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Interphase Mixing in Symmetric Diblock Copolymers Determined by Proton−Deuterium CP/MAS NMR

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ABSTRACT: It has long been recognized that the interphase, i.e., the region between adjacent phases in heterogeneous materials, is a major factor in determining many of the mechanical, optical, and electronic properties of such systems. Interphases are, in general, not abrupt, but exhibit a gradient in the composition from one pure phase to the other. For block copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA), it has been shown, using neutron reflectivity (NR) and fluorescence measurements, that the interphase can extend over several (∼5) nanometers. In this paper, it is shown for block copolymers of perdeuterated polystyrene and poly(methyl methacrylate) (P(d-S-*b*-MMA)) that proton−deuterium CP/MAS experiments can be used for spin counting of deuterons in the interphase. Our approach takes into account the varying compositional profile across the interphase. The results are in reasonable agreement with those derived from NR studies. The basic assumptions underlying our approach to deuteron counting at the interphase are discussed.

I. Introduction

In multicomponent, heterogeneous polymer systems, the interphase, i.e., the region between adjacent phases, is a major factor in determining many of the physical and mechanical properties in such systems. The interphase in block copolymers comprised of incompatible blocks is of particular interest, since such materials are increasingly being used as compatibilizers, surfactants, and adhesives. The width and composition of interphases have been the subject of numerous investigations involving a variety of experimental approaches such as small-angle X-ray scattering,[1,2] dynamic mechanical measurements,[3] transmission electron microscopy,[4] fluorescence spectroscopy,[5] and thermal methods.[6] Very detailed information about the morphology of the interphase in symmetric poly(styrene-*block*-methyl methacrylate) diblock copolymers P(S-*b*-MMA) was recently obtained from neutron reflectivity studies.[7,8] Variable-angle spectroscopic ellipsometry (VASE)[9] and energy transfer studies[10] are emerging as techniques complementary to neutron reflectivity.

Various solid-state NMR approaches designed specifically for the characterization of interfaces are also being used.[11−16] The approaches rely on selectively enhancing the interfacial region by taking advantage of the r^{-6} dependence of polarization transfer or r^{-3} dependence of dipolar recoupling[16] experiments. The work of the Schaefer[15] group has focused on polarization transfer between nuclei and unpaired electrons using dynamic nuclear polarization. Our approach has been based on the polarization transfer between protons and deuterons at the boundary of immiscible phases. In particular, it was shown that studies based on ^{1}H−^{2}H cross-polarization and magic angle spinning (CP/MAS)[12,13] can be made quantitative using a simple approach to deuteron spin counting.[17]

Here ^{1}H−^{2}H CP/MAS NMR is used to determine the fraction of deuterated polystyrene in the interphase region of a series of P(d-S-*b*-MMA) diblock copolymers of different molecular weights. For simplicity, a linear composition gradient across the interphase is assumed and it is shown that the deuterium NMR results interpreted in the light of this assumption yield interphase thicknesses consistent with the results of neutron reflectivity studies.

II. Experimental Section

The block copolymers were purchased from Polymer Laboratories, Inc. Any d-PS homopolymer impurity generated in the synthesis of the copolymer was removed by Soxhlet extraction with cyclohexane. A random copolymer of d-S and MMA was synthesized by T. E. Long in the Corporate Research Laboratories of Eastman Kodak Co. by radical synthesis.

The deuterium NMR spectra were obtained using a Chemagnetics CMX 300 solid-state NMR spectrometer. Spectra were acquired using 5 ms 90° pulses with a CP contact time of 1 ms. The delay between acquisitions was 1 s. A total of 9272 acquisitions were made for each spectrum. High-power proton decoupling was applied in all cases.

III. Results and Discussion

General Description of Deuterium MAS and CP/MAS Spectra. Deuterium NMR has been used extensively to characterize the dynamics and orientation of polymers.[18,19] For solids, micelles, and liquid crystalline materials, the broad Pake doublet observed in the static ^{2}H NMR spectra, i.e., obtained in the absence of mechanical sample spinning, is inhomogeneously broadened and will upon MAS give rise to rotational echoes in the ^{2}H free-induction decay. The Fourier transform of such a free-induction decay consists of a manifold of spinning sidebands whose envelope is related to the shape of the Pake doublet.

The inhomogeneous nature of the ^{2}H Pake doublet was demonstrated experimentally by Ackerman et al.[20] in the case of Bloch decay spectra, i.e., spectra obtained

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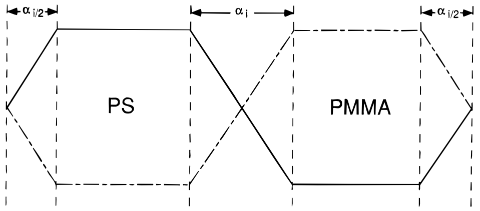

Figure 1. Sketch of the lamellar and interphase structure of d-S-*b*-PMMA assuming a linear concentration profile across the interphase (—) polystyrene; (— - —) poly(methyl methacrylate) profiles; a_i interphase width.

following a simple 90° pulse to the spin system. Subsequently, work from our laboratory[13,14] has shown that uniform intermolecular $^1H-^2H$ cross-polarization across the entire deuterium powder pattern is possible under MAS conditions. While the intensity of a Bloch decay spectrum, I_B, is proportional to the total concentration of deuterium in a sample, the CP/MAS intensity, I_{CP}, is a measure of the number of deuterons in contact with protons.

Deuterium CP/MAS Spectra as a Function of Block Copolymer Molecular Weight. We have examined the $^1H-^2H$ CP/MAS spectra for a series of symmetric d-S-*b*-MMA diblock copolymers studied previously by Anastasiadis et al.[8] using neutron reflectivity. These authors report the volume fraction of the sample occupied by the interphase for three molecular weights, 272K, 80K, and 3012.4K. In the notation of this work, the volume fraction of the interphase is denoted as $2a_i/L$, where *a3i* is the width of the interphase and L the lamellar repeat period. A sketch of the structure is given in Figure 1. Typical free-induction decays displaying rotational echoes are shown in Figure 2.

It can easily be shown that for symmetric blocks of comparable density the volume fraction is also equal to the fraction of a given monomer at the interphase. We denote by $X_S{}^i$ the fraction of all deuterated styrene units (d-S) that are at the interphase. We can generally say that the Bloch decay intensity I_B is proportional to the total d-S units in the sample, whereas I_{CP} is proportional *(with a different proportionality constant)* to the d-S units at the interphase. Hence the ratio R of the two spectral intensities should satisfy

$$R = I_{CP}/I_B = KX_S{}^i = K(2a_i/L) \tag{1}$$

where K is some constant of proportionality. We have plotted R against $X_S{}^i$ for three different molecular weights and hence different values of L as determined in ref 8. While the results shown in Figure 3 follow the linear behavior predicted by eq 1, the experimentally determined quantity R cannot be related to the interphase width a_i without an independent knowledge of the proportionality constant K. To determine the amount of d-S at the interphase, we must be able to relate quantitatively the intensities of CP/MAS spectra to those obtained from Bloch experiments.

Spin Counting of Interphase Deuterons from CP/MAS Spectra. The total Bloch decay intensity, I_B, for the copolymers, as measured for example by the intensity of the first rotational echo, can be written as

$$I_B = I_B{}^i + I_B{}^{PS} \tag{2}$$

where the component $I_B{}^i$ is the component of the deuterium signal intensity arising from d-S within the interphase, and $I_B{}^{PS}$ is the portion of the signal from d-S in the polystyrene domain. The mole fraction, $X_S{}^i$, of d-S in the interphase is given by

$$X_S{}^i = I_B{}^i/(I_B{}^i + I_B{}^{PS}) = I_B{}^i/I_B \tag{3}$$

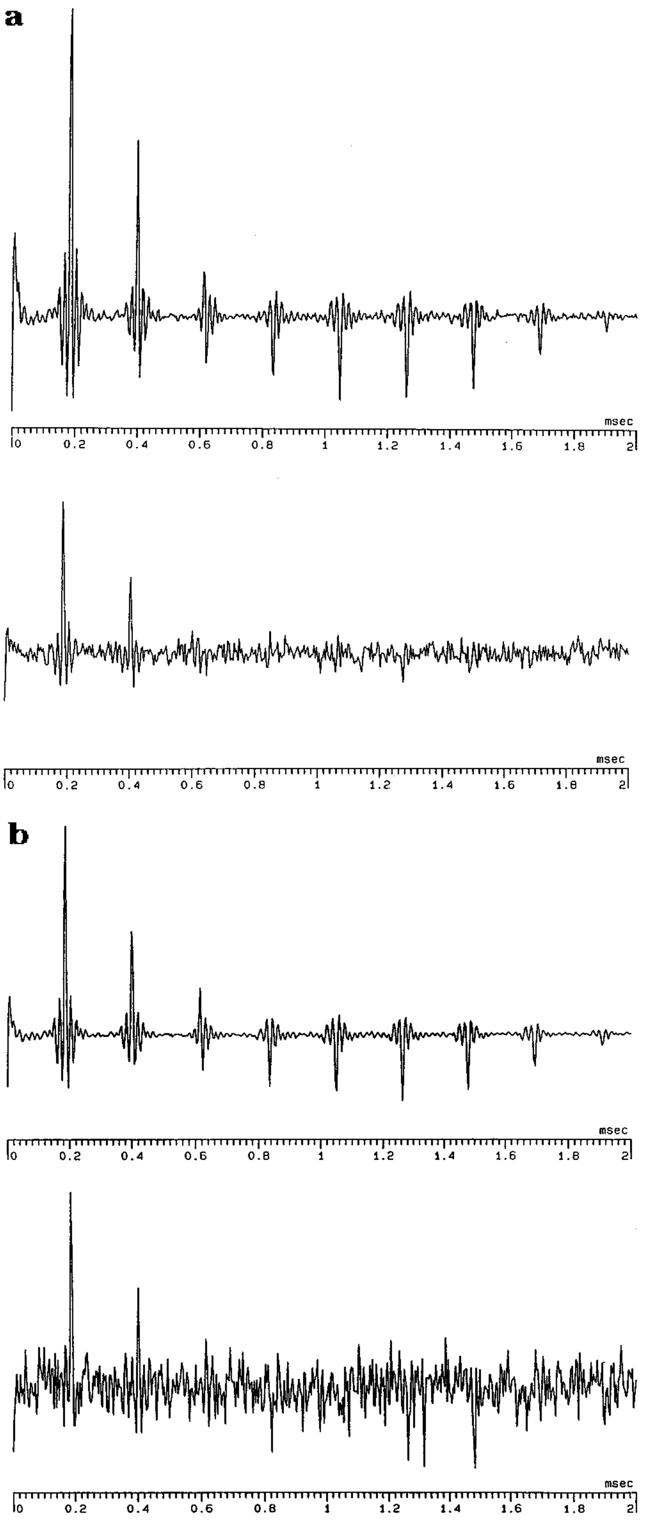

Figure 2. Time-domain Bloch decay (top) and CP/MAS (bottom) spectra for d-S-*b*-MMA: (a) MW = 27 200; (b) MW = 301 400.

To calculate $X_S{}^i$ we need to determine $I_B{}^i$. This quantity cannot be determined directly by experiment. It must be inferred from the CP/MAS spectrum inten-

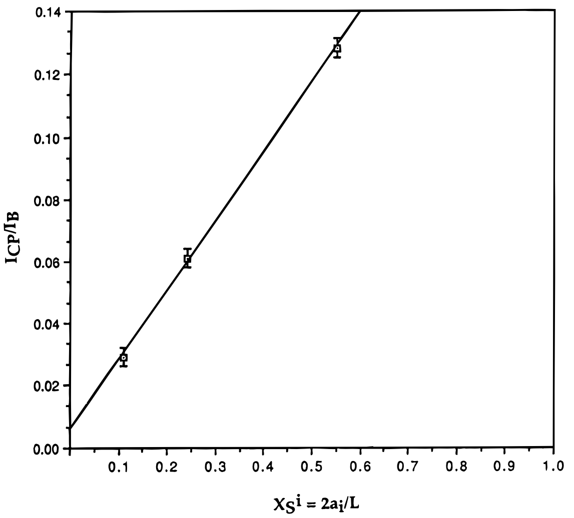

Figure 3. Dependence of the rotational echo intensity ratio I_{CP}/I_B on the mole fraction of S-d_8 units $X_S{}^i$ at the interphase.

sity, I_{CP}. To compare Bloch decay and CP/MAS intensities, we can write

$$I_{CP} = KI_B{}^i \tag{4}$$

where K is the proportionality constant defined by eq 1.

We now introduce a lattice model of the interphase in which protons and deuterons occupy random sites. Let X_H and X_D represent the fraction of sites occupied by protons and deuterons, respectively. In this model, $I_B{}^i$ is simply proportional to X_D; i.e., we can write

$$I_B{}^i = k_2X_D \tag{5}$$

The expression for I_{CP}, on the other hand, is somewhat more subtle, especially since the composition profile varies across the interphase. First, in the limiting cases of X_D or $X_H = 0$, I_{CP} also goes to zero either because there are no deuterons to cross-polarize to, or protons to cross-polarize from. In general, we can write

$$I_{CP} = k_1X_D(1 - X_D) \tag{6}$$

and

$$I_{CP}/I_B{}^i = k_1X_D(1 - X_D)/k_2X_D = kX_H \tag{7}$$

Were one to assume naively that the interphase consists of equal amounts of d-S and MMA monomer units, then X_H would simply equal 0.5 (S and MMA have the same number of hydrogen atoms). However, a more detailed analysis which takes into account the variation of X_H and X_D across the interphase (presented elsewhere[17] and reproduced in the appendix) leads to

$$I_{CP}/I_B{}^i = (1/3)k \tag{8}$$

The proportionality constant k must be obtained independently from a model system. Within the framework of our lattice model, a plausible approach would be to use a series of random copolymers of d-S and MMA, P(d-S-*r*-MMA). In the present work, we have estimated k from a P(d-S-*r*-MMA) where $X_H = X_D = 0.5$.

Now, using eq 8, one can calculate $I_B{}^i$ for the three different molecular weight block copolymers investigated. From eq 3 then an NMR estimate for $X_S{}^i$ was calculated and compared to that obtained from neutron reflection studies. The results of such a calculation are summarized in Table 1.

Table 1. Comparison of NR and NMR Results

	$X_S{}^i$	
dS-*b*-MMA mol wt	by NR	by CP/MAS
27 200	0.57	0.44
80 000	0.24	0.21
301 400	0.12	0.10

It is interesting to note that $X_S{}^i$ determined from the NMR studies is consistently lower than that obtained in the NR studies, implying that the interfacial width determined by NMR is smaller. In the NR studies it was stated that the interfacial width of 50 Å was larger than the interfacial width of 40 Å predicted from mean field theoretical arguments. Subsequent studies[21,22] showed that the value of the interfacial width measured by NR includes a contribution from capillary waves since the NR measures composition variations normal to the interface laterally averaged over the coherence length of the neutron, which is on the order of microns. Taking this into account, the NR results and mean field theoretical arguments are in excellent agreement. Now consider the CP/MAS NMR results reported here. From the values of $X_S{}^i$, interfacial widths of 38, 44, and 40 Å are found with increasing polymer molecular weight. These results are in surprisingly good agreement with mean field arguments. There can be no capillary wave contribution to the NMR results due to the very local nature of the polarization transfer process. Consequently, as observed, the widths obtained from NMR are expected to be lower than those obtained from NR from theoretical arguments.

Given the various approximations made to determine $X_S{}^i$, particularly the reliance on a single random copolymer composition to estimate k, the agreement between the NMR data, the NR results, and mean field theoretical arguments is particularly gratifying.

IV. Conclusions

It has been shown that CP/MAS NMR can be used to obtain quantitative information on the interfacial width in diblock copolymers. In particular, these studies focused on the case of a lamellar microphase-separated morphology. In comparison to mean field theory and neutron reflectivity results, the insensitivity of the technique to capillary waves was shown. This implies that the curvature of the interface does not interfere with the evaluation of the interfacial width, and the extent of segmental mixing is directly measured. Consequently, measurement of the interfacial width for cylindrical and spherical microphase-separated morphologies is possible. In addition, by use of the selective labeling of one component, intermixing of that component, and only that component, can be accessed by this method. Experiments on asymmetric diblock copolymers and ternary polymer mixtures are currently in progress.

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Appendix. Accounting for the Interphase Concentration Profile

Let the deuterium mole fraction, X_D, vary linearly from unity to zero over the interphase thickness a_i. Let

λ be the variable along a_i; then X_D varies across the interphase as

$$X_D(\lambda) = (1 - \lambda/a_i) \tag{A.1}$$

The contribution, $dI_B^i(\lambda)$, of a deuterium signal from a volume element $d\lambda$ of the interphase to the Bloch decay intensity can be written as

$$dI_B^i(\lambda) = k_2 X_D(\lambda)\, d\lambda = k_2(1 - \lambda/a_i)\, d\lambda \tag{A.2}$$

The total contribution *from the interphase to the BD/MAS signal* is then given by

$$I_B^i = k_2\int(1 - \lambda/a_i)\, d\lambda = (k_2/2)a_i \tag{A.3}$$

where the limits of integration are from zero to a_i.

Similarly, from eq 7 the contribution $dI_{CP}(\lambda)$ of the deuterium signal from a volume element of the interphase to the cross-polarization can be written as

$$dI_{CP}(\lambda) = k[1 - X_D(\lambda)]\, dI_B^i \tag{A.4}$$

Substituting dI_B^i from eq A.2 and carrying out the integration, we obtain for the total contribution *from the interphase to the CP/MAS signal*

$$I_{CP} = kk_2\int(\lambda/a_i)(1 - \lambda/a_i)\, d\lambda = kk_2(1/6)a_i \tag{A.5}$$

Thus the ratio of the CP/MAS to the Bloch decay signal yields

$$I_{CP}/I_B^i = k/3 \tag{A.6}$$

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