales, from milliseconds to seconds. An additional comparison is made with differential scanning calorimetry and xenon NMR results, which also address this problem. In addition, the WISE data permit an estimate of the aPP domain size.

Introduction

It is common to modify the properties and redirect the usefulness of many polymers by the use of plasticizers. Usually these plasticizers are small molecules, much smaller than the polymer molecules that they modify. Generally, they may be thought of as dissolving in the polymer or at least taking up residence in regions where free volume is found. If they form a well-defined second phase, there may be a problem with the stability of the mixture. However, plasticizers can also be polymeric or at least oligomeric molecules. Such additives may be used to form a uniform polyblend in which the final properties are in some way average properties of the two constituents. More commonly, the polymeric additives will be chosen to form a second phase or to interact with a system that is already multiphase. Thus, a polymer can act as a surfactant if it bridges the interface between two phases, or it can create multiple, interacting phases if it only partially dissolves in the host polymer. The role of surfactant can be well portrayed by a suitable block copolymer. The interactive filler polymer may be a homopolymer. Polymers are added to asphalt to improve its properties and to obtain better adhesion to aggregates for road building. Elastomers are particularly sensitive to modification by nonmiscible polymeric additives. Depending on the application, say in road building, price may be an important consideration in the choice of additive. A reliable method for screening the properties of different additives and understanding out why they work as they do is useful. NMR studies can be an important means to that understanding.

Most polymer blends are not thermodynamically stable.[1] Given enough time, the internal molecular disorder of the polymer systems will eventually result in phase separation on a macroscopic scale. Before this happens, a heterogeneous system may possess many interesting mechanical properties particularly when the

dynamical heterogeneities are on the range of a few tens of nanometers.[1,2]

A variety of thermoanalysis techniques have been applied to the determination of polymer blend miscibility as well as microscopy and some special diffraction and spectroscopic techniques. However, these methods do not yield comprehensive information about the scale of the molecular mobilities. The differential scanning calorimetry (DSC) technique, which is the most commonly performed, only indicates phase domains smaller than 10 nm. One purpose of this paper is to compare these methods with a variety of NMR methods for this identification and also compare the different NMR methods themselves.[3,4]

Solid-state NMR provides a way to measure sizes of structural inhomogeneities (domains) down to a molecular size scale. These methods are all based on proton spin diffusion. In the usual spin-diffusion experiment, differences in proton $T_{1\rho}$'s (or other relaxation times) of a multicomponent system are influenced by the short-range spatial proximity between protons and therefore able to distinguish the degree of intimacy of a mixture of polymer chains.[5−10] More recently, domain sizes have been estimated from a spin-diffusion experiments in which tailored spin-polarization gradients are generated and the polarization gradients subsequently monitored as spins return to equilibrium.[11−16]

Another recently developed tool to reveal the local environment in polymer blends is ^{129}Xe NMR.[17] In this technique, use is made of the fact that the xenon chemical shift is highly sensitive to the local environment, especially the free volume.[18,19] With xenon absorbed in a phase-separated two component blend, two lines will be seen if the phases are different enough. In addition, it may be possible to obtain diffusion coefficients (exchange rates) for absorbed xenon if domain sizes are small enough.[20−23]

In this paper we will focus on a modified interpretation of the heteronuclear two-dimensional wide-line separation (2D-WISE) experiment to obtain information about spin diffusion within a nanophase-separated

[†] North Carolina State University.
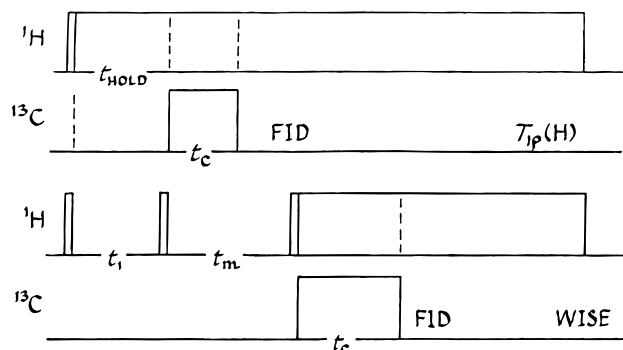[‡] Universidade Federal do Rio de Janeiro.

Figure 1. Two cross-polarization pulse sequences for the detection of spin-diffusion: (top) the sequence to measure the proton rotating frame relaxation time $T_{1\rho}$; (bottom) the 2-D WISE-NMR experiment.
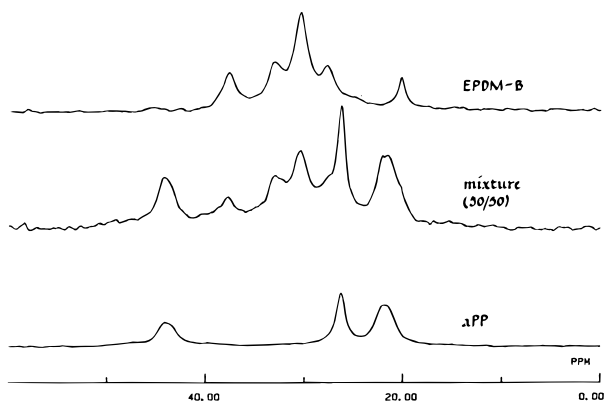

Figure 2. The 50 MHz CPMAS ^{13}C NMR spectra of pure EPDM-B, pure aPP, and a 50/50 blend of EPDM-B and aPP.

polymer blend, ethylene—propylene—diene terpolymer (EPDM), and atactic polypropylene (aPP), to estimate domain size.

Experimental Section

Binary polymer blends consisting of atactic polypropylene (aPP) (supplied by Polibrasil S.A, Brazil) and two different ethylene propylene-diene terpolymers (EPDM-A and EPDM-B) (supplied by Nitriflex S.A, Brazil) were used. The molecular weight distribution (M_W/M_N) of the samples was determined by GPC (2.8 for EPDM-A, 11.8 for EPDM-B and 3.6 for aPP). The blending was obtained by processing EPDM/aPP mixtures in a Haake S40 plastograph, at 120 °C.

A Chemagnetics CMC200S, 200 MHz solid-state NMR spectrometer with a Chemagnetics wide-bore magnet was used for all the NMR experiments. The cross-polarization pulse sequences used in the experiments are shown in Figure 1. All the observations were on ^{13}C at 50.1 MHz. A proton rf field of 50 kHz was employed throughout the experiments. The magic angle spinning speed was of the order of 3 kHz. Spectral width was 300 ppm (15 kHz).

Results

CPMAS Spectra. Figure 2 illustrates representative CPMAS spectra of EPDM-B, aPP, and the EPDM-B/aPP 50/50 blend. EPDM yields a ^{13}C spectrum with lines near 38, 33, 30, 28, and 20 ppm relative to TMS, while the aPP groups have their resonance lines at 44, 26, and 22 ppm. The magic-angle ^{13}C lines of the EPDM-B/aPP blends have slightly different line shapes compared to those of the corresponding pure polymers. Furthermore, the CH_3 carbon resonances are largely overlapped and the CH/CH_2 resonances are partially overlapped in the blend. At room temperature, both pure

aPP ($T_g = -16$ °C) and EPDM ($T_g = -50$ °C) are above their glass transition temperatures T_g and therefore present a high mobility with EPDM more mobile than aPP. Above T_g, conformational exchanges and rotational diffusion are not frozen on the time scale of the NMR measurements, and this is reflected by the relatively good resolution in the carbon-13 spectra.

Proton $T_{1\rho}$ Experiment. In earlier studies of these systems using the traditional DSC techniques, EPDM/aPP blends appear to be homogeneous up to 50% of aPP in the blend, but this does not necessarily imply homogeneity of the blend on a nanometer scale.[4] In another study we report observations from ^{129}Xe experiments which clearly indicated that in EPDM/aPP blends are homogeneous only up to 30% aPP.[24]

A first experimental NMR approach was to examine the usefulness of the proton spin—lattice relaxation time $T_{1\rho}$ in the rotating frame for the characterization of the individual components of EPDM/aPP blends. Carbon-resolved proton $T_{1\rho}$ relaxation can be characterized by matched spin-locked, cross-polarization transfer experiments as shown in the sequence in Figure 1. After the initial, rapid buildup of carbon polarization, the carbon signal tracks the polarization in the proton reservoir and thus follows its decrease via the proton $T_{1\rho}$ process.[6-9] Since proton $T_{1\rho}$ is sensitive to molecular motions in the mid-kilohertz frequency range and also sensitive to proton spin diffusion, we expect that changes in this parameter detected for the EPDM/aPP blend can be discussed in terms of incomplete spin diffusion and phase separation.[8] Proton $T_{1\rho}$'s were determined from relaxation curves with 12 data points (t_{hold} values), each replicated 500 times. The results for the pure polymers and various blends of EPDM-B/aPP are listed in Table 1. Results for EPDM-A are similar.

The pure polymers EPDM and aPP clearly have different relaxation rates which arises primarily from a difference in molecular motion. In the EPDM/aPP blends, the proton $T_{1\rho}$'s observed through the 38, 33, and 30 ppm lines (see EPDM average) are approximately the same as the EPDM $T_{1\rho}$ in the pure EPDM polymer which suggests that much of the EPDM is well phase separated from aPP and spin diffusion is efficient enough within the EPDM phase to give it the appearance of a single relaxation time. The small drop that occurs on going from pure EPDM to blend probably indicates a slight slowing of motion in the EPDM caused by the presence of the incompatible domains of aPP. The influence of the boundary with aPP is not felt by the EPDM which relaxes quickly enough not to benefit much from outside. On the other hand, the aPP shows evidence of communication with the EPDM phase since there is a pulling of the aPP rate toward that of EPDM as EPDM concentration increases. There are probably two reasons why EPDM affects aPP more than aPP affects EPDM. First, EPDM is a much better source of relaxation. Second, the aPP phase may be of smaller extent. These results suggest that the phases are separated but that there is some communication between spins in the two components.

It is instructive to compare these observations with those that can be made in a system in which it is possible to follow how two clearly different phases each influences the other by means of communication throughout the entire relaxation process.[8] Ideally, relaxation of each phase begins as if the other were not there and then alters its relaxation decay until both phases are

Table 1. ^{13}C-Detected, Proton $T_{1\rho}$/ms (at 50 kHz) for Various Blends of EPDM-B and aPP, as a Function of Chemical Shift^a

W/W ratio EPDM/aPP	EPDM 38 ppm	EPDM 33 ppm	EPDM 30 ppm	aPP 44 ppm	aPP 26 ppm	EPDM average	aPP average
100/0	3.2	3.0	3.0			3.1	
90/10	2.4	2.6	2.7	5.0	4.0	2.6	4.5
70/30	2.7	2.6	2.4	(11.1)	6.0	2.6	6.0
60/40	2.7	2.5	2.7	(17.1)	7.6	2.6	7.6
50/50	3.0	2.9	2.6	10.4	9.1	2.8	9.8
30/70	3.8	2.8	2.2	11.7	11.0	2.9	11.3
0/100				18.2	18.3		18.2

^{a} Data in parentheses are unreliable, excessive scatter.

relaxing at the same, intermediate rate. The point of changeover is determined by the strength of the cross-relaxation process relative to the two different relaxation processes.

These systems and many others do not allow such a clean interpretation. First there are the experimental limitations of this study. Broad, overlapping lines and finite instrument time limited the precision with which the details of the relaxation process could be determined. Under the best of circumstances it is difficult to characterize multiple relaxation processes with meaningful certainty. Here we were limited to estimating a single first-order relaxation time for each decay. This time then becomes more of a qualitative assessment of the amount of communication between the phases. We follow the relaxation far enough that the effects of cross-relaxation can make itself felt but not nearly far enough that the final phase of the relaxation, when all phases relax at the same rate, can be characterized. In interpreting data with these limitations, we, nevertheless, allow ourselves to be guided by the features of the ideal two-phase relaxation process.

There is a second complication present in our study. The model which we are trying to argue for is one in which one phase, the EPDM, is pure and of large extent. By contrast, the aPP is not so much a separate pure phase as a separating region between the EPDM domains. It is probably not nearly as pure as the EPDM. Thus, the system is only approximated by the idealized two-phase model. Add to that the fact that pure EPDM relaxes much faster than aPP, and it becomes clear why EPDM is seen to influence aPP while the reverse is not so easily seen.

The uncertainties in the interpretation of a system of this complexity are expected to be found in most mixed phase systems. The compromises that have been made will have to be made where a large number of relaxation processes are assembled for comparison. Since we do not have the comfort that comes from being able to describe the multiple cross-relaxation processes in detail, there is always a chance that the changes we see are not entirely from communication between phases but also involve altered rates of relaxation from other causes. Ultimately, the believability of the model depends on how well it fits all the facts together.

WISE Experiment. Estimation of the Spin-Diffusion Rate Constant. The pulse sequence for the 2D-WISE experiment shown in the Figure 1 consists of three 90° pulses applied in the proton channel followed by a CP transfer to the carbon system.[11] The first pulse flips the magnetization into the $x-y$ plane. During a time, t_1, the magnetizations in regions with different T_2's (spin−spin relaxation times) dephase with different relative rates. At an appropriate delay, t_1, the magnetization of a rigid domain may be lost completely while

the magnetization of mobile domain is barely affected. A second pulse applied after a time t_1 brings the remaining magnetization back to the z-direction, and is then followed by a mixing time t_m, during which the overall magnetization is allowed to approach equilibrium via spin−lattice relaxation in the laboratory frame.[11,12] The final part of the sequence monitors the resulting magnetization by spin locking it for CP transfer to the carbon system for observation. Thus, an abnormal (and somewhat controllable) polarization can be created for the start of the mixing time. The WISE technique only works properly if different domains in the sample have significantly different spin−spin relaxation times (T_2) and also when T_1 is long enough compared to the mixing (cross-relaxation) process between the domains.[12] The 2D-WISE technique described in this paper was chosen because of the sensitivity of the technique to show spin-diffusion rates in the EPDM/aPP system. It works because of the fact that different phases in these two polymers have significantly different proton spin−spin relaxation times and some interphase communication, at least at the phase boundary.

To examine the ability of WISE to identify and characterize phase separation, we selected two systems: 50/50 EPDM-A/aPP, which seems clearly phase separated, and 90/10 EPDM-B/aPP, which shows little evidence for phase separation in most studies.

Beginning with the 50/50 EPDM-A/aPP system, we first chose to use WISE to characterize the proton T_1 process for the two components of this system This is done by choosing t_1 long enough (10 ms, in this case) to eliminate any $x-y$ component of magnetization following the first pulse. Then the second pulse serves to dispatch any z component of magnetization that may have built up during t_1. The evolution during t_m is a simple T_1 recovery following a saturating 90° pulse. These results are shown in Figure 3, where we have plotted the difference between the individual intensities and the asymptotic value at long time. We are clearly in a phase-separated system since the two different phases, observed by means of the carbon system, have different relaxation behavior. The initial slopes for aPP and EPDM-A correspond to T_1 of 700 and 300 ms, respectively.

The situation changes when we choose $t_1 = 40$ μs. This time is short enough that most of the EPDM-A polarization in the $x-y$ plane is still available to be put back into the z direction. For the same time, the aPP polarization has already been lost. The evolution that begins the t_m period now has a quite different starting point: aPP has been saturated while EPDM-A is nearly at its equilibrium value in the z direction. We see, in Figure 4, that the character of the recovery toward equilibrium has been changed. The solid lines drawn on this figure were transferred from Figure 3, with
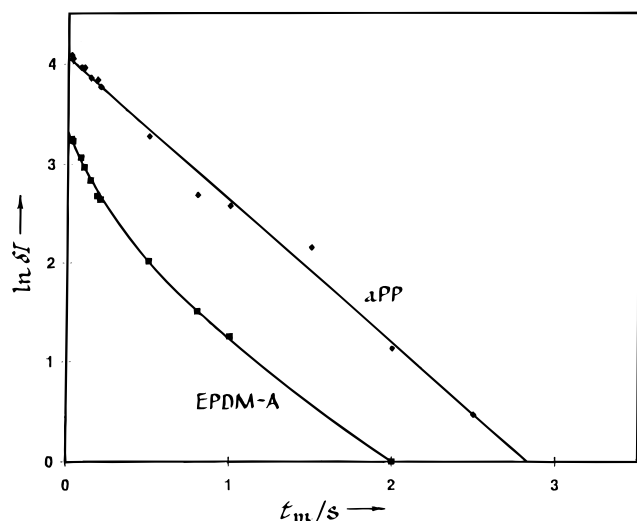
Figure 3. Carbon detected proton relaxation in a 50/50 blend of EPDM-A and aPP (WISE experiment with $t_1 = 10$ ms).
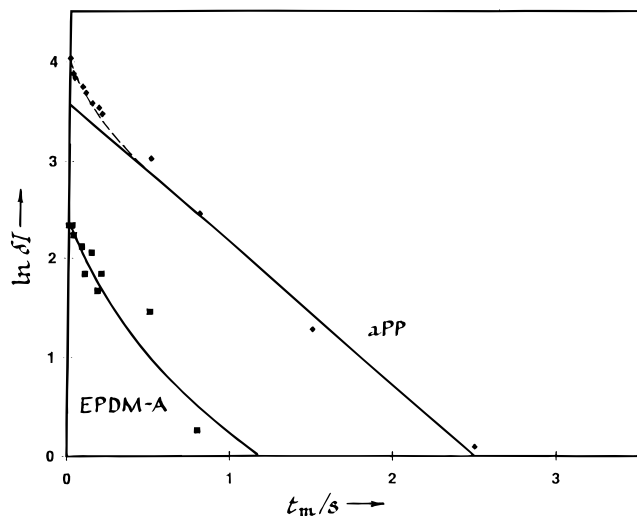

Figure 5. Return to equilibrium for two individual components in a 90/10 blend of EPDM-B and aPP (WISE experiment with $t_1 = 40$ μs).

Figure 4. Carbon detected proton relaxation in a 50/50 blend of EPDM-A and aPP (WISE experiment with $t_1 = 40$ μs).

vertical adjustment to account for the fact that EPDM-A began much closer to equilibrium. Clearly, the recovery of the aPP toward equilibrium has benefited from its ability to communicate, by cross-relaxation, with nearly fully polarized EPDM-A. The additional relaxation seen in Figure 4 (dashed line) corresponds to a process with time constant ~170 ms. We attribute this to communication between part of the aPP phase and the EPDM-A phase. As with the $T_{1\rho}$ results, only the more slowly relaxing aPP seems to benefit from proximity to the EPDM-A, which is itself not affected. Note that, to be able to see this communication, we require a process slower than the underlying relaxation process. In this system, with its weak communication, we nearly missed it and can only properly interpret the process when WISE provides a comparison with the conventional T_1 process. We get similar results in EPDM-B samples of similar composition.

It must be emphasized that this is not a conventional use of the WISE sequence. We have used it merely to control the starting points of the T_1 recoveries of the two identifiable domains in our sample. In this way we could find a starting point that would amplify the effects of cross-relaxation and make it easier to identify. Conventional 2D-WISE correlates the proton line width
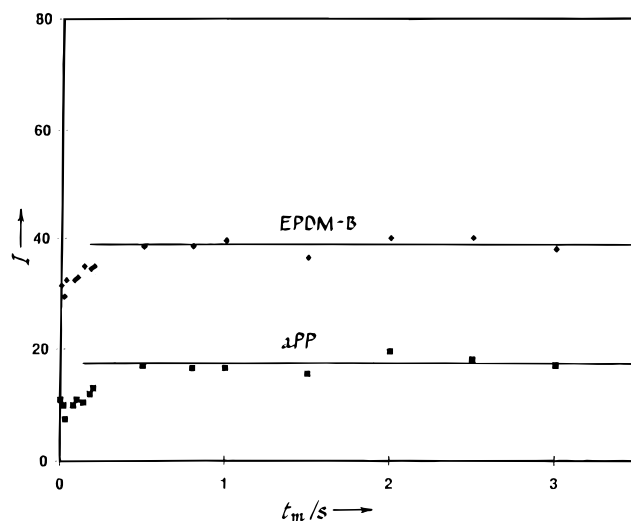
with the individual carbon resonances. Communication is seen as the extension of the mixing time t_m blurs the separation by proton line width. This is a powerful experiment, but it requires that far more data be collected. The method we have used gets some of the same information at a considerable saving of time.

Only the $T_{1\rho}$ data on 90/10 EPDM-B/aPP suggest that there may be some phase separation. Figure 5 shows the raw data for a WISE recovery. We tried to discriminate against aPP by using $t_1 = 40$ μs but did not succeed very well. This material is more rubbery than the others. The recovery process during t_m is indistinguishable between the two components and is characterized by a time constant ~200 ms. On this time scale, it appears that we have a single phase. As remarked before, even on the time scale of $T_{1\rho}$, times the order of 5 ms, it is hard to see independent phase behavior for this rubbery material.

Estimating Domain Size. The WISE results for the 50/50 blend of EPDM-A and aPP suggest that the EPDM-A phase is able to assist the recovery of the aPP by supplying polarization to that phase. Furthermore, this process takes place with a time constant of ~170 ms. The following calculation can make a crude estimate of the aPP domain sizes. From the literature of diffusion we have identified an expression for diffusion into a spherical domain of radius a initially void of the diffusing species.[25] A simplified, asymptotic form of this expression is

$$M(t) = M_0[1 - \exp(-D\pi^2 t/a^2)] = M_0[1 - \exp(-t/\tau)]$$

where M and M_0 represent the instantaneous and equilibrium amounts of magnetization contained in the domain, respectively, and D represents the diffusion constant for the magnetization. We have also written $\tau = a^2/\pi^2 D$ to represent the time constant for filling the domain, from which $a = \pi(D\tau)^{1/2}$ yields an estimate of the domain size. Another geometry will result in a similar, dimensionally equivalent expression.[12,14] We estimate $a = 13$ nm from $\tau = 170$ ms and $D = 0.1$ nm^2 ms, taken from the literature,[12] in lieu of a better order of magnitude estimate. This calculation is based on the idea that aPP has very little polarization at the start of the t_m evolution. This estimate is a lower limit, because

some of the aPP polarization is not affected by the choice of initial conditions.

Conclusion

Two different solid-state NMR methods have been used to investigate the intimacy of mixing within nonmiscible polymer blends. In this study, these two NMR techniques agree with each other to a degree but also clearly see phase separation in the EPDM/aPP system from different points of view. Proton $T_{1\rho}$ data indicate that there is some phase separation with communication in all of the blends we studied although that separation seems to be fading and the effectiveness of communication increasing at the smallest concentrations of aPP. On the other hand, the WISE data showed two phases with some communication between them in the middle range of concentration where the discrimination based on T_2 was effective. At the smallest concentrations of aPP, where the T_2 difference was absent, there was no trace of evidence of phase separation detected by T_1 or the WISE experiment. This difference between the two methods is not unexpected because of the different time scales inherent in the two methods: milliseconds for the $T_{1\rho}$ experiments and seconds for the WISE experiment. At the same time, spin diffusion will not necessarily be identical for both the T_1 and $T_{1\rho}$ processes. It will not be exactly the same since the coupling between spins in the rotating frame is half that in the laboratory frame. More importantly, it is likely that more than one motion and more than one correlation time are involved in the spin diffusion processes. If $T_{1\rho}$ fails to see communication between phases, it may be because it does not allow enough time for that communication to make itself known. If WISE does not detect phase separation, it may be because it allows too much time for the phases to communicate and present an averaged appearance. Most of the blends we have studied fall conveniently between these two extremes. Cross-relaxation is slow enough that we only see it beginning to perturb the $T_{1\rho}$ measurement. At the same time, it is fast enough that we would not be able to identify its effect on T_1 relaxation without the control of the initial conditions afforded by the WISE experiment. Between the two techniques there is greater probability that evidence for phase separation will be seen. Xenon data and DSC data provide two additional different but corroborating views of phase separation in this system. Xenon results show phase separation from 30% aPP, and higher, but do not detect communication between domains. DSC measurements do not detect the presence of phase separation until the concentration of aPP reaches 50%.

The conclusion we reach is that, in trying to characterize phase separation and communication in a blend of immiscible polymers, the more different points of view that can be obtained, the fuller the picture of the phase separation is likely to be.

References and Notes

(1) Dickie, R. A. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 1, p 353.
(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer−Polymer Miscibility*; Academic Press: New York, 1979.
(3) Kroschwitz, J. I. *Polymers: Polymer Characterization and Analysis*; John Wiley & Sons: New York, 1990; p 856.
(4) Silva, N. M.; Ferreira, M. I. P.; Tavares, M. I. B. *Polym. Test.* **1995**, *14*, 329.
(5) Bovey, F. A. *High-Resolution NMR of Macromolecules*; Academic Press: New York, 1972.
(6) Schaefer, J.; Stejskal, E. O.; Buchdahl. R. *Macromolecules* **1977**, *10*, 384.
(7) Fyfe, C. A. *Solid State NMR for Chemists*; C. F. C. Press: Guelph, Ontario, Canada, 1983.
(8) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.
(9) Silva, N. M.; Tavares, M. I. B. *Polym. Bull.* **1995**, *35*, 165.
(10) Schmidt-Rohr, K.; Clauss, J.; Blümich, B.; Spiess, H. W. *Magn. Reson. Chem.* **1990**, *28*, 3.
(11) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: Ltd.: London, 1994; p 408.
(12) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.
(13) Goldman, M.; Shen, L. *Phys. Rev.* **1960**, *144*, 321.
(14) Campbell, G. C.; Vanderhart, D. L. *J. Magn. Reson.* **1992**, *96*, 69.
(15) Eckman, R. R.; Henrichs, P. M.; Peacock, A. J. *Macromolecules* **1997**, *30*, 2474.
(16) Fiebel, S.; Harris, R. K.; Kenwright, A. M. *Magn. Reson. Chem.* **1997**, *35*, 290.
(17) Walton, J. H.; Miller, J. B.; Roland, C. M.; Nagode, J. B. *Macromolecules* **1993**, *26*, 4052.
(18) Kennedy, G. J. *Polym. Bull.* **1990**, *23*, 605.
(19) Bartik, K.; Luhmer, M.; Heyes, S. J.; Ottinger, R.; Reisse, J. *J. Magn. Reson.* **1995**, *B109*, 164.
(20) Mansfield, M.; Veeman, W. S. *Chem. Phys. Lett.* **1994**, *222*, 422.
(21) Simpson, J. H.; Wen, W. Y.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1996**, *29*, 2138.
(22) Walton, J. H. *Polym. Polym. Compos.* **1994**, *2*, 35.
(23) Junker, F.; Veeman, W. S. *Macromolecules* **1998**, *31*, 7010.
(24) Morgan, D. R.; Silva, N. M.; Tavares, M. I. B.; Stejskal, E. O., private communication.
(25) Crank, J. *The Mathematics of Diffusion*; Oxford at the Clarendon Press: 1956; Chapter VI, p 87.

MA980798V