Hydrogen-Bonded Polymer Blends: The Influence of Annealing on the Interface Composition of Thin Films

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ABSTRACT: The interface compositions, before and after annealing, of hydrogen-bonded polymer blends have been investigated by neutron reflectivity. The polymer blends under this study are the blends of deuterated poly(methyl methacrylate) (d-PMMA) and poly(styrene-*co*-vinylphenol) (MPS), which contains 5, 10, or 15 mol % vinylphenol monomer units, and the blends d-MPS (5%)/poly(butyl methacrylate) and d-MPS (5%)/PMMA. In the formation of blends, the excess volume of mixing was found to be negative for blends of MPS (5%) but positive for blends of MPS (10%) and MPS (15%). The volumes of all blends are decreased by annealing. The concentrations of MPS at both interfaces, air/polymer and polymer/substrate, tended to increase after annealing for all blends except the blend MPS (5%)/d-PMMA which showed a significant extent of composition changes.

Introduction

Hydrogen-bonded polymer blend is an interesting and potentially useful system, where the inhomogeneity can be manipulated by controlling the number of hydrogen bonds in the blend.[1] This paper is aimed at exploring the effect of annealing on the thin-film properties of this type of blend by neutron reflectivity, which has been used to describe the composition profiles of polymer thin films.[2] Composition profiles reveal changes in the interface structures as well as volumes due to annealing. Various polymer systems have been studied by neutron reflectivity, including block copolymers of polystyrene and poly(methyl methacrylate),[3] isotopic blends of polystyrene,[4,5] a bilayer of chlorinated polyethylene/poly(methyl methacrylate),[6] a bilayer of polystyrene/d-polystyrene,[7] and polymer trilayers.[8] The theoretical calculation of reflectivity spectra is usually performed by using an assumed composition profile and a multilayer algorithm.[3,9] For example, the interface composition profile of an annealed bilayer of poly(methyl methacrylate) and polystyrene can be described approximately by a hyperbolic tangent function.[3] The mathematical function describing a particular interface is not unique but is model dependent because neutron reflectivity with a uniform layer model does not usually distinguish two similar composition profiles with some minor differences. However, the information of model-fitted interface composition revealed by this technique can contribute to the understanding of the surface properties, such as wetting, friction, and adhesion,[10,11] of these polymer blends.

The miscible blend under current investigation is composed of modified polystyrene and deuterated poly(methyl methacrylate) (d-PMMA). Polystyrene is modified to include a certain percentage of vinylphenol units; miscibility between the two polymers is achieved by the formation of hydrogen bonds between the vinylphenol units of the modified polystyrene and the ester group of d-PMMA. For example, polystyrene is not miscible with poly(methyl methacrylate) but becomes miscible when it is modified to contain ~5% of copolymerized vinylphenol units. Although the 5% modified polystyrene (MPS-5) forms a single-phase blend with PMMA at room temperature, thermally induced phase separation can be seen at elevated temperatures. The thermally induced phase separation, commonly known as the lower critical solution temperature phenomenon, is reversible in many miscible blends, that is, the heterogeneous structure reverts to a single phase upon cooling. However, in a blend of MPS-5 and PMMA, light-scattering results indicated that reversion to single phase was very slow and was not observed even when a slow cooling rate of 0.1 °C/min was used. Because of this characteristic, the interface profile can be frozen easily after phase separation. The interface structures of these phase-separated blends reveal information which is relevant to the understanding of the role of specific interaction between two different polymers. The information of excess volume of mixing can also be obtained from neutron reflectivity measurements and compared with the density measurements previously reported for a similar blend.

Experimental Section

MPS polymers containing 5, 10, or 15 mol % vinylphenol monomer units are designated in the text as MPS-5, MPS-10, and MPS-15, respectively. Deuterated MPS containing 5% vinylphenol monomer units is designated as d-MPS-5. Miscible binary blends under this study consist of equal weights of its components. These blends are d-MPS-5/PMMA, d-MPS-5/PBMA, MPS-5/d-PMMA, MPS-10/d-PMMA, and MPS-15/d-PMMA. Deuterated PMMA was purchased from Polymer Laboratory, Inc., and used as received. MPS-5 was prepared by the free radical copolymerization of styrene and *p*-acetoxystyrene in dioxane at 60 °C for 17 h. The resulting polymer was precipitated in methanol and subsequently hydrolyzed with hydrazine hydrate. After hydrolysis, the solution was neutralized and filtered, and the polymer was again precipitated in methanol. The molecular weight and polydispersity of this polymer were characterized by GPC, and the density was measured by a floating method. The characteristics of MPS-5 and d-PMMA are summarized in Table I.

Thin films for neutron reflectivity studies were prepared by spin-coating a 3% toluene solution of the polymer blend onto a polished silicon disk (50-mm diameter, 7.5 mm thick) purchased from Semiconductor, Inc., Boston, MA. The film thickness was controlled by the spinning speed, ~2000 rpm in this case, and the viscosity of the solution. Because the exact thickness is not critical in this experiment, a rough estimate of the thickness was obtained from the known weight, density, and area of the film. The actual thicknesses, in the range 1200-1800 Å as determined later by neutron reflectivity experiments, are 10-40% less than the initial estimate. The samples were placed in a vacuum oven

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Table I
Characteristics of the Polymers

polymer	M_n	M_w/M_n	density (g/cm^3)	$10^6(b/V)$ (Å^{-2})
MPS-5	84 900	1.70	1.0513	1.42
MPS-10	82 300	1.62	1.0612	1.44
MPS-15	85 600	1.47	1.0700	1.46
d-PMMA	87 500	1.03	1.2830[a]	7.02
d-MPS-5	137 400	1.60	1.1275	6.20
PMMA	74 000	1.07	1.1880	1.07
PBMA	94 800	2.15	1.0700	0.29

[a] This value is obtained by using the density of h-PMMA (1.188 g/cm^3 at 25 °C) from *Polymer Handbook* (Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989) and correcting for the 8% increase in monomer mass.

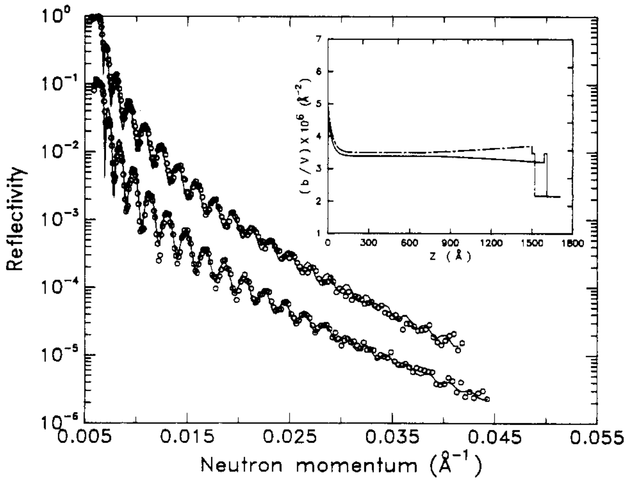

Figure 1. (Top) curve representing the reflectivity from the 50/50 d-MPS-5/PBMA blend before annealing. The circles are the measured data, whereas the solid line represents the calculated reflectivity using the scattering length density profile (solid line) shown in the inset. The origin of the abscissa is the air/polymer interface, with the substrate located at 1600 Å. (Bottom) curve representing the reflectivity after the sample is annealed at 130 °C for 9 h and 195 °C for 12 h. The composition profile after annealing is shown in the inset as a dashed-dotted line. For clarity, the bottom curve has been shifted 10^{-1} downward.

at 100 °C for 3 days to remove the solvent. These dried samples were visually observed to have a uniform gloss and color. Neutron reflectivity spectra were measured on the same specimen before and after different stages of annealing.

The neutron reflectivity experiments were performed on the reflectometer SPEAR at the Manuel Lujan, Jr., Neutron Scattering Center (LANSCE) at the Los Alamos National Laboratory. The nominal angle of incidence for these experiments was ≈1.0°, subject to the placement of sample. The incident and reflected beams define a vertical scattering plane. With a temporary water moderator, we used a wavelength frame of $1 < \lambda < 16$ Å, which yields an accessible range of incident perpendicular wavevectors (at an incident angle of 1.0°) $0.007 < \mathbf{k} < 0.11$ Å^{-1} where $\mathbf{k} = (2\pi/\lambda) \sin \theta$. Since the neutrons were generated by spallation, the neutron wavelengths were resolved using standard time-of-flight techniques. As defined by the detector resolution, the electronic timing resolution, and neutron pulse width, the resolution for these experiments was in the range $3\% < \delta\mathbf{k}/\mathbf{k} < 5\%$ for wavevectors ranging from 0.007 to 0.11 Å^{-1}, respectively. With SPEAR in this configuration, the minimum measurable reflectivity is $R \approx 10^{-6}$. Typical counting times for these samples were approximately 3 h to obtain the statistics shown in Figures 1-5.

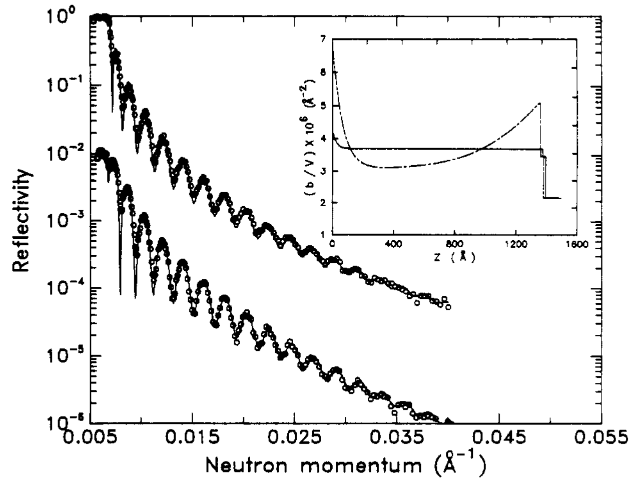

Figure 2. Profiles representing the reflectivities from the 50/50 d-MPS-5/PMMA blend before (top) and after (bottom) annealing. The circles are the experimental data whereas the solid line represents the calculated reflectivity. The solid and dashed-dotted lines in the inset represent the composition profiles before and after annealing, respectively. For clarity, the bottom curve has been shifted 10^{-2} downward.

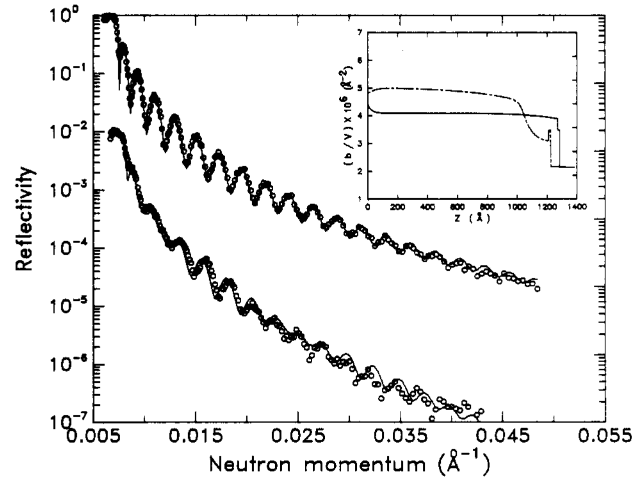

Figure 3. Profiles representing the reflectivities from the 50/50 MPS-5/d-PMMA blend before (top) and after (bottom) annealing. The circles are the experimental data whereas the solid line represents the calculated reflectivity. The solid and dashed-dotted lines in the inset represent the composition profiles before and after annealing, respectively. For clarity, the bottom curve has been shifted 10^{-2} downward.

Results and Discussion

The method used to calculate reflectivity profiles, based on assumed composition profiles, has been described in refs 3 and 9. The roughness at the air/polymer and polymer/silicon interfaces (Table II) is included in the recursion formulation. The specific volumes of the films were calculated from the average scattering lengths and listed in Table III. The plane average profile of roughness at the interfaces is assumed to be a hyperbolic tangent function.[12] The roughnesses at the interfaces, presented in this paper, are the parameters which characterize the width of a hyperbolic tangent profile. Since we did not find a single mathematical function to describe the composition profiles for these annealed blends, a combination of the exponential function and the modified hyperbolic tangent of the following forms is used.

$$E(x) = \exp(-ax) \tag{1}$$

$$E(x) = E_o + (H - E_o)(ae^{bm} - 1)/(ae^{bm} + 1) \tag{2}$$

In the above equations, a and b are adjustable parameters, E_0 is the average scattering length in the profile, H is the high limit of the scattering length in the profile, and $m = (x - n/2)d/D$, where n is the number of layers, d is the thickness of a single layer, and D is the total thickness of the profile. The choice of these functions is empirical and is not necessarily the only way to describe these profiles.

Usually, a thin film is first divided into two or three layers, and each layer is assigned a profile shown in eq 1

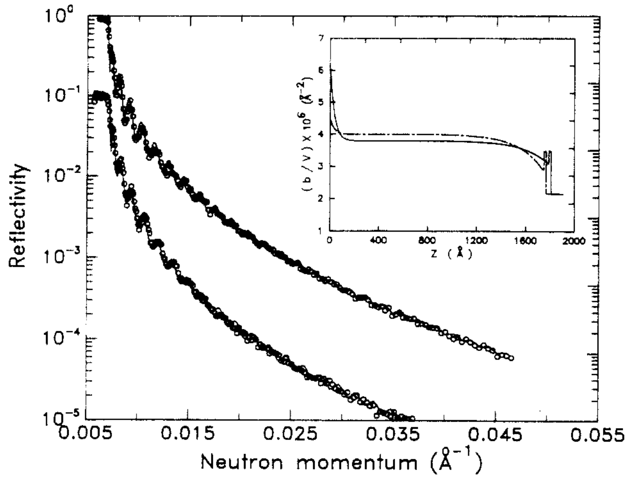

Figure 4. Profiles representing the reflectivities from the 50/50 MPS-10/d-PMMA blend before (top) and after (bottom) annealing. The circles are the experimental data whereas the solid line represents the calculated reflectivity. The solid and dashed-dotted lines in the inset represent the composition profiles before and after annealing, respectively. For clarity, the bottom curve has been shifted 10^{-1} downward.

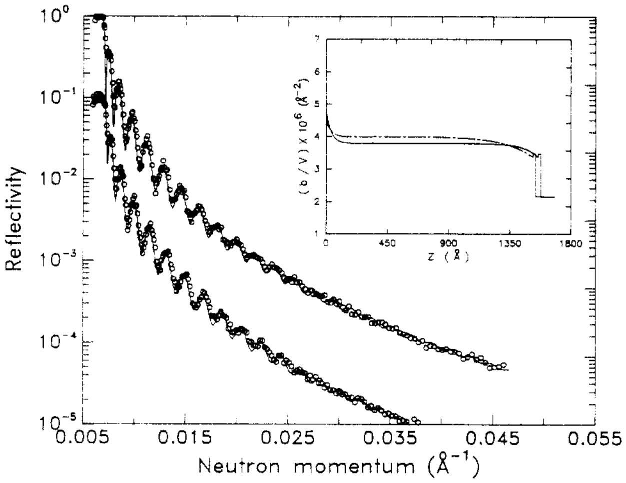

Figure 5. Profiles representing the reflectivities from the 50/50 MPS-15/d-PMMA blend before (top) and after (bottom) annealing. The circles are the experimental data whereas the solid line represents the calculated reflectivity. The solid and dashed-dotted lines in the inset represent the composition profiles before and after annealing, respectively. For clarity, the bottom curve has been shifted 10^{-1} downwards.

Table II
Roughness at the Air/Polymer and Polymer/Silicon Interfaces

50/50 blend	polymer/silicon interface (Å)	air/polymer interface (Å) as prepared	air/polymer interface (Å) annealed
d-MPS-5/PBMA	18	10	7
d-MPS-5/PMMA	18	3	6
MPS-5/d-PMMA	15	4	10
MPS-10/d-PMMA	15	4	3
MPS-15/d-PMMA	15	2	2

or 2. After that, each layer is again divided into a certain number of layers with 10–15 Å for each layer. A 15-Å-thick silicon oxide layer is assumed to exist on the silicon surface. The results of fitted reflectivity profiles are shown in Figures 1 through 5. The top and bottom curves in each figure represent the reflectivities of the sample before and after annealing, respectively. Although there may be more than one composition profile which can be used to fit a set of reflectivity data, the simplest one is chosen for these fittings. Because the blends in this study have only two components, the number of choices of composition profiles, which can be used to describe the films before or after annealing, is very few. We did not find other composition profiles which could give a fit equally good as those presented here. The calculated reflectivity profiles represent the best fit that we have attained through trial and error. Further refinement of these fits is possible, but unnecessary because the agreement between experimental and calculated results are already within the experimental error of the reflectivity measurements.

Table III
Calculated and Experimental Specific Volumes of the Blends

50/50 blend	calc[a] (cm^3/g)	exp[b] (cm^3/g)	% change
d-MPS-5/PBMA	0.911	0.853	−6.4
d-MPS-5/PMMA	0.864	0.869	+0.6
MPS-5/d-PMMA	0.865	0.838	−3.2
MPS-10/d-PMMA	0.861	0.905	+5.1
MPS-15/d-PMMA	0.857	0.900	+5.0

[a] Calculated values are obtained from the following equation: $V = W_1V_1 + W_2V_2$, where W_1 and W_2 are the weight fractions of the components in the blend and V_1 and V_2 are the specific volumes of the pure components. In these blends, $W_1 = W_2 = 0.5$. [b] Experimental values are obtained from the average scattering length density profiles.

The initial state of a cast film is defined by the condition under which it is prepared. It is influenced by the choice of solvent, concentration, temperature, and spinning speed. After drying at 100 °C for 72 h, the films were quenched to room temperature which was about 80 °C below the glass transition temperature of the component polymers. Although the initial state is not the equilibrium state, it is the change between the initial and final states that is of interest. Our purpose is to learn how one can use annealing to manipulate the surface properties of these blends.

The various annealing temperatures relative to the phase separation temperature for these blends were investigated by the cloud point measurements. The cloud point of d-MPS-5/PBMA is ~138 °C, as measured by temperature scan light scattering at a heating rate of 0.1 °C/min and a fixed angle of 15°. The cloud point observed visually by heating the sample in a vacuum oven at each temperature for 3 days and using a temperature increment of 10 °C is ~130 °C. The method yields ~125 °C as the cloud point for the MPS-5/PMMA blend. The annealing temperatures listed in Table IV are well within the two phase regions, except for the blends of MPS-10 and MPS-15, which do not undergo phase separation under these annealing conditions. Concerning the surface effect, the surface free energy can contribute to the total free energy of the system and thus affect the spinodal and binodal temperatures,[13,14] but its magnitude is uncertain. In the symmetric diblock copolymer of deuterated polystyrene and PMMA, surface effect causes the elevation of the microphase separation temperature[15] when the thickness of the bilayer is less than half the period of the lamellar microdomain, which is about twice the R_g (radius of gyration) of a single polystyrene[16,17] or PMMA[18] chain in the melt. According to that study, the surface effect in our films should not exert any significant effect on the spinodal and binodal temperatures of the blends because the thickness of our films is at least 12 times R_g. However, the interactional free energy due to hydrogen bonding between MPS and silicon oxide can alter the total free energy significantly. Through the comparison of bulk-phase behavior and the composition change in the thin film, we find that most of the blends studied here have parallel phase behavior in the bulk and in the thin-film states, except the blend d-MPS-5/PBMA. At the annealing temperature of 195 °C, d-MPS-5/PBMA is ex-

Table IV
Sample Thickness before and after Vacuum Annealing

50/50 blend	as-prepared thickness (Å)	annealed thickness (Å)	% change in thickness	annealing condition (h/°C)
d-MPS-5/PBMA (toluene)[a]	1600	1510	−5.6	9/130, 12/195
d-MPS-5/PMMA (toluene)[a]	1375	1370	−0.4	3/170, 7.5/195
MPS-5/d-PMMA (toluene)[a]	1270	1240	−2.4	19.5/170, 7/185
MPS-10/d-PMMA (dioxane)[a]	1800	1760	−2.2	9.3/195
MPS-15/d-PMMA (dioxane)[a]	1590	1530	−3.8	10.5/170, 9.3/195

[a] Solvent used in the preparation of the blend.

pected to be phase separated, but instead it shows only a slight change in its composition profile (Figure 1). One possible factor is that d-MPS-5 preferentially segregates to both interfaces, and this surface effect elevates the phase separation temperature. As a result, the blend remains in a phase-mixed state. Another factor is the chain scission previously found in MPS-5.[19] Both effects can cause the elevation of phase separation temperature.

An interesting phenomenon that is worth mentioning is the comparison between the change of composition profile of d-MPS-5/PMMA and that of MPS-5/d-PMMA. In the case of MPS-5/d-PMMA, d-PMMA segregates to the air/polymer interface while MPS-5 segregates to the polymer/substrate interface. The result is a two-layer structure with a broad phase boundary.[19] In the case of d-MPS-5/PMMA, d-MPS-5 prefers to segregate to both interfaces. The resulting composition profile does not have a three-layer structure, but has a concave shape (Figure 2) due to the broad phase boundary in this type of blend. The contribution of surface effect in the formation of this composition profile is not clear.

All the annealed blends were believed to be close to the equilibrium state at the annealing temperature because there was insignificant change of reflectivity profile after further annealing at the same temperature. In this particular system, phase separation prefers to proceed in the direction perpendicular to the substrate due to the hydrogen bonds between MPS and silicon oxide and the difference in the surface free energy of the component polymers. Inhomogeneity along the lateral direction, if there is any, cannot be determined by the current analysis. Our analysis is based on the **k** range shown in the figures, within which the off-specular reflection arising from inhomogeneity is not significant, and therefore gives a plane average composition profile. Beyond the **k** range studied, the reflectivity is too weak for useful analysis. The information obtained from a plane average composition profile is useful in that it gives the enrichment of a certain component in the blend along the depth of the film.

After annealing, the roughness at the air/polymer interface was found to decrease or remain the same if there was no significant change in the composition profile, whereas the roughness at the air/polymer interface increased. The increase in roughness at the air/polymer interface is most pronounced in the blend MPS-5/d-PMMA. We speculate that the increased roughness in this sample is due to the migration of MPS-5 away from the interfaces, thus leaving vacancies that are not completely filled after further annealing. The roughness values at both interfaces before and after annealing are summarized in Table II, and the annealing conditions are listed in Table IV. One should be reminded that the roughness parameters listed in Table II are the parameters which characterize the width of a hypoberlic tangent profile at the interfaces. They are proportional, but not equal, to the exact physical roughness. Several specimens were annealed first at a lower temperature and subsequently at a higher temperature only because small changes were found in reflectivity profiles after the first annealing.

In the formation of the blend films, a negative excess volume of mixing was found from the average scattering length density profiles for blends of MPS-5, whereas positive values were obtained for blends of MPS-10 and MPS-15. The same behavior was also observed in conventional specific volume measurements for a similar hydrogen-bonded blend system.[20] The results are summarized in Table III. The negative excess volume which is common in many blends can be understood as the result of hydrogen bonds between the free hydroxyl group in MPS and the carbonyl group in PMMA. The reasons for positive excess volumes are more complicated. We reason that the volume shrinkage to be expected from interpolymer hydrogen bond formation is countered, to some extent, by the breakup of the self-association of the hydroxyl groups in MPS and by the poor packing of the inherently immiscible segments of styrene and methyl methacrylate. Under atmospheric pressure, it is reasonable to assume that the average packing distance between styrene and methyl methacrylate units is greater than that between styrene units of different MPS chains or that between methyl methacrylate units of different PMMA chains. From our previous studies of miscibility in hydrogen-bonded blends by solid-state NMR,[1] we also know that the average size of inhomogeneity in the blends decreases as the number of hydrogen bonds increases. On the basis of these data, it can be deduced that the reduction of the size of inhomogeneity will also increase the number of encounters between these inherently immiscible segments of styrene and methyl methacrylate; consequently, the region of poor packing increases and a positive excess volume of mixing results, although interpolymer hydrogen bonding is more extensive in these blends.

The effect of annealing on the thickness of film is shown in the Table IV. The thickness values are reduced for all blends during annealing, except that of d-MPS-5/PMMA, which remains almost constant during annealing. Coincidentally, the excess volume of mixing of d-MPS-5/PMMA is also close to zero. The volume reduction for these blends after annealing might be due to the repacking of polymer chains at the annealing temperature. This can be understood from the process of film preparation. These films were cast from solvent at room temperature. In the process of solvent removal during spinning and subsequent drying at 100 °C, which is slightly below the T_g of the polymers, the segmental mobility of chains in the film is more limited than that at the temperature of annealing; consequently, polymer chains are more efficiently packed at the annealing temperature. Upon quenching from the annealing temperature to room temperature, the state of packing is apparently preserved first by the effect of hydrogen bonding and later by vitrification. For example, the number of hydrogen bonds in a related blend has been shown to increase when the temperature is decreased from 200 °C and to reach a constant value at a temperature close to the T_g of MPS (110 °C).[21] The volume reduction by annealing is most

Table V
Interface Compositions of Blends before and after Annealing

		composition[a]			
		air/polymer interface		polymer/substrate interface	
50/50 blend	bulk	as prepared	annealed	as prepared	annealed
d-MPS-5/PBMA	49/51	73/27	78/22	49/51	58/42
d-MPS-5/PMMA	51/49	61/39	100/0	51/49	79/21
MPS-5/d-PMMA	55/45	49/51	36/64	56/44	70/30
MPS-10/d-PMMA	55/45	15/85	45/55	70/30	74/26
MPS-15/d-PMMA	55/45	40/60	45/55	65/35	65/35

[a] The compositions are calculated from the scattering length density at the intersections of the composition profile and interfaces and are expressed in terms of volume ratio. They were estimated by assuming the densities of the individual components in the blends to be the same as those of pure components.

pronounced in the blend d-MPS-5/PBMA, where a 5.6% decrease in the thickness was found.

The as-prepared films of d-MPS-5/PBMA and d-MPS-5/PMMA show an enrichment of d-MPS-5 at the air/polymer interface, while the blends of MPS-5/d-PMMA, MPS-10/d-PMMA, and MPS-15/d-PMMA show an enrichment of d-PMMA at the air/polymer interface and an enrichment of MPS at the polymer/silicon interface. This indicates the surface tension of PMMA or PBMA is larger than that of d-MPS-5, while the surface tension of d-PMMA is less than that of MPS-5, MPS-10, or MPS-15. The fact that the surface tension of d-PMMA is less than that of MPS-5 is interesting if we compared MPS-5/d-PMMA with the block copolymer of polystyrene and d-PMMA,[3] where the surface tension of d-PMMA is larger than that of polystyrene. This behavior is attributed to the higher density of MPS-5 compared with that of polystyrene. According to Macleod's equation,[22-25] the surface tension is proportional to the *n*th power of density. Consequently, MPS-5 has a greater surface tension than that of polystyrene. Another interesting behavior we observed is the change in the relative magnitude of surface tensions of component polymers when we compare these changes in the blend MPS-5/d-PMMA to those in the blend d-MPS-5/PMMA. After annealing, d-PMMA dominates the surface of MPS-5/d-PMMA, while d-MPS-5 dominates the surface of d-MPS-5/PMMA. Deuteration seems to alter the relative magnitude of surface tensions of these polymers. We speculate that this change comes from the density change by deuteration.

After annealing, all blends show an increase in MPS concentration at both interfaces, except the blend MPS-5/d-PMMA. This blend undergoes phase separation initially to form a two-layer structure and then remixing after prolonged annealing due to the chain scission of MPS-5.[19] Compared with MPS-5/d-PMMA, all other blends in this study do not show such a significant change in their composition profiles. The calculated interface compositions are summarized in Table V. The compositions were estimated by assuming the density of each polymer in the blend to be the same as that of the pure component. Upon quenching to room temperature, the compositions of the blends are frozen in a state corresponding to that at the annealing temperature due to the effect of hydrogen bonding and glass transition. From the last two columns of Table V, one also observes that the differences in MPS concentration caused by annealing are 14, 4, and 0 for MPS-5/d-PMMA, MPS-10/d-PMMA, and MPS-15/d-PMMA, respectively. This indicates the enrichment of MPS on the polymer/silicon interface also depends on the number of hydrogen bonds between MPS and d-PMMA. As the vinylphenol content in MPS increases to provide more interaction sites between MPS and d-PMMA,[21] the concentration change of MPS at the polymer/substrate interface, caused by annealing, decreases. The chain scission of MPS previously reported[19] has only a minor effect on the MPS concentration at the polymer/substrate interface, as shown in Table III of ref 19.

In summary, annealed thin films of hydrogen-bonded blends have different compositions at their air/polymer and polymer/substrate interfaces. The interface compositions of these blends change with annealing due to the following reasons: (1) the adsorption of poly(styrene-*co*-vinylphenol) onto silicon oxide, (2) the difference in the surface tensions of the component polymers in the blend, and (3) the preservation of the annealing state by hydrogen bonds and glass transition. The observed behaviors indicate that the thermal treatment alters the surface properties of hydrogen-bonded polymer blends. The trend in the excess volume of mixing measured by neutron reflectivity for the blends reported here is in agreement with that measured by the density gradient method for a bulk film of a similar hydrogen-bonded blend.

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