Small-Angle Neutron Scattering Studies on the Phase Behavior of Binary Polymer Blends Driven by Photoisomerization

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The effects of tacticity[1−4] and microstructure[5,6] on miscibility have been examined in a number of polymer blends by varying the stereocontent of the polymer components through chemical synthesis. Changing the substituent groups on the monomer repeat units of polymer chains can also modify the miscibility of polymer blends. It would be more convenient for the miscibility control if the parameters expressing the microstructure of polymer chains could be varied continuously by some method complementary to the chemical synthesis. A decade ago, Irie and Iga demonstrated that the lower critical solution temperature (LCST) of the mixture of *trans*-stilbene-labeled polystyrene (PSS) and poly(vinyl methyl ether) (PVME) could be lowered by irradiation with ultraviolet (UV) light.[7] Recently, we have used PSS/PVME mixtures as a model system to experimentally verify the prediction for the soft-mode suppression in polymer blends undergoing reversible reactions.[8] It was also found in these experiments that the PSS/PVME blend was thermodynamically destabilized by irradiation with both 313 and 365 nm UV light. The advantage of these blends is that the microstructure of polymer chains can be continuously altered via *trans* → *cis* conformational transitions upon irradiation with UV light. Since the *cis*-form of stilbene has a propeller-like conformation that is much bulkier than the planar *trans*-form, it is expected that the packing between PVME and PSS chains in the blend becomes inefficient upon photoisomerization, leading to a decrease in miscibility.[7−9] Another reason responsible for this thermodynamical destabilization of the blend may originate from the different interactions between the two forms of stilbene and PVME segments arising from the large change in dipole moment of the molecule. Though it has been demonstrated that the binary interaction parameter, χ, of PS/PVME blends decreases with increasing pressure,[10,11] there is neither direct evidence nor obvious explanation for this thermodynamical destabilization accompanying the *trans* → *cis* photoisomerization of stilbene in PSS/PVME blends. In this work, we directly quantify the change of the interactions between PVME and stilbene-labeled deuterated PSS chains under irradiation by using small-angle neutron-scattering (SANS) experiments.

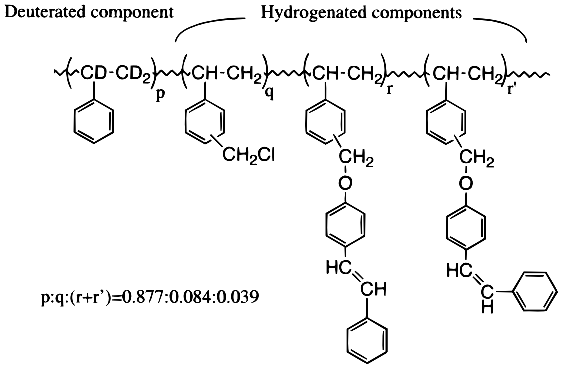

Figure 1. Chemical structure of stilbene-labeled polystyrene (PSDS).

Samples used in this work are deuterated polystyrene (PSD) labeled with *trans*-stilbene (PSDS, $M_w = 3.3 \times 10^5$ g/mol, $M_w/M_n = 2.2$) and poly(vinyl methyl ether) (PVME, $M_w = 9.6 \times 10^4$ g/mol, $M_w/M_n = 1.6$, purchased from Scientific Polymer Products Inc.[12]). Stilbene was labeled on the PSD chains by coupling the potassium salt of *trans*-4-hydroxystilbene (Lancaster, recrystallized twice in toluene) to the PSD containing ca. 12.2 mol % of chloromethyl groups that are introduced randomly into the PSD chain via the radical copolymerization of styrene-d_8 (Cambridge Isotope Laboratory) and (chloromethyl)styrene (CMS, Tokyo Kasei Co.).[13] The chemical structure of PSDS is shown schematically in Figure 1. The molar ratio of deuterated styrene versus residual (unreacted) CMS versus labeled monomer is 0.877:0.084:0.039, respectively, as determined by the combination of elemental analysis and UV−visible spectroscopy. The weight fraction PSDS/PVME (20/80) is used as a fixed composition for all the blends in this work.

SANS measurements were carried out at the Cold Neutron Research Facility of the NIST Center for Neutron Research. Data were collected on the 8 m SANS instrument (NG1) with the neutron wavelength, $\lambda = 9.0$ Å, providing a q range of 0.008 Å$^{-1} < q <$ 0.08 Å^{-1} where $q \equiv (4\pi/\lambda)\sin(\theta/2)$ and θ is the scattering angle. The samples for SANS measurements were sandwiched between two quartz windows with a diameter of 22 mm and a 0.1 mm Teflon spacer used to adjust the sample thickness. The actual sample thickness necessary for the SANS data reduction was measured with a micrometer prior to the scattering experiments. SANS data reduction and analysis were carried out according to procedures described previously.[14]

Irradiation was performed on both sides of the blend with the thickness ca. 0.1 mm at 24 °C by using a high-pressure Hg−Xe lamp (250 W, Moritex, Japan). Exciting wavelengths longer than 300 nm were selected from the incident beam by using appropriate optical filters. Since the cloud points obtained by light scattering for irradiated PSDS/PVME(20/80) blends with different thicknesses ranging from 15 to 100 μm were almost the same within ±1 °C, we conclude that within this range, the effects of the sample thickness on the critical behavior of the blend are insignificant under the irradiation conditions used in this work.

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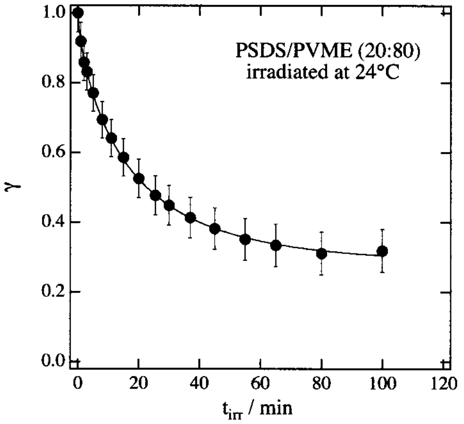

Figure 2. Irradiation time dependence of the *trans*-stilbene fraction in PSDS/PVME (20:80) blends. Unless noted otherwise, bars in the figures represent ± one standard deviation in the measurements assuming normal, random statistical errors representing a confidence interval of 68%.

As irradiation time, t_{irr}, increases, the optical density, OD(t_{irr},λ), decreases, revealing the consequence of the *trans* → *cis* photoisomerization. By using the ratio $\rho \equiv \epsilon_t/\epsilon_c$ of the extinction coefficient ϵ_t of the *trans*-isomer to ϵ_c of the *cis*-isomer of the model compound, 4-methoxystilbene, taken from the literature,[15] the fraction γ of the *trans*-isomer is obtained from

$$\gamma(t_{irr}) = \frac{\left[\rho\dfrac{\mathrm{OD}(t_{irr},\lambda)}{\mathrm{OD}(0,\lambda)} - 1\right]}{(\rho - 1)} \tag{1}$$

Here, *OD* measured at $\lambda = 355$ nm was used. Since the absorption at this λ is almost due to the stilbene moieties and the maximum OD value was less than 0.8, the linearity between OD and γ approximately holds. The irradiation time dependence of γ is shown in Figure 2. From these spectroscopic data, the photoisomerization of stilbene reaches equilibrium when ca. 70% of the *trans*-isomer is converted into the *cis* under the irradiation conditions used in this work. Five (PSDS/PVME) blends were prepared and irradiated with UV light for 0 (nonirradiated), 5, 10, 20, and 40 min. The corresponding γ values are 1, 0.77, 0.59, 0.51, and 0.35, respectively.

The scattering profiles obtained at 84 °C for the as-cast and irradiated PSDS/PVME blends are shown in Figure 3. The scattering intensity, particularly in the low q region, increases with increasing irradiation time, implying that the composition fluctuations in these blends are enhanced by the increase in the fraction of the *cis*-isomer upon irradiation. The scattering profiles, *S(q)*, were analyzed by fitting the experimental data to the random phase approximation (RPA) (eq 2) derived by de Gennes for a two-component polymer mixture:[16]

$$S(q) = k_N\left[\frac{1}{\phi_A v_A \langle N_A\rangle_n \langle g_D(x_A)\rangle_w} + \frac{1}{\phi_B v_B \langle N_B\rangle_n \langle g_D(x_B)\rangle_w} - \frac{2\chi}{v_0}\right]^{-1} + \text{baseline} \tag{2}$$

where $<N_i>_n$ is the number average polymerization index, ϕ_i is the volume fraction, and v_i is the molar volume of the *i*th component. The term $<g_D>_w$ is the weight-averaged Debye function and is given by the following equation provided that the polydispersity of the sample can be expressed by a Schultz–Zimm distribution:[5,6]

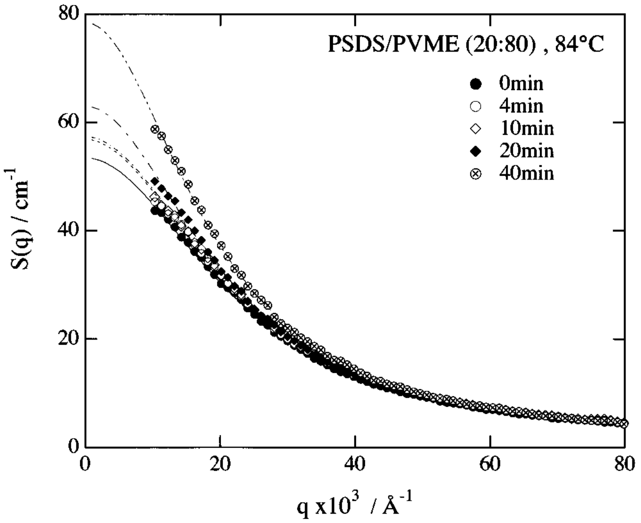

Figure 3. Small angle neutron scattering profiles $S(q)$ observed for as-cast and UV-irradiated PSDS/PVME (20:80) blends at 84 °C. The numbers in the figure indicate the irradiation time. The curves were obtained by fitting the scattering function to eq 2 using a nonlinear least squares regression. The standard deviation of each data point is within the size of the data markers.

$$\langle g_D(x)\rangle_w = \frac{2}{x^2}\left[x - 1 + \left(\frac{h}{h+x}\right)^h\right] \tag{3}$$

Here, $x = q^2\langle N\rangle_n b^2/6$ where b is the statistical segment length. Furthermore, $h = [\langle N\rangle_w/\langle N\rangle_n - 1]^{-1}$ and k_N is the contrast factor given by

$$k_N = N_0\left(\frac{\alpha_A}{v_A} - \frac{\alpha_B}{v_B}\right)^2 \tag{4}$$

In eq 4, N_0 and a_i are, respectively, Avogadro's number and the scattering length of a monomer unit of the *i*th component. The value of k_N for this PSDS/PVME (20/80) blend was estimated as 4.28×10^{-3} mol cm^{-4}. The curve fitting was performed by using a nonlinear least squares regression routine with b, χ, and the incoherent baseline as floating parameters (i.e., a three-parameter fit). Here we assumed $b_A = b_B$ (=b) to reduce the number of fitting parameters. It was found that the b values thus obtained were almost unchanged (within ±4%) with γ and temperature. On the other hand, the baseline only changes within the range 0–0.7 (cm^{-1}), indicating its insignificant contribution to the fitting process. As a consequence, the χ values dominantly affect the profiles of *S(q)*. It should be noted that the χ parameters obtained by the three-parameter fit (χ, b, and baseline) and by a two-parameter fit (χ and b floating; baseline = 0) are almost unchanged (less than 3%), revealing the uniqueness of the fitting process. The curves in Figure 3 represent the results of the RPA fitting. The experimental data can be fitted to the two-component RPA theory because the label content is sufficiently low.

The dependence of the χ parameter of the PSDS/PVME blend on γ at different temperatures is shown in Figure 4. For comparison, the χ parameters of the

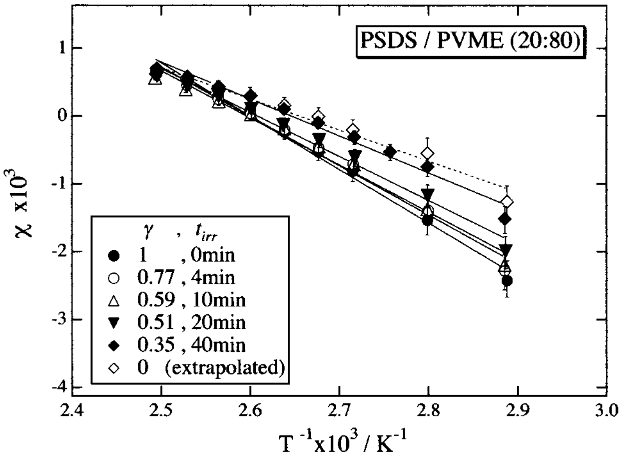

Figure 4. Temperature dependence of the χ parameter of a PSDS/PVME (20:80) blend irradiated over different time intervals. The square symbols in the figure represent the χ_{cis} values estimated by extrapolating the data obtained in Figure 5 to $\gamma = 0$. Bars representing the standard uncertainties are estimated from the uncertainties in the SANS data convoluted with uncertainties in the sample thickness.

as-cast blend with all *trans*-isomers ($t_{irr} = 0$) and all *cis*-isomers estimated by using the procedure described below, are depicted in the same figure. At low temperatures, the χ values increase with the *cis*-stilbene fraction whereas the effects are not significant at high temperatures. It should be noted that the thermally reversible reaction of stilbene is negligible even at high temperatures.[17] Actually, upon annealing under the thermal conditions of the SANS experiments, it was found that less than 5% of the *cis*-isomers in the *cis*-rich blends obtained by irradiation was converted to the *trans*-isomer, as estimated from the recovery of the absorbance.

According to random copolymer theory,[18–20] the χ value of the PSDS/PVME blend can be expressed as

$$\chi(\gamma) = \gamma\chi_{trans} + (1-\gamma)\chi_{cis} - (1-x-y)^2\gamma(1-\gamma)\chi_{tc} \quad (5)$$

where the interaction parameters between the PVME segments and the polymer segments bearing *trans*- and *cis*-isomers are specified as χ_{trans} and χ_{cis}, respectively. Furthermore, χ_{tc} is the interaction parameter between the *trans*- and *cis*-stilbene-labeled segments. x and y are the volume fractions of deuterated styrene and (chloromethyl)styrene in a PSDS chain, respectively. Assuming that the χ_{tc} term of eq 5 is negligible due to the small content of stilbene, i.e., $(1 - x - y)^2 < 0.01$, eq 5 is approximately linear with respect to γ. The dependence of χ on the fraction of *trans*-stilbene at different temperatures is shown in Figure 5. The values of χ_{cis} estimated by extrapolating the data in Figure 5 under the condition $\gamma \rightarrow 0$ were incorporated as a dotted line into Figure 4, revealing the limit under which the miscibility of the PSDS/PVME can be controlled by using photoisomerization of stilbene.

For the temperature dependence of χ, the data shown in Figure 4 indicate that the relation $\chi = A + B/T$ is applicable for the PSDS/PVME blend. From these straight lines, the values of A and B were calculated and listed in Table 1. It has been argued that A represents an entropic and B an enthalpic contribution. Table 1 shows that an increase in the fraction of *cis*-isomers results in a decrease of the entropic contribution, A, and an increase in the enthalpic contribution, B. Since the parameter B is purely enthalpic in nature, the increase of B with a decrease in γ suggests that the *trans* → *cis* photoisomerization has weakened the attractive interactions between PSDS and PVME.

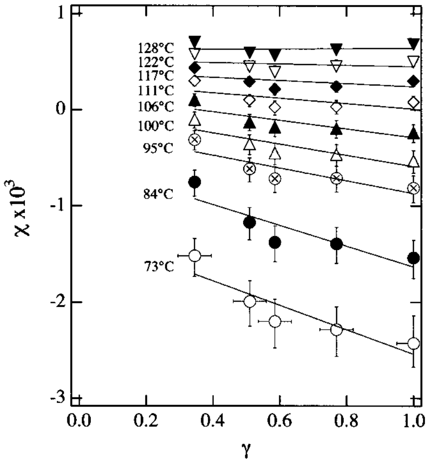

Figure 5. Dependence of the χ parameter on the fraction of *trans*-isomers in a PSDS/PVME (20:80) blend at different temperatures. The error bars shown in the horizontal and vertical directions are the same with those shown in Figure 2 and Figure 4. The former shown at 73 °C represents the typical errors in the horizontal direction for the data at other temperatures.

Table 1. Irradiation Time, t_{irr}, Dependence of the Parameters, A and B, of the Binary Interaction Parameter, $\chi = A + B/T$, for a PSDS/PVME (20:80) Blend

t_{irr} (min)	γ	A	B
0	1	0.0205	−7.89
5	0.77	0.0189	−7.29
10	0.59	0.0180	−6.95
20	0.51	0.0169	−6.50
40	0.35	0.0144	−5.46

In conclusion, we have provided direct evidence for the modification of polymer−polymer miscibility by photoisomerization of stilbene. The continuous alteration of the χ parameter by irradiation provides a systematic characterization of the effects of microstructures on the binary interaction parameter as well as an efficient method of controlling the miscibility of polymer blends with light.

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