# Proton NMR Study of the Intimacy of Mixing in a Hydrogen-Bonded Blend of Polystyrene and Poly(butyl methacrylate)

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*Received July 2, 1991; Revised Manuscript Received December 3, 1991*

ABSTRACT: High-resolution solid-state proton NMR techniques were used to examine the mixing of polystyrene (PS) and poly(butyl methacrylate) (PBMA) chains in a blend where the PS was chemically modified by copolymerization with 1.5 mol % of a modified styrene monomer containing a hydroxyl group. Substitution of this modified PS(OH) polymer "compatibilizes" the otherwise incompatible PS/PBMA blend. Proton spin diffusion techniques were used to examine the level of mixing. Data indicated that there is compositional heterogeneity remaining in this 60/40 PS(OH)/PBMA blend on the 6–12-nm scale, a scale which is comparable to the mean separation between "decorations" on the unperturbed Gaussian PS chain. The compositional heterogeneity is such that the mean PS(OH)–proton fraction in the PS(OH)-rich regions is about 75% and likewise for the PBMA–proton fraction in the PBMA-rich regions. The level of mixing is deemed sufficiently intimate for imparting intermediate material properties to this blend. There is also evidence of some molecular-level mixing in the differential line broadening/line narrowing of PBMA/PS(OH) resonances in the blend spectrum.

## Introduction

The general utility of polymer blends in many materials science applications is limited by the inherent immiscibility (phase separation dictated by thermodynamics) of most polymer pairs.[1] A combination of anything but carefully chosen polymers therefore results in a macroscopically phase-separated morphology and a material whose properties often fall far short of the useful intermediate properties which motivated the blending. One current synthetic effort aimed at compatibilizing (promoting mixing in) blends utilizes the chemical modification of one or more blend components. For example, the introduction of a low concentration of a hydrogen-bonding comonomer into the polymerization of polymer A when polymer B is capable of participating in the hydrogen bonding has created good mixing in certain cases.[2-5] This paper is a study of such a compatible blend.

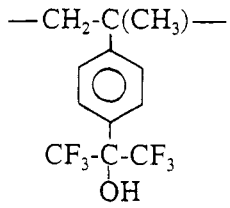
Compatibilized blends present some significant analytical challenges which directly influence the materials development process. One would like to be able to distinguish at least the extreme cases, namely, molecular-scale mixing or phase separation with mixing only at locations corresponding to the positions of added functionalities. Between these extremes there is a range of intermediate possibilities involving partial mixing everywhere along with the existence of sizable concentration fluctuations for each polymer. Ideally, one would like to be able to comment on this intermediate case as well. If blend phase structure is somehow defined by the concentration and placement of added functionalities, then domain sizes in compatibilized blends could be controlled in synthesis by functionalizing to achieve a certain level of mixing. This could provide a means by which properties could be tailored for a given application.

We illustrate here the role which solid-state NMR techniques can play in the structural characterization of compatibilized polymers. Proton spin diffusion[6] experiments employing CRAMPS[7] (*C*ombined *R*otation *A*nd *M*ultiple-*P*ulse *S*pectroscopy) have already proven useful for structural studies of more conventional polymer blends;[8-12] here these experiments are extended to this important class of materials. Specifically, we seek information about the intimacy of mixing in a blend of 60% by weight polystyrene (PS) and 40% by weight poly(butyl methacrylate) (PBMA) in which the PS has been "decorated" by copolymerization with 1.5 mol % of a modified PS monomer bearing a hydroxyl group. Although, as we have verified, pure PS/PBMA blends phase separate, $T_g$ and light scattering measurements[13] indicate miscibility for this 60/40 PS(OH)/PBMA blend. Our experiments provide a more microscopic perspective of compositional inhomogeneity from which the compatibilizing role of the modified homopolymer may be inferred.

## Experimental Section

**NMR Spectroscopy.** All NMR experiments were performed using a Bruker CXP-200 spectrometer[14] with a static field strength of 200 MHz for $^1$H and a slightly-modified Doty 5-mm CRAMPS probe. Spectrometer tuning was performed on a spherical water sample using published procedures.[15] The pulse sequence used for the chemical-shift-based (CSB) spin-diffusion experiment[8,12] consists of a preparation period with a fixed number of MREV-8[16] cycles (applied during an integral number of rotor periods[12]) after which the magnetization, which has precessed in the toggling frame, is stored alternately parallel and antiparallel to the static field direction (with alternate adding and subtracting of the data). This preparation produces a polarization per spin which varies sinusoidally across the spectrum. The period of the sinusoid is inversely proportional to the number of MREV-8 cycles, and the phase of the sinusoid depends on the radio frequency. After the preparation period there is a variable spin-diffusion time, $\tau_{sd}$, followed by spectral readout under MREV-8, and a recycle delay. Experimental parameters used in this work include a 1.5-$\mu$s 90° pulse, a 40.8-$\mu$s MREV-8 cycle time, and 12 cycles of multiple-pulse irradiation for gradient preparation (total time of 490 $\mu$s). The magic-angle spinning (MAS) rate was set to 4084 Hz so that two rotor periods would equal the preparation period.[12]

**Samples.** Preparation of the compatibilized blend film considered here has been previously described.[13] Polystyrene was modified at a level of 1.5 mol % through incorporation of the *p*-(1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)-$\alpha$-methylstyrene comonomer. The corresponding HFMS repeat unit is




The resulting copolymer is designated PS(OH). Although the 60/40 relative weight percent of PS(OH)/PBMA was found to be close to the critical composition,[13] this fact is only relevant to the mechanism of phase separation at higher temperatures; at ambient temperature this blend represents well the "single-phase" state. Approximately 3.5 mg of the blend was used for NMR analysis. Samples of neat PS(OH) (MW = 37 000) and PBMA (MW = 42 000) were also examined as reference materials for the blend.

## Results and Discussion

The $^1$H CRAMPS spectra of the 60/40 PS(OH)/PBMA blend, the pure PS(OH), and PBMA are presented, respectively, in parts a–c of Figure 1. Relative integrals in b and c are 0.53 and 0.47 times the blend integral in accordance with the respective calculated proton fractions. It is clear that the aromatic resonance near 7 ppm in the blend spectrum arises exclusively from the PS(OH) while the aliphatic region has contributions from both polymers; the dominant contribution, however, is from the PBMA. The shoulder near 4.5 ppm is the oxymethylene resonance of PBMA.

The fact that only PS(OH) contributes to the aromatic signal and PBMA dominates the aliphatic signal makes this blend easy to study using the CSB spin-diffusion experiment. The initial polarization gradients resulting from the CSB polarization profiles may be tailored[12] for optimizing the changes in *line shape* associated with the internal spin reequilibration process. This consideration is very important when the spectra of the homopolymers are quite similar, i.e., there is strong overlap. Our experimental data were collected at a time when we had less appreciation for these experimental nuances so we used initial gradients which were adequate but not precisely optimized in this sense. When the line shapes of the individual polymers have as much contrast as they do in our case, spin diffusion between protons on different homopolymer chains may be followed with good sensitivity using a wide range of initial conditions. With our choice of initial conditions, we were able to follow the dissipation of the aromatic/aliphatic gradient to about 0.7% of its original value and, more importantly, the decay of the initial *average* PS(OH)/PBMA polarization gradient to about 2% of its original value.

In Figure 2 we show selected spin-diffusion spectra taken at the indicated spin-diffusion times and scaled by the indicated vertical amplification factors. The spin-diffusion spectra have total integrals which are about $0.07I(M_0)$ where $I(M_0)$ is the intensity of the Boltzmann-equilibrium CRAMPS spectrum, $M_0$. $M_0$ is also shown in Figure 2 for reference; the shape of the $M_0$ spectrum, of course, represents full internal spin equilibrium. In Figure 2 we consider a spin-diffusion time of 50 $\mu$s to approximate our initial condition; spectra at shorter spin-diffusion times may have some contribution from transverse magnetization surviving the storage pulse. Spin diffusion is then followed for longer spin-diffusion times. Aliphatic resonances pass through zero-integral in the first 500 $\mu$s of spin diffusion, and, by 40 ms, the line shape is very close to that of $M_0$.

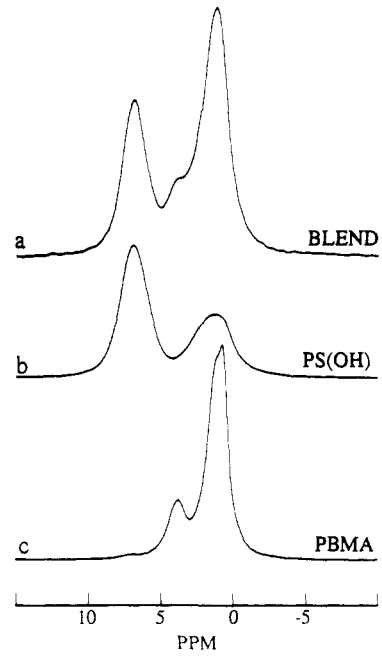



**Figure 1.** 200-MHz $^1$H CRAMPS spectra of (a) the 60/40 PS(OH)/PBMA blend, (b) the PS(OH) homopolymer, and (c) the PBMA homopolymer. Intensities in b and c, relative to the intensity of spectrum a, are chosen to coincide with their respective proton fractions in the blend, i.e., 0.53 and 0.47.

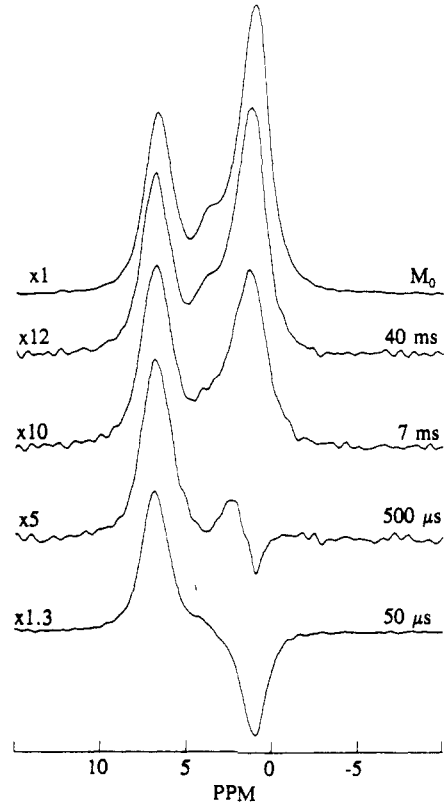



**Figure 2.** Spin-diffusion spectra taken after the indicated spin-diffusion times for the 60/40 PS(OH)/PBMA blend; the $M_0$ spectrum is given as a reference line shape corresponding to full internal spin equilibrium. Relative vertical amplification factors are also given. The 50-$\mu$s line shape approximates the initial condition; internal spin equilibrium has nearly been achieved after 40 ms. The total spin-diffusion integrals are about 7% of the $M_0$ integral.

A period of 40 ms is a long[12] time for achieving full internal spin equilibrium if the PS(OH) and the PBMA are mixed on a molecular scale. Before we can dismiss the

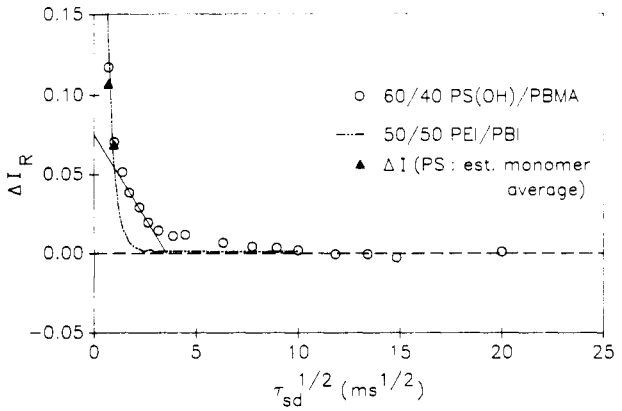



**Figure 3.** Deviations (open circles) of the aromatic intensity from internal spin equilibrium (see eq 1 for a definition of $\Delta I_R$) in the spin-diffusion experiment of Figure 2. Triangles at the abscissa values of the first two points are estimates of the deviations from equilibrium of the average PS(OH) proton polarization. The mixed-dot-dash line is parallel data from ref 12 corresponding to a well-mixed blend with larger monomers and a somewhat smaller spin-diffusion constant; the steeper decay of this line, relative to $\Delta I_R$, implies that the PS(OH)/PBMA blend is not as intimately mixed as the PEI/PBI blend. The solid line is claimed to be associated with spin diffusion between regions of varying composition. From this line both domain dimensions and approximate phase stoichiometries are extracted.

idea that this blend is not ideally mixed, we must consider the possibility, in principle, that this long time is the result of a reduction in the efficiency of spin diffusion via the fast (correlation times shorter than $10^{-6}$ s), near-isotropic motions of intramolecular proton–proton vectors. This possibility was investigated by measuring the Bloch-decay spectrum of the blend. This spectrum showed no narrow features superposed on the resonance whose full width at half-height was about 30 kHz. Thus we conclude that the longer spin-diffusion time required for internal spin equilibration indicates *nonideal* mixing on a molecular scale, and we proceed to such an interpretation and to the extraction of a distance scale for this inhomogeneity of composition.

In order to discuss the spin-diffusion data in a more quantitative form, we plot the parameter, $\Delta I_R$, against $\tau_{sd}^{1/2}$; these are the open circles in Figure 3. $\Delta I_R$ is a difference polarization associated with the aromatic PS-(OH) peak in the blend spectrum and is defined as

$$\Delta I_R = \exp(\tau_{sd}/T_1)[I_R(\tau_{sd}) - I_R']/I_R(M_0) \qquad (1)$$

where $I_R(\tau_{sd})$ is the integral of the aromatic peak in the spin-diffusion spectrum corresponding to $\tau_{sd}$, $I_R'$ is the integral of the aromatic peak in a hypothetical spectrum having the $M_0$ line shape and a total integral equal to the total integral of the spin-diffusion spectrum at $\tau_{sd}$, $I_R(M_0)$ is the aromatic integral in the $M_0$ spectrum, and $T_1$ is the proton longitudinal relaxation time, assumed uniform throughout the blend. The exponential term compensates for polarization changes related to $T_1$; the remaining quantity is a measure of the deviation of the average aromatic proton polarization from internal spin equilibrium, where that deviation is normalized against the Boltzmann-equilibrium polarization.

In Figure 3, only the points corresponding to $\tau_{sd} = 0.5$ ms and longer are plotted. Not shown is the point corresponding to 50 $\mu$s at $\tau_{sd}^{1/2} = 0.22$ ms$^{1/2}$ and $\Delta I_R = 0.55$. This very steep decay over the first 0.5 ms is primarily the result of spin diffusion within the PS(OH) monomer units and between immediately adjoining chains. To jump ahead in this story, the situation that exists is that the decay rate which we associate with inhomogeneous mixing of the PS(OH) and PBMA chains is indicated in Figure 3 by the straight solid line. In view of the fact that decay associated with this straight line extends over only the last 14% of the total range of $\Delta I_R$, we want to be sure that this decay does not represent statistical fluctuations in the intimacy of mixing or statistical fluctuations in the "random-walk" diffusional process. It is quite characteristic of all diffusion curves that they "bend over" as equilibrium is approached.[17] Thus, we present what we believe are sufficient arguments for treating the data in the vicinity of the solid line as evidence of inhomogeneous mixing. The credibility of this claim is crucial to the interpretation given to the data.

The first argument begins with the recognition that $\Delta I_R$ is not exactly the quantity we would like to plot. In order to capture only the interpolymer PS(OH)/PBMA spin diffusion, we would like to plot the deviation from equilibrium of the *average* PS(OH) polarization, rather than the deviation from equilibrium of the *aromatic* PS(OH) polarization. We can approximate the intrapolymer spin diffusion of PS(OH) by conducting the same experiment on pure PS(OH) and measuring how, as a function of $\tau_{sd}$, the aromatic intensity is related to the total intensity, i.e., how the average aromatic polarization is related to the average polarization. We did this, and the solid triangular symbols appearing in Figure 3 represent the deviation of the average PS(OH) proton polarization from equilibrium. Only two triangular symbols appear at the two earliest-time points; the remaining points coincide with the $\Delta I_R$ values and are not plotted. Thus, with the exception of the first two points, these remaining points are an accurate monitor of PS(OH)/PBMA interpolymer spin diffusion. Another result from the spin-diffusion measurements on pure PS(OH) is that the total spin-diffusion integral for this CSB polarization gradient is $0.36I(M_0)$. This integral has relevance for stoichiometric arguments presented later.

The second argument for interpreting the data along the solid line in Figure 3 in terms of inhomogeneous mixing is that parallel data[12] for other intimately mixed blends indicate that equilibrium is achieved significantly faster than in the PS(OH)/PBMA blend. This is illustrated in Figure 3 by the mixed-dot-dash line corresponding to a so-called 50/50 PEI/PBI blend.[18] The latter consists of mostly aromatic, high-$T_g$ polymers with monomer units considerably larger (three or five unfused aromatic rings plus other linkages) than those of PS(OH) and PBMA. Proton density is also lower in the PEI/PBI blend. From both of the foregoing points of view, if the PS(OH) and PBMA chains were as well mixed as the PEI/PBI chains, internal spin equilibrium would have been reached in even a shorter time than was required for the PEI/PBI blend. As can be seen, the data indicate a longer time, consistent with the idea that there is inhomogeneity of mixing in the PS(OH)/PBMA blend.

The third argument is relatively weak but in the context of the other two arguments makes the conclusion stronger. This argument is based on the observation that in Figure 3 $\Delta I_R$ seems to have notable relative slope changes in two places, near $\tau_{sd}^{1/2} = 1.5$ and 3.5 ms$^{1/2}$. This latter bending of the data we associate with the usual "tailing" of spin-diffusion curves[12,19] to times well beyond the $x$-intercept of the linearly decaying portion of the line (solid curve).

Minimum domain dimensions (MDD's), i.e., the shortest distances across domains, corresponding to the regions of compositional heterogeneity in the PS(OH)/PBMA blend are obtained from the solid line of Figure 3. The intercept

of this line with the $\Delta I = 0$ level gives a characteristic spin-diffusion time ($t^*$) which can then be used in a one-dimensional diffusion model which assumes lamellar morphology:

$$\langle x^{*2} \rangle = (4/3)Dt^* \quad (2)$$

where $x^*$ is the root-mean-square (rms) distance covered by spin diffusion in a time $t^*$ and $D$ is the appropriate diffusion coefficient. The $t^*$ associated with the solid line in Figure 3 is 12.3 ms. If we further assume that the diffusion coefficient scales as the cube root of proton density,[6] calculated $D$'s for alkanes[20] may be converted to values appropriate for 60/40 PS(OH)/PBMA. We get $D = 5.4 \times 10^{-12}$ cm$^2$/s. Equation 2 then gives $x^* = 3.0$ nm, implying that the MDD ($\approx 2x^*$) for each region of chemical heterogeneity is about 6.0 nm in this blend; it follows that the overall repeat distance is about $4x^*$ or 12 nm. If the morphology is not lamellar and the MDD's express themselves with a higher dimensionality, e.g., one of the phases consists of rods having a fractional volume of 0.4–0.5, then the data could be interpreted as pointing to rod diameters of 10–12 nm and overall repeat distances of 14–16 nm.[21] We favor a lamellarlike morphology, taking a cue from the morphology which block copolymers adopt when the mass fraction of both components is similar, as it is in this blend. If the morphology is lamellar, however, the lamellae are not well-defined over distances greater than 50 nm since light scattering measurements performed in our laboratory would have identified such features. In any case, our data point to MDD's in the 6–12-nm range and overall repeat distances in the 12–16-nm range.

The MDD, assuming lamellar morphology, correlates quite well with the calculated end-to-end distance,[22] 5.9 nm, for an unperturbed Gaussian PS chain whose length is 67 monomers (the mean distance between HFMS decorations). Considering this distance scale, as well as the approximate nature of the 6.0-nm distance determined from the data, there is support for a morphology related to the mean separation between HFMS labels.

More can be said about chemical heterogeneity in 60/40 PS(OH)/PMBA, specifically with regard to composition. If we consider the solid line plotted in Figure 3, its extrapolation to the $\tau_{sd} = 0$ intercept has the interpretation that this would be the $\Delta I_R$ after spin diffusion within the monomers and after spin diffusion among well-mixed neighboring chains. In other words, it is from this hypothetical starting point that spin diffusion across domains of heterogeneous composition would take place. Having performed the very same spin-diffusion experiment on pure PS(OH) and finding that the total integral, after spin diffusion within the monomer was $0.36I(M_0)$ versus $0.07I(M_0)$ in the blend, means that if the domains of compositional heterogeneity in the blend consisted of pure PS(OH) and pure PBMA phases, the intercept for the solid line in Figure 3 ought to have been 0.29 (=0.36–0.07). The fact that the intercept associated with the solid line is only 0.075 means that during the period of equilibration with the immediately neighboring chains, i.e., those which are well mixed, there was enough communication between PS(OH) and PBMA protons to reduce this intercept from 0.29 to 0.075. Such a reduction would be consistent with the following idealized morphology[12] (although this data cannot point to a unique morphology): there are two phases, a PBMA-rich and a PS(OH)-rich phase. Each phase contains about half the total protons (the proton fractions in the original blend are 0.53 and 0.47 for PS(OH) and PBMA, respectively). In each phase the dominant component contributes about 75% of the protons and the minor component 25%. MDD's and overall repeat distances are those indicated in the foregoing paragraphs.

A final comment addresses the question of whether there is any spectral observation regarding the mixing of the PS(OH) and PBMA chains. First, we were unable to identify the hydroxyl protons which presumably are hydrogen bonded to PBMA carbonyls. Failure to observe these protons arises from unfavorable concentration and spectral overlap considerations. Second, a very close look at Figure 1 reveals that the PS(OH) aromatic peak in the blend is about 0.25 ppm narrower than it is in the pure PS(OH); conversely, the primarily-PBMA aliphatic line in the blend is about 0.25 ppm broader than in the pure PBMA. The slight asymmetry of the main peak in the PBMA spectrum has also been washed out in the blend spectrum, indicating less resolution of the PBMA resonances in the latter spectrum. A narrowing of the PS(OH) spectrum and a broadening of the PBMA resonances can be taken as evidence for some molecular-level mixing, given the further assumption that the atactic PS(OH), if it did phase separate, would not possess characteristics of anisotropic magnetic susceptibility. This latter assumption further assumes that orientational correlation distances associated with the aromatic hexad axes in the PS(OH) glass are very short range. The mechanism for the broadening/narrowing phenomenon upon molecular-level mixing is that intermolecular ring-current shifts[23] associated with the aromatic rings of the PS(OH) would be added to the PBMA line width and diluted in the PS(OH) line width relative to those resonances in the pure polymers.

## Conclusion

High-resolution solid-state proton NMR was used to study the extent of molecular mixing which results when two incompatible polymers, polystyrene and poly(butyl methacrylate), are "compatibilized" via the addition of 1.5 mol % of a hydrogen-bonding comonomer in the PS synthesis. Inferred minimum dimensions for domains of compositional heterogeneity in 60/40 PS(OH)/PBMA are about 6 nm, and the overall repeat distance is 12 nm assuming an idealized lamellar morphology. The 6-nm distance is close to the mean separation (5.9 nm) between hydroxyl labels for the unperturbed Gaussian PS chain. The spin-diffusion data are also consistent with an idealized rod/matrix morphology possessing an interphase surface area similar to that of the lamellar model. There, assuming that the rod phase accounts for 0.4–0.5 of the volume fraction, the rod diameter falls in the 10–12-nm range and the overall repeat distance between rod centers becomes 14–16 nm.

These domains certainly possess some mixed-phase character; i.e., data are consistent with the minor species in each phase contributing about 25% of the protons in that phase. The correspondence between spin-diffusion data and morphology is not unique. The existence of discrete phases with sharp boundaries with these compositions is no doubt too idealized. The real picture is probably that compositional heterogeneity exists on the 6–12-nm scale and that compositional changes are more continuous with the 25% number representing a mean value.

This work illustrates the general utility of proton spin-diffusion experiments based on CSB polarization gradients in the investigation of compatibilized polymer blends. This picture of heterogeneous composition in the compatibilized blend depends heavily on arguments in which in-

trapolymer and intraphase spin diffusion are separated from interphase spin diffusion based on differing time scales for these processes. In this case the observed difference in time scales is deemed adequate but the inexact separation of interphase spin diffusion from nearest-neighbor spin diffusion prevents us from getting a clearer picture of the phase morphology and/or composition. In any case, if the level of mixing in this blend is typical of compatibilized blends, then it seems that mixing is sufficiently intimate to impart useful intermediate properties to these blends.

**Acknowledgment.** We are greatly indebted to Dr. Geoffrey B. McFadden of the Computer and Applied Mathematics Laboratory at NIST for writing the programs for computing spin-diffusion profiles appropriate to 1D (lamellar) and 2D (rod/matrix) morphologies.

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**Registry No.** PS(OH) (copolymer), 120721-72-4; PBMA (homopolymer), 9003-63-8.