Equilibrium Structure of Hydrogen-Bonded Polymer Blends

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Received 27 March 1998; accepted 18 May 1998

ABSTRACT: Deuterium-labeled polystyrene modified by random distributions of the comonomer p-(1,1,1,3,3,3-hexaflouro-2-hydroxyisopropyl)- α -methyl-styrene [DPS(OH)] has been blended with poly(butyl methacrylate) (PBMA) and studied with small-angle neutron scattering (SANS). Miscibility is induced via hydrogen bonding between the DPS(OH) hydroxyl group and PBMA carbonyl groups. The data suggest that the nature of the miscible-phase structure in these blends differs from that of the usual homopolymer blends at small scattering angles, which we attribute to the short-range site specific nature of the hydrogen bond interaction. © 1998 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 36: 2745–2750, 1998

Keywords: polymer blends; hydrogen bonding; small-angle neutron scattering

INTRODUCTION

Hydrogen bonding is an effective way of making miscible blends out of otherwise immiscible polymer components.¹⁻¹¹ If polymers A and B are immiscible over any practical range of temperature, miscibility can often be enhanced if, for example, polymer A is modified by the introduction of a random distribution of a comonomer that can form hydrogen bonds with B-chain segments. The resulting blend is then a lower-critical-solutiontemperature (LCST) system with an effective chain-averaged interaction parameter. Because of the strong site-specific nature of hydrogen bonding, the conventional random-phase approximation would appear to be inadequate. Past studies demonstrate a clear deviation from a Lorentzian scattering profile at small scattering angles in hydrogen-bonded blends of polystyrene and poly-(butyl methacrylate).^{6,12} Such a deviation has been associated with either a transient approach to thermal equilibrium for very dilute bond distributions,^{7,10} or a thermodynamically reversible deviation associated with an equilibrium state at moderate hydrogen-bond densities.¹²

We use small-angle neutron scattering (SANS) to quantitatively investigate the effect of hydrogen-bond density on the structure of long-wave length thermal composition fluctuations in hydrogen bonded polystyrene/poly(butyl methacrylate) blends. In all cases, the blends studied are well above the glass transition temperature but below the extrapolated stability limit. The anomalous low-q scattering that is observed is attributed to the details of the hydrogen bond distribution. Over a fixed window of temperature, this structure is observed to depend strongly on the density of hydrogen bonds.

EXPERIMENT

Materials

The systems we consider are blends of modified, deuterium-labeled polystyrene [DPS(OH)] and poly(butyl methacrylate) (PBMA) and are identical to those used in a previous study.¹² To induce miscibility, the comonomer p-(1,1,1,3,3,3-hexaflouro-2-hydroxyisopropyl)- α -methyl-styrene (HFMS) is introduced at random sites along the DPS chain. Each OH group on the HFMS can form a hydrogen bond with the carbonyl group on any nearby PBMA segment. Random copolymer

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Journal of Polymer Science: Part B: Polymer Physics, Vol. 36, 2745–2750 (1998) © 1998 John Wiley & Sons, Inc. CCC 0887-6266/98/152745-06

	M_W	M_N	$T_g \ (^{\rm o}{\rm C})$
DPS(OH)-1.2 DPS(OH)-3.5 DPS(OH)-10.1	60,300 53,700 36,000	33,400 28,200 21,000	118 ± 5 118 ± 5 123 ± 5
PBMA-LL2	71,000	51,000	42 ± 5

Table I. Characteristics of the Pure Components

of deuterated styrene and HFMS was prepared using 2,2'-azoiso-butyronitrile (AIBN) and toluene as initiator and solvent, respectively.² The purified products were characterized by fluorinecontent, gel-permeation-chromatography (GPC), and infrared analysis and are denoted by DPS-(OH)-x, where x/100 is the comonomer mole fraction or probability that a given styrene segment is modified by the presence of the HFMS. For the DPS(OH)-x components, the average number of OH per chain (and standard deviation) determined by elemental fluorine analysis¹³ is, $6 (\pm 2)$, 16 (±4), and 28 (±5) for x = 1.2, 3.5, and 10.1,respectively.¹⁴ The PBMA-LL2 was prepared using AIBN and toluene as initiator and solvent, respectively, fractionated in toluene and methanol, and characterized with GPC. Glass transition temperatures were determined using differential scanning calorimetry (DSC). For all of the blends described here, DSC identified a single welldefined glass transition temperature. For the pure components, molecular weight¹⁵ distributions and glass transition temperatures are shown in Table I. The blends are all 40/60 DP-S(OH)-x/PBMA-LL2 by weight, with glass transition and spinodal temperatures of $T_g = (63 \pm 5)^{\circ}$ C and $T_s = (145 \pm 18)^{\circ}$ C (x = 1.2); $T_g = (68 \pm 5)^{\circ}$ C and $T_s = (307 \pm 30)^{\circ}$ C (x = 3.5); $T_g = (71 \pm 5)^{\circ}$ C and $T_s = (560 \pm 50)^{\circ}$ C (x = 10.1).

SANS Measurements

Blends for SANS measurements were solvent cast from toluene, dried in a vacuum oven for 2 days at 90 \pm 2°C and at 110 \pm 2°C for one day, meltpressed into 1 mm-thick disks, and annealed for 12 h at 90 \pm 2°C. The 40/60 DPS(OH)/PBMA composition [$\phi_0 = 0.40$ where ϕ_0 is the DPS(OH) volume fraction] is slightly removed from the (theoretical) "critical" composition $\phi_c = B_B^{1/2}/(N_A^{1/2} + N_B^{1/2}) \approx 0.5$ where the cubic term in a Landau expansion of the free-energy of mixing vanishes.⁹ The pressed samples were transparent to visible light, and SANS measurements as a function of temperature and OH content were done on the 8-m instrument at the Cold Neutron Research Facility of the National Institute of Standards and Technology using incident neutrons of wavelength of 12 Å. The two-dimensional scattering profiles were azimuthally averaged and the measured background was subtracted to yield intensity as a function of the scattered wavevector, $\mathbf{q} = 4\pi/\lambda \sin(\theta/2)$, where θ is the scattering angle.

RESULTS AND DISCUSSION

A rigorous theory of the SANS structure factor of hydrogen-bonded polymer blends is not available. Following a previous phenomenological approach,⁹ we consider a spatially varying interaction parameter that models fluctuations in hydrogen bond density, and which can be written as

$$\chi_{HB}(\mathbf{r}) = \bar{\chi} + \rho(\mathbf{r}), \qquad (1)$$

where $\bar{\chi} = \int d\mathbf{r}\chi(\mathbf{r})/V$ and $\int d\mathbf{r}\rho(\mathbf{r})/V = 0$. In this quasi-quenched approximation, hydrogen bonds in the miscible phase form a network, the structure of which is taken to be static on the time scale of thermal composition fluctuations over length scales smaller than or comparable to the effective mesh size. The field $\rho(\mathbf{r})$ models the spatially varying or inhomogeneous part of the interaction. For $\rho = 0$, we recover the usual homopolymer-blend structure factor

$$S_o(q) = \frac{S(0)}{1 + \xi^2 q^2}$$
(2)

in the low-q limit, where S(0) and ξ are the susceptibility and correlation length, respectively. For q larger than a cutoff q_c characteristic of $\rho(\mathbf{r})$, the scattering is well approximated by eq. (2).

Treating eq. (2) as the "form factor" for the free (uncoupled) fluctuations, we can formally define a low-q structure factor associated with the coupling to $\rho(\mathbf{r})$ via $S(q) = I(q)/S_o(q)$, so that $S(q) \rightarrow 1$ for $q > q_c$. As shown in Figure 1, dividing out $S_o(q)$ in this way removes a large part of the temperature dependence, which is consistent with a picture in which the composition fluctuates about a fixed bond configuration. In this work, we fit the residual structure to an expression of the form

$$I(q)/S_o(q) \equiv S(q) = 1 + Aq^{-y}.$$
 (3)



Figure 1. Low-q structure obtained by dividing the measured scattering intensity [I(q)] by a Lorentzian fit of the data above the cutoff wavevector q_c $[S_0(q)]$. The horizontal scale (q axis) is common while the vertical scale is not. In (a), circles correspond to 100°C, diamonds to 110°C, triangles to 120°C, and squares to 130°C. In (b) and (c), circles correspond to 100°C, diamonds to 120°C, and triangles to 140°C.

Physically, the field $\rho(\mathbf{r})$ reflects the fact that thermal fluctuations occur in a spatially varying "potential" set by the distribution of hydrogen bonds and the size of the chains. Over length scales for which these oscillations can be ignored ($q > q_c$), the blend appears homogeneous and eq. (2) is adequate. Over length scales for which these oscillations are important ($q < q_c$), they act as an energetic barrier to extended composition fluctuations. It is important to note that the particular form of eq. (3) used here is simply what works over the q range in question, which may represent the limiting form of a more complicated expression. The fitting results for the total intensity based on eqs. (2) and (3) are summarized in Table II and are displayed along with the data in Figure 2.

Figure 3 shows a double logarithmic plot of the structure factor for the three different hydrogen bond densities at a fixed temperature of 100°C. As the density increases, the energy barrier to thermal fluctuations increases and the mixture moves further away from the spinodal. As a consequence of this, thermal fluctuations are suppressed. The effect of increasing the density of hydrogen bonds at a fixed temperature is represented schematically in Figure 4. At low hydrogen bond densities, the unbound portions of the chains still have enough freedom to fluctuate. As the density increases, this freedom disappears. Previous studies⁵ suggest the formation of an intermolecular complex at sufficiently high OH content in hydrogen-bonded blends of PS(OH) and poly (methyl methacrylate). More data at significantly lower qis needed before we can offer further speculation as to the nature of the equilibrium structure in these blends.

One possible scenario is that spatial variations in the hydrogen bond density give the system a natural tendency to decompose into some type of modulated or microphase-separated state. A recent phenomenological model suggests a stable or metastable intermediate phase between miscibility (low *T*) and macroscopic phase separation (high *T*) when the hydrogen bond density is sufficiently dilute.⁹ Evidence for this type of behavior is shown in Figure 5 for the x = 1.2 sample. The slope of a Zimm plot of $I^{-1}(q)$ vs. q^2 is the interfacial coefficient $\kappa = \xi^2/S(0)$ that gives the free-

x	T (°C)	ξ (Å)	$S(0) (cm^{-1})$	у	A (Å ^{-y})
1.2	100	33.9 ± 2.0	39.6 ± 4.0	2.0 ± 0.1	$-(6.0\pm2.0) imes10^{-6}$
	110	38.8 ± 2.0	50.5 ± 4.0	1.9 ± 0.1	$-(1.2\pm 0.3) imes 10^{-5}$
	120	46.7 ± 3.0	71.4 ± 4.0	1.8 ± 0.1	$-(2.0\pm0.5) imes10^{-5}$
	130	61.2 ± 4.0	124.6 ± 4.0	1.9 ± 0.1	$-(1.4\pm0.3) imes10^{-5}$
3.5	100	14.0 ± 0.4	6.2 ± 0.4	3.6 ± 0.3	$(2.6\pm 0.5) imes 10^{-10}$
	120	15.1 ± 0.6	7.1 ± 0.4	3.8 ± 0.3	$(1.4\pm 0.4) imes 10^{-10}$
	140	16.9 ± 0.6	8.5 ± 0.4	3.5 ± 0.3	$(1.0\pm 0.3) imes 10^{-9}$
10.1	100	5.9 ± 0.3	1.4 ± 0.1	3.6 ± 0.4	$(1.6\pm 0.5) imes 10^{-8}$
	120	6.4 ± 0.3	1.4 ± 0.1	3.9 ± 0.4	$(4.1 \pm 2.0) imes 10^{-9}$
	140	6.7 ± 0.3	1.6 ± 0.1	4.2 ± 0.4	$(1.7\pm 0.7) imes 10^{-9}$

Table II. Fitting Parameters for the Fits of the Data Shown in Figure 2



Figure 2. Zimm plots of the inverse scattering intensity vs. wavevector squared for (a) 1.2% OH content, (b) 3.5% OH content, and (c) 10.1% OH content. The curves are the fits to the data described in the text and the insets show the low q behavior. The spinodal temperatures deduced from the temperature dependence of the susceptibility and correlation length¹² are (a) 145°C, (b) 307°C, and (c) 560°C.



Figure 3. At a fixed temperature of 100°C, the total scattering intensity exhibits an order of magnitude increase between 1.2 and 10.1% OH content. The curves are the fits described in the text.

energy cost of a composition gradient, $\frac{1}{2} \kappa |\nabla \phi|^2$. The sudden increase in ξ at 140°C (inset) approximately 5 K below the extrapolated spinodal suggests a change in the interfacial energy, which might be associated with microphase separation or a shift in the distribution of hydrogen bonds. That a composition gradient suddenly costs more free energy seems consistent with a transition into a lower free-energy, modulated phase.

CONCLUSIONS

In conclusion, we present a quantitative study of the effect of hydrogen bond density on the equilibrium-phase structure of hydrogen-bonded DPS/ PBMA blends using small-angle neutron scattering. The results suggest that the randomphase-approximation approach to miscible-phase scattering from thermal composition fluctuations might become invalid at sufficiently large length scales, which we attribute to the strong site-specific nature of the hydrogen bonding. As the OH content increases at a fixed temperature, thermal fluctuations become suppressed and the low-qscattering becomes dominated by the structure of the crosslink distribution. The data strongly suggest that the nature of the miscible-phase structure in these blends differs from that of the usual homopolymer blends at small scattering angles, and this difference warrants further theoretical investigation.



Figure 4. Schematic representation of a hydrogen-bonded polymer blend. White beads with varying amounts of the HFMS comonomer (small black beads) correspond to DPS(OH), while gray beads correspond to PBMA. When the OH content is low (a), the crosslinks form a diffuse network that limits the extent of long-wavelength fluctuations. As the comonomer density is increased at fixed temperature (b), these fluctuations are further suppressed as the system is moved away from the spinodal. When the comonomer density is sufficiently high (c) virtually all thermal fluctuations are absent and the low-*q* scattering is dominated by the structure of the hydrogen bond distribution. In (c), self-association of modified styrene segments starts to emerge, further complicating the picture. Recent studies suggest the formation of an intermolecular complex above 9% OH content.⁵



Figure 5. An increase in the slope of a Zimm plot $[I^{-1}(q) \text{ vs. } q^2]$ at a well-defined temperature suggests a change in the interfacial structure of the 1.2% OH blend. The positive intercept at $T = 140^{\circ}$ C indicates that this temperature is still below the spinodal $(T_s = 145^{\circ}$ C), suggesting that this change in slope might be associated with microphase separation. The inset shows the interfacial coefficient κ as a function of temperature, where the units are expressed in terms of $K_n RT_c$, where K_n is the SANS contrast factor between DPS and PBMA and R is the molar gas constant.

The authors would like to acknowledge L. Sung, A. Topp, and D. Liu for assistance in the acquisition and analysis of the experimental data.

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- 13. This analysis was carried out by Galbraith Laboratories, Inc. Certain commercial equipment, instruments, materials, or laboratories are identified in this article in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that materials, equipment, or services identified are necessarily the best available for the purpose.
- 14. Error bars in graphs and uncertainties in quoted numerical results represent the best estimate of two standard deviations in experimental uncertainty.
- 15. According to ISO 31-8, the term "Molecular Weight" has been replaced with "Relative Molar Mass" denoted by the symbol M_r . The conventional notation, rather than the ISO notation, has been used in this publication.