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Deuterium Effects on Blend Miscibility of an Alternating Copolymer and a Homopolymer

Mary E. Galvin* and Sharon Heffner

AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974

Karen I. Winey*

Materials Science and Engineering Department, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104-6272

ABSTRACT: This paper reports a deuterium effect involving poly(styrene-*co*-methyl methacrylate) alternating copolymer/poly(methyl methacrylate) homopolymer blends, AB/A, in which deuteration of the methyl methacrylate (MMA) monomer unit influences blend miscibility. Two blend compositions were investigated, 35%/65% and 50%/50%, using DSC and TEM. Perdeuteration of the MMA units of the copolymer promotes miscibility, perdeuteration of the MMA units of the homopolymer reduces miscibility, and the absence of perdeuteration exhibits intermediate miscibility. These results are interpreted using the concept that intramolecular repulsion within a copolymer can promote copolymer/homopolymer miscibility. Using the sequence-independent models for copolymer/homopolymer blends, we have determined $\chi_{PS,D\text{-}PMMA} > \chi_{PS,H\text{-}PMMA}$, which is consistent with measurements of these interaction parameters by others.

Introduction

Polymer science has experienced the advent of new techniques (small-angle neutron scattering, forward-recoil spectrometry, and various nuclear magnetic resonance techniques) which use the nuclear contrast between hydrogen and deuterium. Results from such experiments have substantially improved the understanding of polymer miscibility, chain conformations, polymer–polymer diffusion, chain microstructure, and local molecular motions. The increased use of isotope labeling has also uncovered the reality of isotope effects. As one early example, Bates et al. discovered blends of protonated 1,4-polybutadiene and perdeuterated 1,4-polybutadiene phase separate and exhibit an upper critical solution temperature.[1] Subsequently, researchers have continued to label polymer systems with deuterium but have done so with appropriate caution. Previous studies of the deuterium effect have focused on homopolymer/homopolymer blends, A/B, and block copolymers. Considerably less is known about the deuterium effect in copolymer/homopolymer blends.

Early theories of copolymer blends were modifications of the Flory–Huggins theory of homopolymer blends in which the interaction parameter was defined as a weighted sum of the interaction parameters for the monomer units present.[2-4] Furthermore, the distinction was made between intramolecular and intermolecular interactions, so as to explain the experimentally observed "copolymer effect". The copolymer effect refers to copolymer blend systems in which no combination of monomers exhibits miscibility in the respective homopolymer blends, but blend miscibility may be observed when the monomers are combined in copolymers. The following is a common example of the copolymer effect: Poly(styrene-*co*-acrylonitrile) copolymers are miscible with homopoly(methyl methacrylate) over a range of copolymer compositions, while the related homopolymer blends (PS/PMMA, PS/PAN, PMMA/PAN) are not miscible.[5]

However, both the copolymer composition and the monomer sequence are necessary to define a copolymer. The monomer sequence (for instance, blocky, alternating, or random) refers to the order in which the monomers of a copolymer are covalently bonded together and has been the subject of recent copolymer blend theories.[6-11] Previous work by Galvin and Winey has demonstrated the importance of the sequence distribution in a well-defined copolymer/homopolymer/homopolymer (AB/A/B) system in which the copolymers had either a random or alternating sequence.[12-14] Further study of these blends was initiated using solid-state NMR techniques which involved deuterium labeling. This paper reports a deuterium effect in poly(styrene-*co*-methyl methacrylate) alternating copolymer and homopoly(methyl methacrylate), AB/A, blends. Furthermore, the deuteration of the A type monomers of the copolymer produces a different behavior than deuteration of the A type monomers of the homopolymer.

Experimental Methods

Polymers. Narrow molecular weight poly(methyl methacrylate) (PMMA) and perdeuterated poly(methyl methacrylate) (D-PMMA) were purchased from Polymer Laboratories. The alternating copolymers were polymerized in toluene by coordinating either methyl methacrylate or perdeuterated methyl methacrylate with ethylaluminum sesquichloride from Aldrich. Styrene monomer was added to the methyl methacrylate-aluminum mixture, and the polymerization commenced. Details of this polymerization and the subsequent purification and fractionation are presented elsewhere.[12] The poly(perdeuterated methyl methacrylate-*co*-styrene) alternating copolymer (D-ALT) was not fractionated, because of the small quantity of copolymer.

Polymer Characterization. Size-exclusion chromatography was performed using a Waters 150 GPC with bimodal Zorbax columns. The results are shown in Table 1. Note that the weight-average molecular weights of H-ALT and D-ALT are closely matched, though the polydispersity of D-ALT is larger. ^{1}H solution NMR spectra confirm that the copolymers have compositions of 50 mol % styrene and 50 mol % methyl methacrylate. According to Heffner's peak assignments, ^{13}C solution NMR spectra of the copolymers indicate atactic and strictly alternating sequences of monomers.[15] Specifically, the approximate ratio of coheterotactic to cosyndiotactic to coisotactic peaks is 2:1:1. ^{1}H solution NMR shows that the homopolymers of methyl methacrylate are also atactic with the approximate ratio of heterotactic to syndiotactic to isotactic triads being 1:1:0.[12,16]

Blend Preparation and Evaluation. Dilute solutions were prepared with ~30 mg of combined copolymer and homopolymer

Table 1. Homopolymer and Copolymer Characteristics

designation	polymer	M_w	M_w/M_n	T_g (°C)
H-ALT	poly(methyl methacrylate-*co*-styrene) alternating copolymer	530 000	1.5	102
D-ALT	poly(perdeuterated methyl methacrylate-*co*-styrene) alternating copolymer	535 000	2.7	102
H-PMMA.1	poly(methyl methacrylate)	30 000	1.1	120
H-PMMA.2	poly(methyl methacrylate)	53 000	1.04	120
D-PMMA	poly(perdeuterated methyl methacrylate)	39 000	1.1	120

and with ~3 mL of anhydrous tetrahydrofuran. The solvent was evaporated from the blend over 12 h in an atmosphere of nitrogen. The blends were subsequently annealed under nitrogen at 140 °C for 5 days. Glass transition temperatures were recorded on a Perkin-Elmer DSC7 at a heating rate of 20 °C/min. The polymer films were embedded in partially cured epoxy and microtomed at room temperature with a Diatome diamond knife and a Reichert Ultracut S microtome. To provide contrast, the microtomed sections were stained with RuO_4 which preferentially stains the styrene monomer units. The specimens were examined by transmission electron microscopy using either a JEOL 100CX at 100 kV or a Philips 400T at 120 kV.

The TEM images exhibiting two phases were digitized using a UMAX 630 MAX COLOR scanner with a transmission adapter at a resolution of 100–200 dpi. The image contrast was optimized using Adobe Photoshop 2.0.1 before analysis. The area of each phase was determined using public domain software, NIH Image 1.44, which measures the area occupied by a selected range of gray levels. Dividing this measured area by the area of the entire micrograph gives the area fraction of the selected phase in the image. The rules of stereology state that the area fraction of a phase equals the volume fraction in an isotropic sample. TEM, unlike reflective optical microscopy, for instance, produces a projected image from which we approximate the area fraction. The error associated with projection is substantial only when the domain size is comparable to the thickness of the film through which the electrons pass. In these polymer blend samples the domain sizes (~1000 nm) are typically much larger than the thickness of the microtomed sections (50 nm). Consequently, we equate the measured area fractions from the TEM images to the volume fractions of the bulk samples.
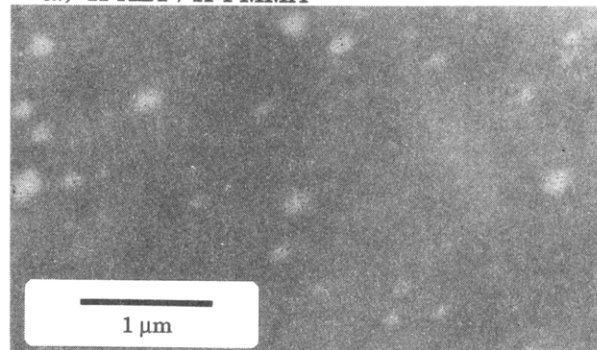
Results

Figure 1 shows the transmission electron microscopy (TEM) results for blends containing 35% alternating copolymer and 65% homopolymer. Three types of blends were prepared: no perdeuteration (H-ALT/H-PMMA), perdeuteration of the MMA units of the copolymer (D-ALT/H-PMMA), and perdeuteration of the PMMA homopolymer (H-ALT/D-PMMA). In the absence of deuteration the 35%/65% blend exhibits immiscibility as evidenced by the isolated, light-gray domains which contain more MMA units than the continuous, medium-gray phase (Figure 1a). The phase rich in MMA units constitutes approximately 3% by volume of the blend, though this value is somewhat unreliable due to the error associated with projecting small domains through a comparably sized sample. In contrast the DSC of this blend detects only one T_g, 106 °C, which typically implies miscibility (see Table 2). The TEM and DSC results for this blend are readily reconciled by acknowledging that a small volume of a second phase, less than ~10% of the blend, cannot be detected with conventional calorimetry methods.
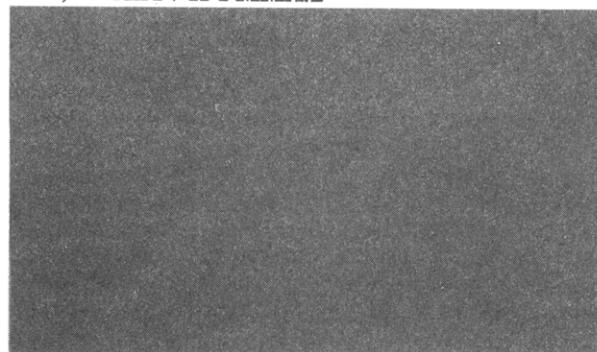
Perdeuteration of the MMA units of the alternating copolymer produces a miscible polymer blend of D-ALT/H-PMMA.2 at a composition of ~35% copolymer. The TEM images exhibit uniform contrast (see Figure 1b), and the DSC scans show one glass transition temperature, 99 °C. However, perdeuteration of the MMA units of the homopolymer, H-ALT/D-PMMA, produces an immiscible polymer blend at the same blend composition. Figure 1c shows the TEM images having light-gray domains which contain more MMA units than the surrounding medium-

35% Copolymer / 65% Homopolymer

a.) H-ALT / H-PMMA

1 μm

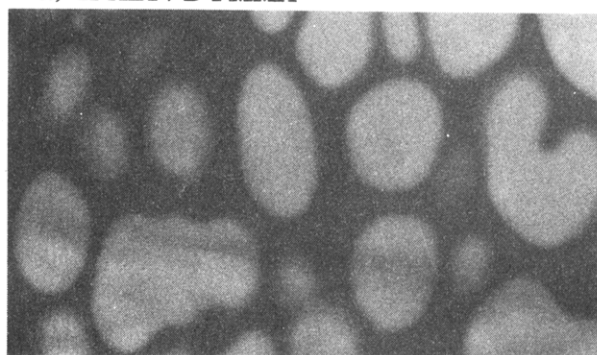### b.) D-ALT / H-PMMA.2

c.) H-ALT / D-PMMA

Figure 1. Transmission electron micrographs of blends containing ~35% alternating copolymer and ~65% homopolymer: (a) no perdeuteration, two phases, 35% H-ALT/65% H-PMMA.2; (b) perdeuteration of the MMA units in the copolymer, one phase, 34% D-ALT/66% H-PMMA.2; (c) perdeuteration of the homopolymer, two phases, 36% H-ALT/64% D-PMMA.

gray phase and are on the order of microns in size. The volume fraction of the copolymer-rich (medium-gray) phases is 42 ± 2 vol %. The DSC results for the ~35% H-ALT/65% D-PMMA indicate two glass transition temperatures, 97 and 115 °C, which also indicates the immiscibility of this blend.

In comparing the phase behavior of D-ALT/H-PMMA.2 and H-ALT/D-PMMA blends, notice that the weight-average molecular weights of the copolymers are comparable, while the weight-average molecular weight of H-PMMA.2 is higher than that of D-PMMA, 53 000 versus

**Table 2. TEM and DSC Results of Alternating Copolymer/
Homopolymer Blends**

| blend | 35% ALT/65% PMMA | | 50% ALT/50% PMMA | |
	TEM	T_g(DSC) (°C)	TEM	T_g(DSC) (°C)
H-ATL/H-PMMA.2	2 phases	106[a]	1 phase	107
D-ALT/H-PMMA.1		99		
D-ALT/H-PMMA.2	1 phase	99	1 phase	110
H-ALT/D-PMMA	2 phases	97, 115	2 phases	100, 119

[a] Only one T_g is observed via DSC for this phase-separated blend, because the volume fraction of the minority phase is quite small (~3 vol %).

39 000, respectively. Thus, an additional blend was prepared to evaluate the importance of this homopolymer molecular weight difference on the blend miscibility. The blend 35% D-ALT/65% H-PMMA.1 (M_w = 30 000) exhibits a single T_g, as did the blend of 35% D-ALT/65% H-PMMA.2 (see Table 2). The observed differences in phase behavior between D-ALT/H-PMMA.2 and H-ALT/D-PMMA blends cannot be attributed to the homopolymer molecular weight.

The TEM and DSC results for blends containing 50% alternating copolymer and 50% homopolymer are presented in Figure 2 and Table 2. Unlike the 35%/65% blend, the 50%/50% blend is miscible in the absence of perdeuteration as determined by both TEM images having a uniform gray level (Figure 2a) and by DSC showing a single T_g, 107 °C. However, as in the case of blends containing ~35% alternating copolymer, perdeuteration of the MMA units of the alternating copolymer and perdeuteration of the MMA units of the homopolymer produce miscible and immiscible blends, respectively. The copolymer-rich (medium-gray) phase constitutes 59 ± 2 vol % of the 50% H-ALT/50% D-PMMA blend as determined by image analysis. The DSC results for this blend indicate two glass transition temperatures: 100 and 119 °C.

Discussion

The blend miscibility in alternating copolymer/homopolymer blends is influenced by the presence of perdeuterated components and whether the perdeuteration is of the copolymer or the homopolymer. In the absence of perdeuteration, there is a phase boundary between 35% and 50% copolymer for the H-ALT/H-PMMA.2 blend system. The miscibility range is extended by perdeuterating the MMA units of the alternating copolymer as evidenced by the D-ALT/H-PMMA.2 blends being miscible at both compositions studied. In contrast the miscibility range is significantly reduced by perdeuterating the MMA units of the homopolymer. Using the lever rule or conservation of mass, the overall blend compositions, and the observed volume fractions, the compositions of the equilibrium phases were determined to be 0% and 84% alternating copolymer for the H-ALT/D-PMMA blend system. Thus, we conclude that H-ALT/D-PMMA blends containing up to 84% copolymer exhibit two phases, which is a larger immiscibility range than observed in either H-ALT/H-PMMA or D-ALT/H-PMMA blends. This deuterium effect significantly limits the experimental techniques available for exploring the interaction parameters of this system.

The following is a discussion of our results in terms of the copolymer effect presented in the introduction. The earliest theories of copolymer/homopolymer miscibility include the importance of the composition of the copolymer.[2-4] More recently, theories have added the importance of sequence distribution of the monomer units

50% Copolymer / 50% Homopolymer

a.) H-ALT / H-PMMA
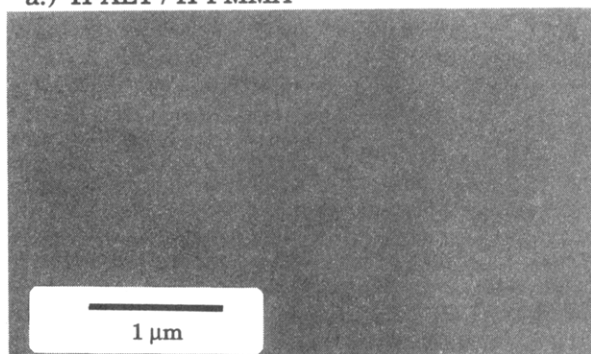
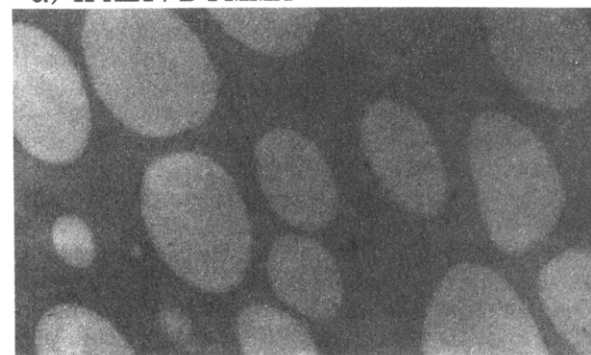b.) D-ALT / H-PMMA.2
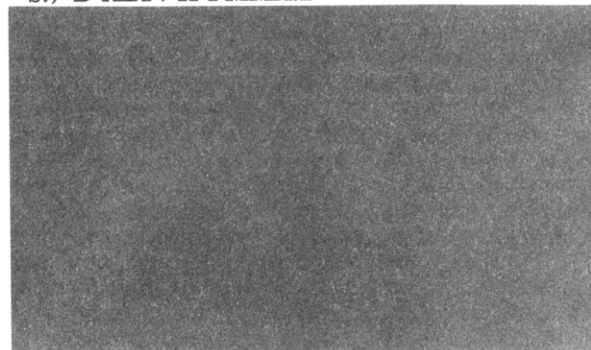
c.) H-ALT / D-PMMA

Figure 2. Transmission electron micrographs of blends containing 50% alternating copolymer and 50% homopolymer: (a) no perdeuteration, one phase; (b) perdeuteration of the MMA units in the copolymer, one phase; (c) perdeuteration of the homopolymer, two phases.

in the copolymers.[6-11] Here we will focus on the first class of theories, because all the copolymers of this study have the same monomer sequence, specifically a strictly alternating sequence.[12,15] The familiar mean-field, Flory-Huggins equation can be written for the free energy of mixing of a copolymer and a homopolymer as

$$\Delta G/RT = (\varphi_1/N_1) \ln \varphi_1 + (\varphi_2/N_2) \ln \varphi_2 + \chi_{blend}\varphi_1\varphi_2 \quad (1)$$

where N_i's are the degrees of polymerization, φ_i's are the volume fractions, and χ_{blend} is the net segmental interaction parameter for the system. According to these early theories, the interaction parameter for a copolymer blend, χ_{blend}, depends on the composition of the copolymer and the monomer–monomer interaction parameters of the components.[2-4] For example, the net interaction parameter of A_xB_{1-x}/C type blends is given by

$$\chi_{blend} = x\chi_{AC} + (1-x)\chi_{BC} - x(1-x)\chi_{AB} \quad (2)$$

where x is the fraction of A monomers in the copolymer ($0 < x < 1$) and χ_{ij} is the interaction parameter between i and j homopolymers. The prefactors describe the relative number of nonbonded interactions between the different monomer types; positive prefactors refer to the intermolecular interactions of the mixed state, and negative prefactors refer to the intramolecular interactions of the unmixed state, though in both cases the interactions do not include interactions with nearest bonded neighbors. Because the interaction parameter describes the interactions between nonbonded neighbors, this expression is independent of the bonded neighbors within the copolymer. In other words, this expression is independent of the sequence distribution. Additional limitations are implicit in this approach: the monomer–monomer interaction parameters are composition and molecular weight independent, polymers are monodisperse, and free volume changes are neglected. This formalism generally explains the copolymer effect in which a AB/C blend system has three positive homopolymer/homopolymer interaction parameters (χ_{AB}, χ_{AC}, and χ_{BC}), but the interaction parameter for the blend is negative which corresponds to favorable mixing. Specifically, if the interaction between A and B monomers of the copolymer are sufficiently unfavorable, that is, having a large positive interaction parameter, then blends of AB/C will be miscible over some composition range so that the unfavorable interactions between A and B can be screened by the homopolymer C. Such copolymer/homopolymer blends exhibit blend miscibility in the absence of specific interactions.

For our experiments involving alternating copolymer, the copolymer composition, x, equals 0.5 and the following expressions are derived:

Type 1.　$PS_{0.5}H$-$PMMA_{0.5}/H$-$PMMA$

$$\chi_{blend.1} = 0.25\chi_{PS,H\text{-}PMMA} \qquad (3)$$

Type 2.　$PS_{0.5}D$-$PMMA_{0.5}/H$-$PMMA$

$$\chi_{blend.2} = 0.50\chi_{PS,H\text{-}PMMA} - 0.25\chi_{PS,D\text{-}PMMA} + 0.50\chi_{H\text{-}PMMA,D\text{-}PMMA} \qquad (4)$$

Type 3.　$PS_{0.5}H$-$PMMA_{0.5}/D$-$PMMA$

$$\chi_{blend.3} = -0.25\chi_{PS,H\text{-}PMMA} + 0.50\chi_{PS,D\text{-}PMMA} + 0.50\chi_{H\text{-}PMMA,D\text{-}PMMA} \qquad (5)$$

Theoretically, the miscibility of blends of type 1, 2, and 3 will only be identical if these χ_{blend} values are equal. This would be the case if both $\chi_{H\text{-}PMMA,D\text{-}PMMA}$ was zero and $\chi_{PS,H\text{-}PMMA}$ approximately equaled $\chi_{PS,D\text{-}PMMA}$. However, our experimental results show that blends of type 3 are immiscible while blends of type 2 are miscible, which implies that the interaction parameter for type 3 blends is larger, $\chi_{blend.3} > \chi_{blend.2}$. Combining this expression with eqs 4 and 5 leads directly to the conclusion that the monomer–monomer interactions between PS and D-PMMA are more unfavorable than the monomer–monomer interactions between PS and H-PMMA, $\chi_{PS,D\text{-}PMMA} > \chi_{PS,H\text{-}PMMA}$.

The sequence-independent copolymer blend theories suitably organize our experimental results in the alternating copolymer and homopolymer blends. Enhanced intramolecular repulsion between styrene and perdeuterated methyl methacrylate monomer units within the perdeuterated alternating copolymer promotes miscibility in the D-ALT/H-PMMA blend system relative to the H-ALT/H-PMMA blend system. In other words, the D-ALT/H-PMMA system exhibits a copolymer effect. In H-ALT/D-PMMA blends the enhanced intermolecular repulsion between styrene monomer units of the copolymer and perdeuterated methyl methacrylate monomer units of the homopolymer promotes immiscibility.

Russell recently published interaction parameters for poly(styrene-b-methyl methacrylate) diblock copolymers having perdeuterated PS and/or PMMA blocks as determined using the random-phase approximation and SANS results.[17] In addition, Russell adopted the equation of state results of Callaghan and Paul[18] for PS/PMMA homopolymer blends to an equivalent nondeuterated diblock copolymer. The temperature-dependent interaction parameters are given as follows:

$$\chi_{P(S\text{-}b\text{-}MMA)} = 0.021 + 3.20/T$$

$$\chi_{P(S\text{-}b\text{-}D\text{-}MMA)} = 0.0292 + 3.188/T$$

Evaluating these interaction parameters at 140 °C, corresponding to the annealing temperature of this study, gives

$$\chi_{P(S\text{-}b\text{-}MMA)} = 0.029$$

$$\chi_{P(S\text{-}b\text{-}D\text{-}MMA)} = 0.037$$

These values are consistent with the inequality that this study established from the miscibility in alternating copolymer/homopolymer blends. The interaction between styrene monomers and deuterated methyl methacrylate monomers is more unfavorable than between styrene monomers and methyl methacrylate monomers.

Conclusions

Blend miscibility in the PS–PMMA alternating copolymer/PMMA homopolymer blend system changes with the substitution of hydrogen with deuterium. Perdeuteration of the MMA units of the copolymer promotes miscibility exhibiting a copolymer effect, and perdeuteration of the MMA units of the homopolymer reduces miscibility with respect to the absence of perdeuteration. Using sequence-independent models for copolymer/homopolymer blends, we have determined $\chi_{PS,D\text{-}PMMA} > \chi_{PS,H\text{-}PMMA}$. This inequality is consist with recent experimental determinations of the interaction parameters. This deuterium effect severely complicates future attempts to measure sequence-dependent interaction parameters using SANS or other techniques requiring deuteration as required for a quantitative comparison with theories by Balazs,[6,7,9,10] Cantow,[8] or others.

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