Determination of Domain Sizes in Compatibilized Polystyrene−(Ethylene-Propylene Rubber) Blends by Measurements of ^{1}H Spin Diffusion

Kevin S. Jack, Almeria Natansohn,* and Jiahu Wang

Department of Chemistry, Queens University, Kingston, Ontario, Canada K7L 3N6

Basil D. Favis and Patrick Cigana

Centre de recherche appliquée sur les polymères, Ecole Polytechnique de Montréal,
Montréal, Québec, Canada H3C 3A7

Received October 10, 1997. Revised Manuscript Received January 26, 1998

The size of domains in a series of compatibilized polystyrene−(ethylene-propylene rubber) blends were measured by solid-state NMR spin diffusion measurements. The average diameter of ethylene propylene rubber (EPR) particles in the blends was observed to decrease as the concentration of interfacial agent was increased up to ca. 15% (weight/volume of EPR) and remained constant upon further addition of interfacial agent. Comparison of the domain sizes obtained from NMR measurements with those obtained from scanning electron microscopy measurements suggests that the NMR technique can be used to confirm large-scale phase separation and investigate the trends in domain sizes in immiscible blends. It was found, however, that in these blends the spin diffusion is slow due to the large size of the domains; as a consequence the uncertainty of the size obtained from ^{1}H spin diffusion is fairly large. It was also found that mechanical grinding of the NMR samples can produce changes in the phase structure of the blends.

Introduction

Polymer blends comprised of rubbery and glassy polymers have been of commercial importance for many decades. For example, it is well known that the addition of a small amount of a rubber to a glassy polymer can lead to an improvement of the impact properties of the blends in comparison with those of the pure glassy homopolymer, e.g., high-impact polystyrenes [polystyrene−(styrene-butadiene rubber) blends] and polycarbonate−(acrylonitrile-butadiene-styrene rubber) blends. It is also widely known that these impact-modified blends adopt a phase-separated morphology, in which the rubbery component is dispersed in a glassy matrix and that the mechanical properties of these blends strongly depend on the sizes of the dispersed-phase particles and the strength of adhesion between the phases in the blends. These factors can be controlled to some extent by varying the chemical nature of the rubbery component and/or the composition of the blend; however, it is often found that a significant improvement of the mechanical properties can be more readily achieved by the addition of a compatibilizer or interfacial agent. In order to predict and/or control the desired properties of compatibilized blends it is important to be able to quantify the effects that the addition of interfacial agents have on the morphology of the blends.

Solid-state NMR measurements of ^{1}H spin diffusion have been shown to be a powerful and convenient technique for probing the phase structure in multiphase polymer systems.[1−9] From NMR measurements it is possible to quantify both the average size of domains and interfacial thickness in polymeric materials, and very importantly, no prior modification of the materials is required for this technique. In the past decade, the investigation of the morphology of multiphase polymer systems by ^{1}H spin diffusion has become an active field of research. Recent examples of investigations of the phase structure of semicrystalline polymers,[4] polymer blends,[8,10,11] block copolymers,[6,12,13] and core-shell latexes[14−16] can be found in the literature.

Direct measurements of ^{1}H spin diffusion can be obtained by monitoring the redistribution of ^{1}H magnetization within a blend, following the selective excitation of magnetization in one of the phases.[7] For

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(1) Caravatti, P.; Neuenschwander, P.; Ernst, R. R. *Macromolecules* **1986**, *19*, 1889.

(2) Goldman, M.; Shen, L. *Phys. Rev.* **1966**, *144*, 321.

(3) Cheung, T. T. P.; Gerstein, B. C.; Ryan, L. M.; Taylor, R. E.; Dybowski, C. R. *J. Chem. Phys.* **1980**, *73*, 6059.

(4) Demco, D. E.; Johansson, A.; Tegenfeldt, J. *Solid State NMR* **1995**, *4*, 13.

(5) Packer, K. J.; Pope, J. M.; Yeung, R. R.; Cudby, M. E. A. *J. Polym. Sci. Polym. Phys. Ed.* **1984**, *22*, 589.

(6) Clauss, J.; Schmidt-Rohr, K.; Spiess, H. W. *Acta Polymer.* **1993**, *44*, 1.

(7) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Soid-State NMR and Polymers*; Academic Press: London, 1994; pp 402−439 and references therein.

(8) VanderHart, D. L.; McFadden, G. B. *Solid State NMR* **1996**, *7*, 45.

(9) VanderHart, D. L. *Makrmol. Chem. Macromol. Symp.* **1990**, *34*, 125.

(10) VanderHart, D. L.; Manley, R. S. J.; Barnes, J. D. *Macromolecules* **1994**, *27*, 2826.

(11) VanderHart, D. L. *Macromolecules* **1994**, *27*, 2837.

(12) Cho, G.; Natansohn, A.; Ho, T.; Wynne, K. J. *Macromolecules* **1996**, *29*, 2563.

(13) Cai, W. Z.; Schmidt-Rohr, K.; Egger, N.; Gerharz, B.; Spiess, H. W. *Polymer* **1993**, *34*, 267.

S0897-4756(97)00670-4 CCC: $15.00

multiphase polymers comprised of hard and soft phases, e.g., impact-modified blends, the Goldman−Shen[2] or "dipolar-filter"[17] pulse sequences are, arguably, the simplest and most suited NMR methods for measuring ^{1}H spin diffusion. In both of these pulse sequences, the initial selection of magnetization is based on differences in the molecular mobility (specifically differences in ^{1}H T_2) of the phases. Quantitative measurements of the size of domains and interfacial thickness in the polymers systems are obtained either by simulations of the experimental diffusion curves[6,18] or from approximate theories.[6,19]

Favis et al. have done extensive work in establishing the relationships between the phase size and interfacial state of immiscible polymer blends. The emulsification curve, which relates the dispersed-phase particle size to the amount of interfacial agent added to the blend, has proven to be a powerful tool for evaluating the efficacy of an interfacial agent for a given interface.[20] One of the systems investigated was a blend of polystyrene (PS) and ethylene-propylene rubber (EPR), a random copolymer of ethylene and propylene. It was shown that triblock[21] and diblock[22] copolymers of PS and hydrogenated polybutadiene were effective emulsifiers for the PS-EPR system. One of the interfacial modifiers investigated was a PS-*b*-(hydrogenated butadiene) diblock copolymer (SEB). This modifier was used to emulsify a blend comprising 80 vol % PS and 20 vol % EPR. In this paper, solid-state NMR measurements of ^{1}H spin diffusion are used to investigate the phase structure of the same PS-EPR-SEB blend system. As the phase structure of these blends has previously been investigated by scanning electron microscopy (SEM),[22] the information obtained by the two techniques will be directly compared.

As mentioned above, a number of quantitative investigations of the phase structure of polymer blends and copolymers using ^{1}H spin diffusion techniques have been published in the past few years. These investigations have primarily been concerned with polymer systems in which the size of the dispersed phase is of the order of a few nanometers to tens of nanometers. Although spin diffusion measurements in an immiscible blend have previously been reported,[6] no systematic investigations by NMR spectroscopy of blends in which large-scale separation of the phases occurs have been reported. In this work the size of domains that are investigated are ca. 1 order of magnitude larger than those which are thought to be suited to measurements by ^{1}H spin diffusion.[7] The applicability of NMR measurements of ^{1}H spin diffusion for studying the domain structure of immiscible blends is, therefore, also discussed here.

Scheme 1. Chemical Structures of PS, EPR, and CAP4741

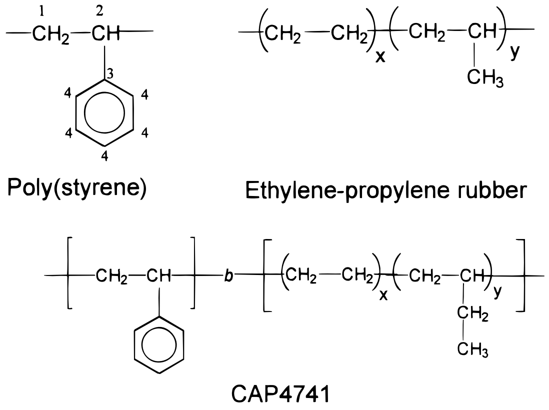

Table 1. Some Physical Properties of the Materials Investigated in This Work

material	M_n (g/mol)	M_w/M_n (g/mol)	T_g (°C)
PS	125 000	2.20	108
EPR	69 000	2.51	−38
CAP4741	67 000		

Experimental Section

Materials. The polymer blends investigated in this work are based on blends containing 80 vol % of polystyrene, supplied by Dow Chemicals (Styron D685), and 20 vol % of ethylene-propylene rubber, supplied by Exxon Chemicals (Vistalon V-504); see Scheme 1. EPR is a random copolymer containing 54 wt % of ethylene. The interfacial agent (CAP4741) investigated in this work is a pure diblock copolymer comprising of 30 wt % PS and 70 wt % of hydrogenated butadiene, supplied by Shell Chemicals. The molecular weight and glass transition temperatures of these polymers are presented in Table 1.

Sample Preparation. PS-EPR blends containing from 0−30% of CAP4741, were produced by mixing in a Brabender mixer, as described elsewhere.[22] The concentration of CAP4741 in each of the blends is expressed in terms of the mass of CAP4741 per volume of the EPR phase. Thus a blend containing 30% CAP4741 contains 30 g of CAP4741 per 100 mL of EPR, which is equivalent to 30 g per 500 mL of PS-EPR.

Samples for NMR measurements were prepared by cutting the blended polymer into very small pieces (ca. 2−3 mm) with a knife. Additionally, a second series of samples was prepared by grinding pieces of the blended polymer in a ball mill for ca. 30 min at room temperature. The mechanically ground samples are referred to as the "milled samples" in this work. The consistency of these samples was that of a powder with particle dimensions of hundreds of micrometers. Unless otherwise stated, the NMR measurements presented in this paper were obtained for the unmilled samples.

^{13}C NMR spectroscopy. ^{13}C cross polarization magic angle spinning (CPMAS) NMR spectra were collected on a Bruker ASX-200 spectrometer, operating at 50.3 MHz. Spin-locking field strengths of 64 kHz ($\pi/2$ pulse time = 3.9 μs), cross polarization times of 1 ms, and MAS spinning rates of 3.3 kHz were used in the acquisition of all of the ^{13}C NMR spectra reported in this work. All spectra were recorded at 297 K.

^{1}H T_1 relaxation times were measured via cross polarization to ^{13}C using an inversion-recovery pulse sequence. Each ^{1}H T_1 experiment consisted of the measurement of 16 separate recovery times, and the recycle delay between acquisitions was 8.0 s.

^{1}H spin diffusion measurements were obtained via cross polarization to ^{13}C using the dipolar filter pulse sequence,[17] shown schematically in Figure 1. A gradient of ^{1}H magnetization is initially created by the "selection" portion of the pulse sequence which consists of 12 $\pi/2$ pulses (3.9 μs pulse time)

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[14] Landfester, K.; Boeffel, C.; Lambla, M.; Spiess, H. W. *Macromolecules* **1996**, *29*, 5972.

[15] Spiegel, S.; Landfester, K.; Lieser, G.; Boeffel, C.; Spiess, H. W.; Eidam, N. *Macromol. Chem. Phys.* **1995**, *196*, 985.

[16] Landfester, K.; Spiess, H. W. *Macromol. Rapid Commun.* **1996**, *17*, 875.

[17] Egger, N.; Schimdt-Rohr, K.; Blumich, B.; Domke, W.-D.; Stapp, B. *J. Appl. Polym. Sci.* **1992**, *44*, 289.

[18] Wang, J. *J. Chem. Phys.* **1996**, *104*, 4850.

[19] Cheung, T. T. P.; Gerstein, B. C. *J. Appl. Phys.* **1981**, *52*, 5517.

[20] Favis, B. D. *Polymer* **1994**, *35*, 1552.

[21] Matos, M.; Favis, B. D.; Lomellini, P. *Polymer* **1995**, *36*, 3899.

[22] Cigana, P.; Favis, B. D.; Jerome, R. *J. Polym. Sci. Polym. Phys.* **1996**, *34*, 1691.

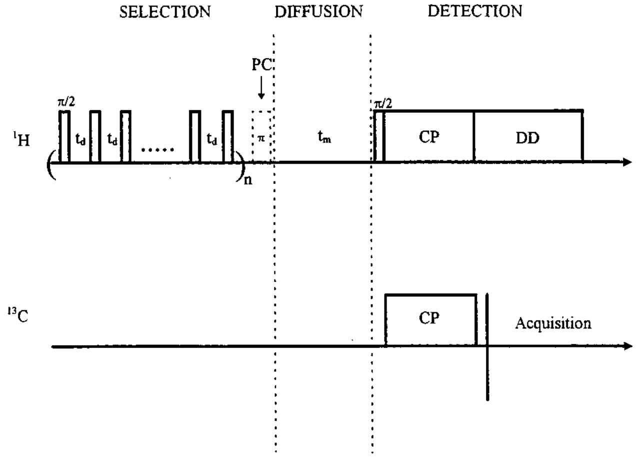

Figure 1. Schematic representation of the dipolar filter pulse sequence. For the experiments in this work $t_d = 16$ μs and $n = 7$. PC represents the phase cycling used to suppress T_1 relaxation effects (see ref 6).

separated by short delays. An interpulse delay of 16 μs and 7 repetitions of the first 12 pulses of the pulse sequence were used to completely eliminate the ^{1}H NMR signal due to the rigid PS phase. The dipolar filter experiments used to measure ^{1}H spin diffusion in the blends comprised of 16 individual mixing times ranging from 500 μs to 500 ms. For each mixing time ca. 3000 transients were collected with a recycle delay of 2 s. Furthermore, errors due to small changes in experimental conditions (e.g., small changes in the tuning characteristics of the probe) during the spin diffusion experiments were minimized by collecting the NMR signal for each mixing time in blocks of 256 transients.

Results and Discussion

Scanning Electron Microscopy. The morphologies of the PS-EPR-CAP4741 blends investigated in this work have previously been investigated by scanning electron microscopy.[22] All of the blends where shown to adopt a morphology which consists of spherical EPR particles dispersed in a PS matrix. The average diameter of EPR particles in the blends was observed to decrease upon addition of CAP4741 up to a loading of ca. 20% CAP4741 (wt/vol EPR), and no significant decrease in the average EPR particle size upon further addition of CAP4741 was observed (see Figure 7 in this paper). The surface-average EPR particle size, as determined by SEM, in PS-EPR blends ranges from 1.8 μm in the uncompatibilized blend to ca. 0.5 μm in blends containing more than 20% CAP4741.

^{13}C NMR Spectra. Figure 2 shows the ^{13}C CPMAS spectra of PS, EPR, and a PS-EPR blend containing 80 vol % of PS. The peak labels on the spectra are consistent with those presented in Scheme 1. Comparison of the ^{13}C NMR spectrum of the PS-EPR blend with those of the homopolymers shows no evidence for intimate mixing of the homopolymer chains, i.e., the ^{13}C CPMAS spectrum of PS-EPR can be constructed by addition of the ^{13}C CPMAS spectra of the constituent homopolymers. Such an observation is consistent with the large-scale phase separation detected by SEM.

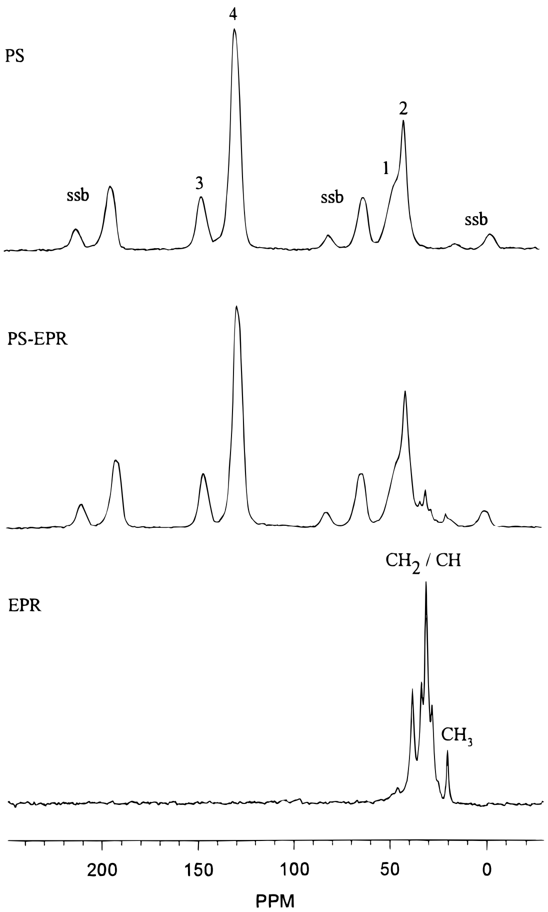

Figure 2. CPMAS spectra of PS, EPR, and a PS-EPR blend containing 80 vol % PS. The numbers are assignments for the carbons shown in Scheme 1. Spinning side bands in the CPMAS spectrum of PS are denoted by ssb.

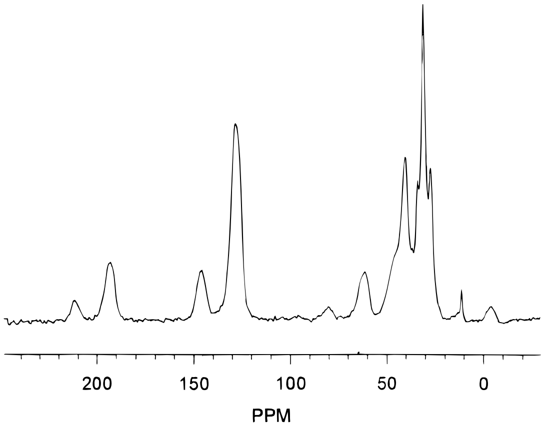

Figure 3. CPMAS spectrum of CAP4741.

It can be seen from Figure 2 that the peaks assigned to the aromatic carbons of PS (145 and 128 ppm) are well resolved from the peaks in the ^{13}C CPMAS spectrum of EPR. Likewise, the methyl peaks (20 ppm) and methylene peaks (30 ppm) in the CPMAS spectrum of EPR are resolved from those of PS. In this work, the magnetization of protons in the PS and EPR phases of the blends are monitored, indirectly, by measuring the intensities of the resonances in the ^{13}C CPMAS spectra at 128 and 30 ppm, respectively.

The ^{13}C CPMAS spectrum of CAP4741 is presented in Figure 3. CAP4741 is a diblock copolymer comprising of 30 wt % PS and 70 wt % of hydrogenated butadiene. From a comparison of Figures 2 and 3 it can be seen that the only resonance in the CPMAS spectrum of the PS-EPR blend that is not present in the CPMAS spectrum of CAP4741 is that assigned to methyl groups in EPR at 20 ppm (Figure 2). Furthermore, the peak at 128 ppm, used to monitor the diffusion of spin magnetization in the blends, contains contributions from both pure PS and the PS block of CAP4741; however, it is assumed that the majority of the PS block of CAP4741 is intimately mixed in the PS phase of the blends.

^{1}H T_1 Relaxation Time Measurements. It has previously been demonstrated, by a large number of authors, that measurements of ^{1}H T_1 and ^{1}H $T_{1\rho}$ relaxation times can be used to obtain information about the size of domains in polymer blends.[5,23–25] It is well known that diffusion of ^{1}H magnetization within polymer blends tends to average the ^{1}H relaxation times measured for the homopolymers in the blends. The extent by which the ^{1}H relaxation times of the homopolymers are averaged upon blending is related to the average distance between the homopolymer chains, i.e., the size of domains in the blend.[5,23,24] For example, measurements of ^{1}H T_1 relaxation times in a blend comprising of two dissimilar polymers will yield a single "averaged" T_1 relaxation time if the size of the domains is smaller than some "critical" value, providing that the intrinsic relaxation times of the constituent polymers of the blend are significantly different. If the size of domains is much larger than this critical value, measurements of the ^{1}H T_1 relaxation behavior of the blend will yield two relaxation times which are similar to those of the components of the blend. For blends containing domain sizes on the order of this critical value, two relaxation times will also be measured; however, the values of the relaxation times will be intermediate to those of the homopolymers and the single averaged value expected for more intimate mixing. Domain sizes determined by this method are generally semiquantitative; that is, measurements of ^{1}H T_1 relaxation times are used to obtain upper or lower limits for the size of domains in blends. In the case where the measured relaxation times are partially averaged by spin diffusion, however, it is possible to quantify the size of domains through simulations of the effects of spin diffusion on the measured relaxation times.[5,26] The size of domains which are probed by relaxation time measurements (i.e., this critical value) can be estimated from the diffusion coefficients and the relaxation times of the homopolymers.[23,24] Typically domain sizes on the order of "tens of nanometers" and a "few nanometers" can be probed by ^{1}H T_1 and $T_{1\rho}$ relaxation time measurements, respectively.[23,24]

^{1}H T_1 relaxation times measured for PS, EPR, CAP4741 and two compatibilized PS-EPR blends are presented in Table 2. It can be seen that the ^{1}H T_1 relaxation times of PS (1600 ms) and EPR (240 ms) in the pure homopolymers are not significantly altered upon blending. Spin diffusion is, therefore, very inefficient in averaging the ^{1}H T_1 relaxation times of the homopolymers, and the mean size of EPR domains in the blend is much greater than a few tens of nanometers.[23,24] If one now considers the addition of a small amount of CAP4741 to the PS-EPR blend, it can be seen from Table 2 that the ^{1}H T_1 relaxation times of the PS phase and the EPR phase in the compatibilized blends are the same as those in the uncompatibilized blend, i.e., the same as those in the pure homopolymers. The minimum possible mean-sizes of EPR domains in the compatibilized blends are, therefore, much greater than a few tens of nanometers. As discussed above, the ^{1}H T_1 relaxation time measurements for the PS-EPR blends provide an estimate for the minimum possible size of domains present in the blend and cannot be used to quantify the change in domain sizes that occur upon the addition of compatibilizer to the blends.

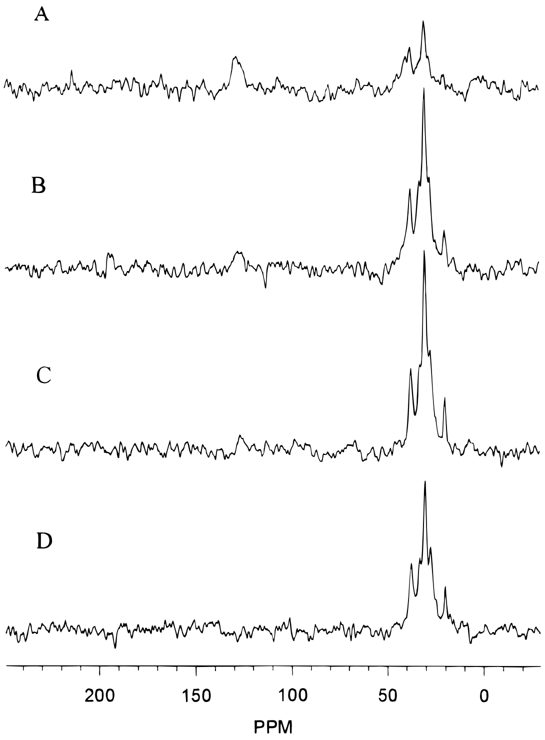

Figure 4. Dipolar filter spectra obtained for a PS-EPR blend containing 30% CAP4741 at various mixing times (A = 300 ms, B = 64 ms, C = 9 ms, D = 0.5 ms).

Table 2. ^{1}H T_1 Relaxation Times Measured for the PS (128 ppm) and EPR (30 ppm) Phases in PS, EPR, CAP4741, and PS-EPR Blends

	^{1}H T_1 Relaxation Times (ms)	
sample	PS phase	EPR phase
PS	1600	
EPR		240
PS-EPR	1470	270
PS-EPR + 10% CAP4741	1420	280
PS-EPR + 25% CAP4741	1410	270

^{1}H Spin Diffusion Measurements. In an attempt to quantify the size of domains present in blends of PS-EPR, measurements of ^{1}H spin diffusion were obtained using the dipolar filter pulse sequence.[17] Figure 4 shows spectra obtained for a PS-EPR blend containing 30% CAP4741 at various mixing times, using this pulse sequence. The dipolar filter pulse sequence, as shown in Figure 1, can be conveniently separated into three parts: selection, diffusion (mixing time), and detection. During the selection portion of the pulse sequence, ^{1}H magnetization in the rigid PS regions of the blend is eliminated leaving only ^{1}H magnetization in the mobile EPR particles. It can be seen by comparing the spectrum in Figure 4D collected with a mixing time of 0.5 ms with the spectra of PS and EPR (see Figure 2) that

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(23) McBrierty, V. J. *Comprehensive Polymer Science*; Allen, G., Ed.; Oxford, 1989; Vol. 1, p 397.

(24) Chu, C. W.; Dickinson, L. C.; Chien, J. C. W. *J. Appl. Polym. Sci.* **1990**, *41*, 2311.

(25) Asano, A.; Takagoshi, K.; Hikichi, K. *Polymer* **1994**, *35*, 5630.

(26) Wang, J.; Jack, K. S.; Natansohn, A. *J. Chem. Phys.* **1997**, *107*, 1016.

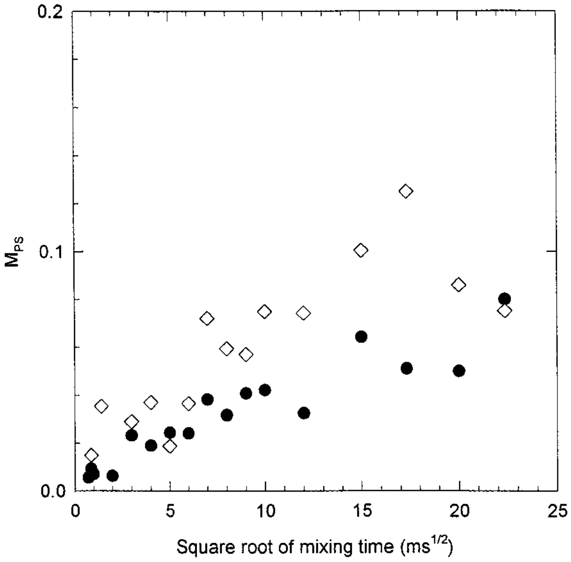

Figure 5. ^{1}H spin diffusion curves measured for PS-EPR blends containing 5% (circles) and 30% (diamonds) CAP4741.

the spectrum shown in Figure 4D is similar to that of pure EPR; the NMR signal ascribed to PS is completely eliminated during the initial selection period of the pulse sequence.

The diffusion of ^{1}H spin magnetization within the blend is monitored by inserting a variable mixing time between the selection and detection steps. From the spectrum collected after a mixing time of 300 ms, presented in Figure 4A, it can be seen that a small amount of ^{1}H magnetization has diffused from the EPR phase into the PS phase of the blend, as is evident by the increase in the ^{13}C NMR peak at 128 ppm. It can also be seen that the spectrum collected with a 300 ms mixing time is very different from the equilibrium CPMAS spectrum of the blend (the equilibrium CPMAS spectrum of the blend containing 30% CAP4741 is similar to that of PS-EPR shown in Figure 2 and is not shown here). Qualitatively, the very limited amount of spin diffusion that is observed during a 300 ms mixing time implies that the sizes of domains in this blend are very large. Previously reported measurements of ^{1}H spin diffusion for polymers in which the sizes of domains are ca. 20 nm show that the distribution of magnetization in the blend reaches equilibrium during a mixing time of 300−500 ms.[6,27,28]

In Figure 5 spin diffusion curves measured for the blends containing 5% and 30% CAP4741 are presented. These spin diffusion curves were produced by plotting the *corrected* integrated intensities from 130 to 124 ppm (i.e., from the protonated aromatic carbons on PS chains) as a function of the square root of the mixing time. For each mixing time (t_m) the integrated intensity has been multiplied by a factor of $\exp(t_m/T_1)$; where T_1 is equal to the ^{1}H T_1 measured for the peak at 128 ppm. Multiplication of the integrals by this exponential factor is applied to approximately *correct* for the reduction in NMR signal intensity resulting from the phase cycling used in the dipolar filter pulse sequence (see Figure 1), as explained by Schmidt-Rohr and Spiess.[7]

To extract quantitative measurements of domain sizes in PS-EPR blends using the initial rate approximation[6] (see below), it is necessary to extrapolate the initial linear portion of the integrated magnetization to the value at equilibrium. As mentioned above, the application of the phase cycle used to reduce T_1 effects in the measured spin diffusion curves, however, leads to a reduction in the absolute signal intensity measured by a factor of $\exp(t_m/T_1)$; where t_m is the mixing time. For mixing times longer than ca. 500 ms, the experimental uncertainty in the NMR signal becomes large, limiting the value of mixing times which can be reliably measured for these blends to $t_m \le 500$ ms. It is, therefore, not possible in the PS-EPR blends to determine the equilibrium magnetization value experimentally. Instead, the equilibrium PS magnetization (M_{PS}^{∞}) was calculated from the initial magnetization in the rubbery phase using the equation[7]

$$M_{PS}^{\infty} = f_R^H M_R^0 \left(\frac{M_{PS}^{CP}}{M_R^{CP}} \right) \tag{1}$$

where f_R^H = fraction of protons in the rubbery phase (EPR+CAP4741) of the blend, M_R^0 = magnetization in the rubbery phase at $t_m = 0$, and M_{PS}^{CP}/M_R^{CP} is the ratio of magnetization in the PS phase to that in the rubbery phase at equilibrium; i.e., in a standard CPMAS spectrum without dipolar filter selection. For the spin diffusion measurements presented here, M_{PS} represents the integral from 130 to 124 ppm and M_R was sampled using the integral from 30 to 26 ppm. Additionally, it was observed that M_R initially increases in intensity at small mixing times and then begins to decrease as the mixing time is further increased. This behavior was also observed in a dipolar filter experiment performed on pure EPR, suggesting that the initial increase in magnetization, observed in the dipolar filter spectra of the blends, is most likely associated with intra- and/or intermolecular ^{1}H spin diffusion within the EPR domains of the blend, e.g., from the methyl protons to the methylene protons or between regions of differing mobility. The value of M_R^0 was, therefore, taken from the spectrum measured after the equilibration of magnetization was completed. Furthermore, it can be seen from Figure 5 that the rate of increase of the corrected diffusion curves begins to slow down at large mixing times. Such a decrease in rate is inherent in both the ^{1}H spin diffusion process and the phase cycling used to suppress ^{1}H T_1 relaxation effects.[6,26] Therefore, only mixing times ≤100 ms (10 $ms^{1/2}$), i.e., the initial linear region, were used in the extrapolation of the ^{1}H spin diffusion curves presented below.

In Figure 6, the spin diffusion curves for the blends containing 5% and 30% CAP4741 are replotted using an expanded scale for the square root of the mixing time. The solid lines in this figure were obtained from a linear least-squares analysis of the initial linear portion of the spin diffusion data and are extrapolated to the value of the equilibrium magnetization ($M_{PS} = 1$). $\sqrt{t_m^*}$ is defined as the square-root mixing time at which the extrapolation reaches equilibrium magnetization, as shown in Figure 6. It can be seen from Figure 6 that the determination of $\sqrt{t_m^*}$ requires extended extrapolations of the initial diffusion curves. These very large

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(27) Cho, G.; Natansohn, A. *Can. J. Chem.* **1994**, *72*, 2255.

(28) Jack, K. S.; Natansohn, A.; Wang, J.; Register, R. A. *Macromolecules*, in press.

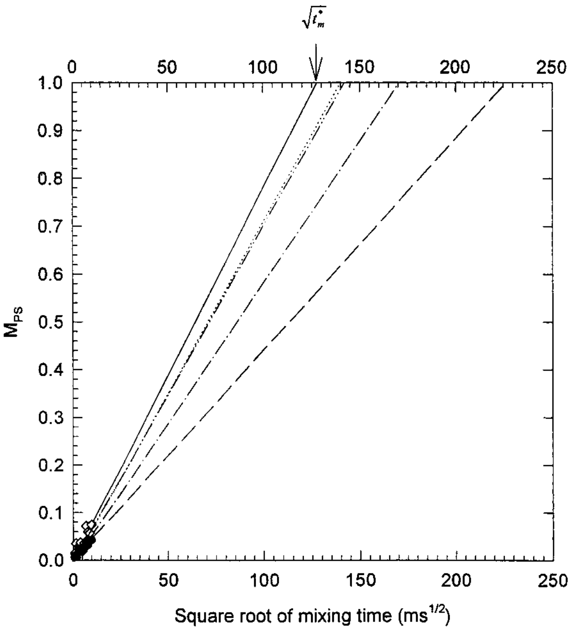

Figure 6. Determination of $\sqrt{t_m^*}$ by the extrapolation of the spin diffusion curves to the equilibrium magnetization value for PS-EPR blends containing 5% (dashed line), 10% (dash-dotted line), 15% (dash-double dotted line), 25% (dotted line), and 30% (solid line) CAP4741. Spin diffusion curves for the blends containing 5% (circles) and 30% (diamonds) CAP4741 are also shown.

extrapolations lead to large uncertainties in the determination of $\sqrt{t_m^*}$ and hence the size of domains measured in the blends. An in-depth discussion of the uncertainties associated with the determination of domain sizes in immiscible blends is presented below. The extrapolated lines for the blends containing 10%, 15%, and 25% CAP4741 are also shown on Figure 6. Spin diffusion data for these blends are not shown for reasons of clarity.

The theory of ^{1}H spin diffusion in multiphase polymers and methods for determining the size of domains in polymer blends from measurements of ^{1}H spin diffusion have previously been described in detail.[6,8,18] For blends in which the interfacial thickness is small with respect to the size of domains, i.e., those which can be described by a two-phase model, it has been shown that the average size of the dispersed phase can be obtained using the initial rate approximation:[6,7]

$$d_{\text{dis}} = \frac{\rho_A^H\phi_A + \rho_B^H\phi_B}{\phi_A\phi_B}\,\frac{\sqrt{D_A D_B}}{\sqrt{D_A}\rho_A^H + \sqrt{D_B}\rho_B^H}\,\frac{4\epsilon\phi_{\text{dis}}}{\sqrt{\pi}}\sqrt{t_m^*} \qquad (2)$$

In eq 2, ρ^H, ϕ, and D represent the proton densities, volume fractions, and diffusion coefficients, respectively, for the two phases (A and B) in the blend, ϵ is the dimensionality, and ϕ_{dis} is the volume fraction of the dispersed phase. $\sqrt{t_m^*}$ is determined from the extrapolation of the initial linear portion of the spin diffusion curve as is shown in Figure 6.

For the PS-EPR blends the values of ρ^H and ϕ can be easily calculated from the composition of the blends and the densities of the materials. Furthermore, SEM measurements of these blends have shown the dimensionality (ϵ) to be equal to 3, i.e., EPR forms approximately spherical domains.[22] The spin diffusion coefficient for PS (D_{PS}) has previously been measured by Clauss et al.[6] and is reported to be 0.8 nm^2/ms. The spin diffusion coefficient for EPR (D_{EPR} = 0.1 nm^2/ms) was obtained from a comparison of NMR and small-angle X-ray spectroscopy measurements of domain sizes in a PS-*b*-EPR diblock copolymer.[29] The values of $\sqrt{t_m^*}$ obtained from Figure 6 and the average size of EPR domains (d_{EPR}), calculated using Equation 2, for each of the blends investigated are shown in Table 3. For the uncompatibilized blend, no spin diffusion was observed up to a mixing time of 500 ms. As explained above, it is not possible to make reliable measurements of spin diffusion for t_m > 500 ms due to the reduction in signal intensity associated with the phase cycle used in the dipolar filter experiments. It is estimated that the total recovery of PS magnetization in the blend must be less than ca. 3% for mixing times of up to 100 ms (10 ms$^{1/2}$) and that the size of the EPR domains must, therefore, be greater than ca. 670 nm.

Table 3. Domain Sizes Measured from ^{1}H Spin Diffusion Measurements for PS-EPR Blends

% CAP4741 (wt/vol EPR)	$\sqrt{t_m^*}$ (ms$^{-1/2}$)	d_{EPR} (nm)	d'_{EPR} (nm)
0	>330	>670	>830
5	227	458	570
10	171	345	430
15	142	286	355
25	140	282	350
30	128	258	360

Finally, the two-phase model for the phase structure of a polymer blend, from which eq 2 is derived, contains cubic symmetry.[6] SEM studies of these blends, however, show the geometry of the EPR particle to be approximately spherical. To compare the two sets of measurements, the cubic dimensions obtained by NMR (d_{EPR}) have been converted to spherical diameters (d'_{EPR}) using the equation

$$d'_{EPR} = d_{EPR}\sqrt[3]{6/\pi} \qquad (3)$$

That is, d'_{EPR} and d_{EPR} are the dimensions of spheres and cubes, respectively, of equal volume.

Comparison of Domain Sizes Determined by NMR and SEM. Figure 7 shows a plot of the average diameter of EPR domains determined by NMR (d'_{EPR}) as a function of compatibilizer added to the blends. It can be seen from this figure that there is good agreement between d'_{EPR} and the number-average domain size (d_n) measured by SEM. This agreement suggests that the ^{1}H spin diffusion measurements are, in a qualitative sense, sensitive to the reduction in the average size of EPR domains in the PS-EPR blends upon addition of CAP4741, even though the size of domains are relatively large. This result can also be seen by comparing, for example, the dipolar filter spectra of the blends containing 0 and 30% CAP4741.

To quantitatively compare the domain sizes determined by NMR and SEM in the PS-EPR blends, it is necessary to consider the physical meaning of d'_{EPR} for a blend in which there exists a distribution of domain sizes. It has been shown that the average domain size (d_A) determined by the initial rate approximation is related to the distribution of domain sizes by[6,7]

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(29) Jack, K. S.; Lai, C.; Natansohn, A.; Wang, J.; Register, R. A. In preparation.

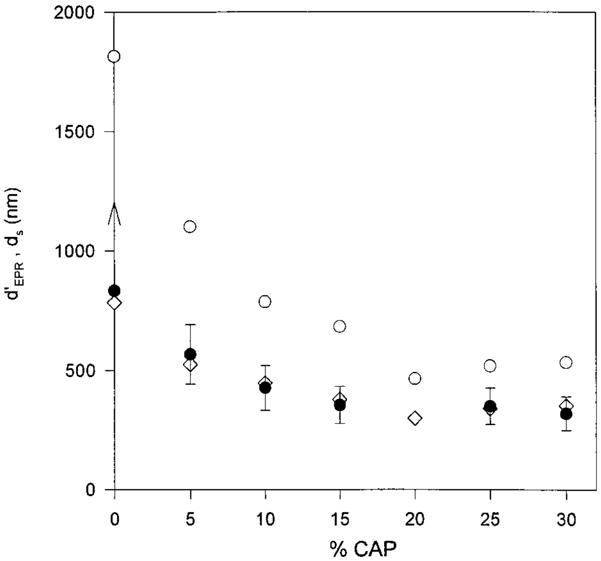

Figure 7. The surface-average size of EPR domains in the PS-EPR blends as measured by NMR (d'_{EPR}, filled circles) and SEM (d_s, hollow circles) and the number-average domain size measured by SEM (d_n, diamonds). The value for d'_{EPR} in the uncompatibilized blend represents a lower bound for the possible average size of domains in this blend.

$$d_A = \langle d_A^{\epsilon}\rangle / \langle d_A^{\epsilon-1}\rangle \qquad (4)$$

For the PS-EPR blends investigated here where $\epsilon = 3$ and A = EPR, d'_{EPR} is equivalent to $\langle d_{EPR}^3\rangle / \langle d_{EPR}^2\rangle$ (i.e., the surface-average size of EPR domains) and should, therefore, be compared with the surface-average domain sizes measured by SEM. The surface-average sizes of EPR domains in the PS-EPR blends measured by SEM (d_s) are plotted as a function of the amount of interfacial agent added to the blend in Figure 7. It can be seen from this figure that d'_{EPR} is consistently smaller than d_s for all of the blends measured. Possible explanations for the differences in the averaged domain sizes detected by NMR and SEM are discussed below.

As described above, the determination of domain sizes using the initial rate approximation requires the extrapolation of the initial buildup of magnetization to the equilibrium value. From Figure 5, it can be seen that the magnetization in the compatibilized PE-EPR blends has recovered to <12% of the equilibrium value for the longest mixing time that could reliably be measured. Furthermore there is a moderate degree of uncertainty associated with the calculation of the value of the equilibrium magnetization. The determination of $\sqrt{t_m^*}$, as shown in Figure 6, is thought to be the dominant source of random error in the determination of domain sizes by this method. The random error associated with the determination of $\sqrt{t_m^*}$, and hence the measurement of d'_{EPR}, is estimated from the uncertainty in the least-squares analysis of the diffusion curves to be ca. 20–25%. The error bars shown on Figure 7 represent this random error. The uncertainties in the size of EPR domains in PS-EPR are larger than those normally obtained from ^{1}H spin diffusion measurements of multiphase polymers,[6,13,15,17,30] due in part to the much larger domain sizes being measured in this work. Additionally, these errors are larger than those obtained from SEM measurements of PS-EPR blends (ca. 10%). These random uncertainties in the measurement of d'_{EPR}, however, cannot account for the differences between d'_{EPR} and d_s. Instead, two possible sources of systematic error must also be considered.

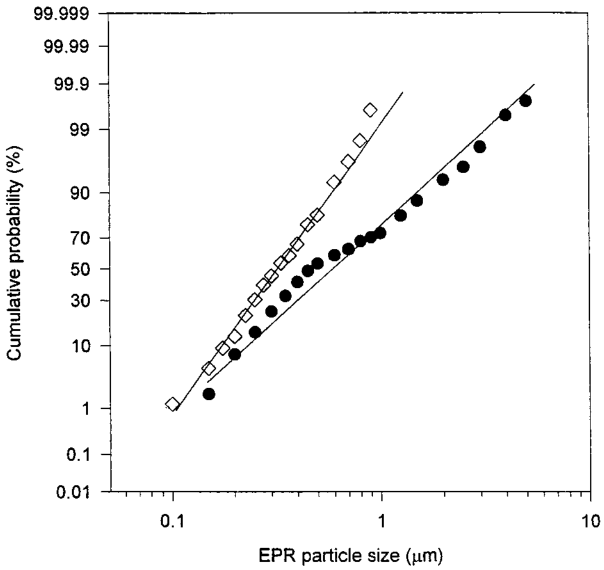

Figure 8. Log-normal particle-size distributions of EPR particles in an uncompatibilized PS-EPR blend (circles) and a blend containing 25% CAP4741 (diamonds).

(1) The first, and most likely, source of systematic error is the difference in sensitivity of the NMR technique as a function of the size of domains in the blend. Measurements of ^{1}H spin diffusion are most sensitive to domain sizes in the range of ca. 1–200 nm.[7] For domain sizes larger than a few hundred nanometers, the amount of spin magnetization that diffuses during the initial linear region of the spin diffusion curve will be below the detection limit of the spectrometer and will not contribute to the average domain size measured. In a polymer containing a broad distribution of domain sizes, it is expected that the NMR measurements would, therefore, underestimate the average domain size, compared with SEM measurements. Furthermore, it is expected that the underestimation of the average domain size by NMR would be greater in the uncompatibilized PS-EPR blend, in which the number of larger domains is greater, c.f. the compatibilized blends; see Figure 7.

To illustrate this last point more clearly, log-normal particle-size distributions for the uncompatibilized PS-EPR blend and the blend containing 25% CAP4741 are shown in Figure 8. These particle-size distributions were obtained from SEM measurements of the blends. It can be seen from this figure that the uncompatibilized blend contains a much broader distribution of EPR particles and has a greater proportion of larger particles compared with the compatibilized blend. For example, ca. 85% of EPR particles in the blend containing 25% CAP are smaller than 500 nm, whereas only ca. 40% of the EPR particles in the uncompatibilized blend are smaller than this size. It is expected, therefore, that the average domain size measured by NMR will be closer to that measured by SEM as the amount of compatibilizer in the blends is increased.

(2) The second possible source of systematic error that we have considered is the influence of ^{1}H spin lattice

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(30) Schmidt-Rohr, K.; Clauss, J.; Blumich, B.; Spiess, H. W. *Mag. Res. Chem.* **1990**, *28*, S3.

relaxation on the initial linear portion of the ^{1}H spin diffusion curves. Very recently, we[26] have demonstrated that ^{1}H T_1 relaxation can have a significant effect on the ^{1}H spin diffusion curves measured in multiphase polymers when the rate of ^{1}H spin diffusion is comparable to the rate of ^{1}H T_1 relaxation, even if the phase cycling for the reduction of T_1 effects is used in the acquisition of data. However, from numerical simulations using models for the phase structure of PS-EPR blends that contain moderately sized domains and include ^{1}H T_1 relaxation terms, it can be shown that the determination of domain sizes using the initial rate approximation does not lead to significantly large errors.

It should be noted that although the uncertainties in the NMR measurements are larger than those obtained by SEM, these uncertainties are not solely related to the large size of domains in the blends but are also due to instrumental limitations and the physical properties of the materials being investigated. For example, the random uncertainties in the determination of $\sqrt{t_m^*}$, associated with the extrapolation of the initial linear portion of the spin diffusion curves, are affected by noise in the experimental data. In addition to this inherent noise, the multiplication of the experimental data by $\exp(t_m/T_1)$ leads to further scatter in the data. By obtaining ^{1}H spin diffusion measurements for these samples at higher magnetic field strengths, it may be possible to reduce these sources of error in two ways. First, the inherent gain in sensitivity at higher field strength will lead to a gain in the signal-to-noise ratio of the experimental data. Second, the ^{1}H T_1 of the homopolymers at the higher field strength may be larger, thereby decreasing errors due to ^{1}H T_1 correction and also increasing the longest accessible mixing time. Furthermore, the sensitivity of these ^{1}H spin diffusion experiments is also a function of the composition of the blends investigated. For blends which contain higher compositions of rubber, the fraction of ^{1}H magnetization removed by the dipolar filter will be less.

Finally, regarding the possibility of existence of an interface, which could be very sharp without compatibilizer but which could have a significant volume at high compatibilizer content, the current method to identify the presence of such an interface using NMR is to analyze the shape of the magnetization growth in the dipolar filter experiment. A sigmoidal shape at relatively low mixing times is an indication of the presence of such an interface, and the dipolar filter growth curve can then be analyzed using a three-domain model.[8,17,18] In our system, the magnetization growth in the dipolar filter experiment is linear, suggesting that the interface, if existent, can be neglected in the spin diffusion process.

Effect of Sample Preparation on the Morphology of PS−EPR Blends. To investigate the effect that sample preparation has on the morphology of PS-EPR blends, a series of samples was prepared for spin diffusion measurements by milling at room temperature. This procedure is often used for CPMAS measurements of glassy polymers, as the powders produced by milling allow for a higher, more uniform, density of sample in the NMR rotor, thus increasing the sensitivity of the experiments and facilitating magic angle sample spinning. For the PS-EPR blends studied in this work, it was not possible to mill the samples at 97 K, i.e., in liquid nitrogen, as it has previously been shown that the EPR particles could separate from the PS matrix at this temperature.[22]

Measurements of ^{1}H spin diffusion in the milled PS-EPR blends were collected under identical conditions as those used for the unmilled samples. It was observed that ^{1}H spin diffusion proceeds more rapidly in the milled samples compared with the unmilled samples. This increase in the rate of ^{1}H spin diffusion upon milling of the sample was observed for each of the blends investigated in this work, including the blend which contained no compatibilizer. It is, therefore, concluded that the milling process used in the preparation of the sample leads to a change in the phase structure of the blend.

Conclusions

Measurements of the average sizes of the dispersed EPR particles in blends of PS-EPR were attempted using NMR measurements of ^{1}H spin diffusion. It was found that the quantitative agreement between the average domain sizes measured by NMR and SEM was poor and that the most probable cause for these differences was the reduced sensitivity of the NMR method to large domain sizes. It is concluded that the NMR method used here is not suitable to quantify the average sizes of domains present in blends that contain a significant fraction of domains greater than a few hundreds of nanometers. Qualitatively, however, the ^{1}H spin diffusion measurements were sensitive to the reduction in the average EPR particle size upon addition of interfacial agent to the blend. This finding suggests that the NMR method may be valuable for studying the relative efficacy of different concentrations of interfacial agent, types of interfacial agents, or processing conditions for compatibilizing polymer blends. Although the uncertainties associated with the NMR method are larger than those obtained from the more established SEM method, it is possible to envisage situations where the latter method is not possible, e.g., where there is limited contrast between the components of the blend under the SEM microscope. Furthermore, it is possible that both the random and systematic uncertainties associated with these measurements could be reduced by future developments in NMR spectroscopy, thus increasing the applicability of the NMR technique. Finally it has been shown that mechanical grinding of polymer blends can lead to changes in the morphology of the blend. It is, therefore, important to ensure that ^{1}H spin diffusion measurements of blends are obtained from samples which have not been mechanically altered.

Acknowledgment. This research was funded in part by the Environmental Science and Technology Alliance of Canada (ESTAC) and by the Natural Sciences and Engineering Research Council (NSERC) of Canada. We thank both NSERC and ESTAC for their financial support. A.N. thanks Canada Council for a Killam Research Fellowship.

CM970670C