Small-Angle Neutron Scattering and Light Scattering Study on the Miscibility of Poly(styrene-*ran*-butadiene)/Polybutadiene Blends

Shinichi Sakurai,[†] **Tatsuo Izumitani,**[‡] **Hirokazu Hasegawa, and Takeji Hashimoto***

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Charles C. Han

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received January 23, 1991; Revised Manuscript Received April 15, 1991

ABSTRACT: The miscibility of binary blends of polybutadiene (PB) and poly(styrene-*ran*-butadiene) (SBR) was studied on the basis of segmental interaction parameters. In this analysis PB was assumed to be a random copolymer comprising 1,2-linkages (V) and 1,4-linkages (B) and SBR to be the one comprising styrene (S) and butadiene with V and B. The segmental interaction parameters between V and S (χ_{VS}), B and S (χ_{BS}), and V and B (χ_{VB}) were determined on the basis of the copolymer blend theory from the effective interaction parameters (χ_{eff}'s) for the blends of PB and SBR, and those for poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (SBS), with different copolymer compositions and microstructures of polybutadienes. The values χ_{eff} were determined from either the small-angle neutron or X-ray scattering of the mixtures in the single-phase state. By use of these segmental interaction parameters, χ_{VS}, χ_{BS}, and χ_{VB}, the miscibility of the SBR/PB blends was predicted for a given set of V, B, and S contents in PB and SBR. The predictions of the miscibility for several SBR/PB blends agreed well with the results of the light scattering experiments.

I. Introduction

The miscibility of different kinds of rubber is an interesting and important problem for the rubber industry. Miscible blends are favored in some cases,[1] but phase-separated blends with well-controlled domain size which could improve physical properties are favored in other cases.[2] The progress of technology made it possible to synthesize *tailor-made* polymers with a predetermined molecular weight, microstructure, and copolymer composition.[3,4] If one can predict the miscibility of a blend with given molecular weights, microstructures, and copolymer compositions of the constituent polymers, it will be a great advance in designing rubber/rubber blends with the desired properties.

Most of the synthetic polydienes are effectively copolymers[5–8] comprising different microstructures, even though they are made of only one kind of monomer. Therefore, the blends of polydienes should also be considered as blends of copolymers. In our previous paper,[5] we reported on the use of the small-angle neutron scattering (SANS) to determine the interaction parameters between various comonomers and to predict phase behavior for binary copolymer blends. We have also shown that the theory of random copolymer mixtures developed by ten Brinke et al.[9] and by Paul and Barlow[9] works well for the blend systems of protonated polybutadiene (HPB) with perdeuterated polybutadiene (DPB), and protonated polyisoprene with DPB having various microstructures, and predicts successfully the miscibility of binary blends of polydienes having different microstructures.

In this paper we demonstrate that the theory can also qualitatively predict the miscibility of poly(styrene-*ran*-butadiene) (SBR) and polybutadiene (PB) blends (SBR/PB). The "effective" segmental interaction parameter χ_{eff} for a blend of SBR with DPB was measured by SANS (section III.A). The data on χ_{eff} for the SBR/PB blends can be expressed by the weighted sum of "fundamental" segmental interaction parameters between different repeating units, i.e., styrene (S), butadiene with 1,2-linkage (V), and butadiene with 1,4-linkage (B), on the basis of the copolymer blend theory. Here we use the word fundamental in order to distinguish the specific segmental interaction between the different microstructures such as χ_{VS} from the average segmental interaction χ_{eff}. The fundamental segmental interaction parameters, χ_{VS} between V and S, χ_{BS} between B and S, and χ_{VB} between V and B, can be obtained by solving three simultaneous equations on χ_{eff} (section III.B). With these fundamental interaction parameters, it is possible to calculate χ_{eff} for a blend of SBR/PB with any given composition and microstructure (section III.C). By comparing the calculated χ_{eff} with the value of χ at the spinodal point, χ_s, the miscibility of the blend can be predicted. The predictions of the miscibility for several SBR/PB blends agreed well with the results of the light scattering (LS) experiments (section III.D).

II. Experimental Section

A. Sample Preparation and Characterization. One DPB, three HPBs, and three SBRs were used in this study. All the polymers were synthesized by living anionic polymerization. The HPB and SBR specimens were kindly supplied by Japan Synthetic Rubber Co. (JSR). The synthesis of DPB has been reported in detail elsewhere.[10]

The characterization data on the polymer samples are listed in Table I. The microstructure of the DPB was determined by ^{13}C NMR spectrometry.[6,7] The microstructures of the HPBs and those of polybutadiene sequences in the SBRs were evaluated by the method of Morero et al.[11] from their infrared (IR) spectra. The content of the 1,2-linkage in the butadiene segment of the SBR sample was fixed at 46 or 61%, while that of the polybu-

---

[†] Present address: Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan.

[‡] Present address: Research Center, Daicel Chemical Industries, Ltd., 1239, Shinzaike, Aboshi-ku, Himeji, Hyogo 671-12, Japan.

0024-9297/91/2224-4844$02.50/0

Table I
Sample Characteristics

sample code	polymer structure[a]	microstructure of PB,[b] %			styrene cont,[c] %	10^{-4}MW[d]		
		1,2	cis 1,4	trans 1,4		M_w	M_n	M_w/M_n
H-9	DPB	12[e]	36[e]	52[e]	0		4.94[f]	1.07[g]
PB-1	HPB	20	28	52	0	18.9	16.2	1.17
PB-2	HPB	46	19	35	0	19.0	16.5	1.16
PB-3	HPB	85	6	9	0	31.3	16.5	1.90
SBR-1	SBR	61	16	23	20	11.8	10.0	1.18
SBR-2	SBR	46	21	33	15	19.0	15.7	1.21
SBR-3	SBR	61	14	25	20	58.4[h]	51.8[h]	1.13[h]

[a] DPB, HPB, and SBR denote a deuterated polybutadiene, a protonated polybutadiene, and a styrene–butadiene random copolymer, respectively. [b] By infrared measurement (Morero method). [c] By infrared measurement. [d] By GPC with a column that was calibrated by an empirical relationship of $M_w[\eta]$ vs the elution volume where $[\eta]$ is the intrinsic viscosity. The absolute values M_n and M_w were obtained by the relationship between $[\eta]$ and molecular weight. [e] By ^{13}C NMR spectrometry. [f] By membrane osmometry. [g] By GPC. [h] By GPC with a light scattering photometer.

Table II
Mixing States for As-Cast Blend Films

blend	compstn, wt	appearance	SANS	LS
SBR-1/H-9	70/30	clear	homogeneous	
SBR-3/H-9	50/50	clear	homogeneous	
SBR-1/PB-1	50/50	turbid		spinodal ring observed
SBR-1/PB-2	50/50	turbid		spinodal ring observed
SBR-1/PB-3	50/50	turbid		strong scattering
SBR-2/PB-1	50/50	clear		homogeneous
SBR-2/PB-2	50/50	turbid		spinodal ring observed
SBR-2/PB-3	50/50	turbid		strong scattering

tadiene sample varied from 12 to 85%. The styrene content of the SBR sample was determined by the IR measurement. The number-average molecular weight (M_n) of H-9 (DPB) was measured by membrane osmometry and its heterogeneity index (M_w/M_n) by GPC. The weight-average molecular weight (M_w), M_n, and M_w/M_n of all the other polymer samples except SBR-3 were determined by GPC with the use of a column that was calibrated by an empirical relationship between $M_w[\eta]$ and the elution volume, where $[\eta]$ is the intrinsic viscosity. The absolute values M_n and M_w were obtained by the relationship between $[\eta]$ and the molecular weight. M_n, M_w, and M_w/M_n for SBR-3 was determined by GPC with a light scattering photometer.

Test specimens were prepared by casting the SBR/DPB or SBR/HPB blends from toluene solutions at 30 °C, subsequently dried in a vacuum oven at room temperature for several days, prior to the measurements. The weight fraction of SBR in the blends was fixed at 50% except the SBR-1/H-9 (SBR/DPB) blend, which contains 70 wt % SBR-1. Hereafter we use the code of SBR-1/H-9 (70/30) to specify the blend of SBR-1/H-9 containing 70 wt % SBR-1.

B. SANS Experiment. SANS experiments were performed by using the SANS spectrometer at the National Institute of Standards and Technology.[12] A neutron wavelength, λ, of 0.60 nm ($\Delta\lambda/\lambda \simeq 0.2$), an iris collimation with a two-aperture configuration mounted in the 4.5-m evacuated flight path, and a two-dimensional detector with a sample-to-detector distance of 3.6 m were used for this study. The scattered intensity was corrected for the electronic and background noise, sample transmittance, and the incoherent scattering and then circularly averaged to obtain its dependency on magnitude of the scattering vector, q ($(4\pi/\lambda)\sin(\theta/2)$; θ being the scattering angle). The incoherent scattering intensity was evaluated from individual SANS measurements of pure SBR-1 and pure H-9 and then subtracted from the net scattered intensity of their blend to obtain the coherent scattering intensity. The SANS profiles were obtained in the q range between 0.128 and 1.270 nm^{-1}. The absolute scattered intensity was obtained with the use of a secondary standard sample (in cm^{-1}).

The SBR-1/H-9 blend specimen cast from ca. 5 wt % polymer solution was placed in a 1.0-mm-thick spacer. Air bubbles in the specimen were removed under vacuum. This is necessary because any air bubble in the specimen expands during the heating process and changes the scattering volume. The specimen was sandwiched between two sheets of 0.2-mm-thick copper (99.99% purity) and was mounted in a sample holder. The SANS measurements were performed at 20, 51.8, 80.1, 110.1, and 139.9 °C. The temperature of the specimen was controlled within ±0.3 °C of the set temperature in a heating block throughout the measurement.

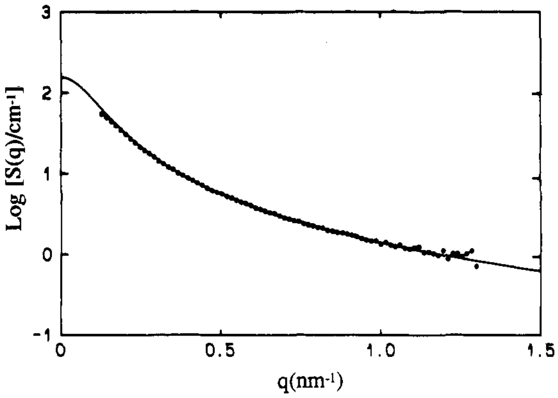

Figure 1. SANS profile of SBR-1/H-9 (70/30) blend at 20 °C (open circles) and best-fit theoretical scattering curve (solid line).

III. Results and Discussion

Turbidities of the as-cast films of the blends were examined, and the results are shown in Table II. The films of SBR-1/H-9, SBR-3/H-9, and SBR-2/PB-1 blends were clear and therefore homogeneous, while the others were turbid and therefore phase separated. Since the glass transition temperature (T_g) of SBR-3 measured by DSC is −48 °C and the T_g's of all the other samples are lower than −48 °C, the as-cast blend films, which were stored at room temperature for several days, are assumed to be at equilibrium. The mixing states for the as-cast films of SBR/DPB(H-9) and SBR/HPB (PB-1, PB-2, PB-3) were further investigated by means of SANS and LS, respectively.

A. SANS Analysis of SBR/DPB Blends. In Figure 1 open circles show the coherent elastic SANS profile of the SBR-1/H-9 (70/30) blend at 20 °C. The sample is clear and therefore considered to be a homogeneous mixture. The scattering profile can be analyzed on the basis of the scattering theory for a single-phase mixture.

de Gennes[13] has obtained the structure factor, $S(q)$, for a binary polymeric mixture in the single-phase state, in the context of the *mean-field* model and the random phase approximation (RPA). Generalizing the de Gennes theory for systems having molecular weight polydispersity given by the Schultz–Zimm distribution, the structure factor, $S(q)$, is given by[5]

$$\frac{k_N}{S(q)} = \frac{1}{\phi_A\langle z_A\rangle_n v_A S_A(q)} + \frac{1}{\phi_B\langle z_B\rangle_n v_B S_B(q)} - \frac{2\chi}{v_0} \qquad (1)$$

with

$$k_N = N_A\left(\frac{a_A}{v_A} - \frac{a_B}{v_B}\right)^2 \qquad (2)$$

and

$$S_i(q) = \frac{2}{x_i^2}\left[\left(\frac{h_i}{h_i + x_i}\right)^{h_i} - 1 + x_i\right] \qquad (3)$$

where

$$x_i = q^2\langle R_{gi}^2\rangle = q^2\langle z_i\rangle_n b_i^2/6 \qquad (3a)$$

and

$$h_i = ((\langle z_i\rangle_w/\langle z_i\rangle_n) - 1)^{-1} \qquad i = \mathrm{A\ or\ B} \qquad (3b)$$

$\langle z_i\rangle_n$ and $\langle z_i\rangle_w$ denote the number- and weight-average degrees of polymerization for the ith component (i = A or B), a_i is the neutron scattering length for component i with the molar volume v_i, volume fraction ϕ_i, and Kuhn statistical segment length b_i. N_A is Avogadro's number, χ is the binary interaction parameter between monomers A and B, and v_0 is the molar volume of the reference cell defined as $v_0 = (\phi_A/v_A + \phi_B/v_B)^{-1}$. Since the scattering length of the deuterated polymers is much larger than that of the protonated polymers, the SANS intensity from the mixtures is strong enough to give statistical accuracy for analysis in terms of eq 1. Note that eq 1 is valid for the mixture comprising statistically random copolymers such as SBR,[14] if χ and k_N are replaced by the effective quantities, i.e., χ_{eff} and $k_{N,eff}$, respectively.

All SANS profiles were fitted with eq 1 with χ_{eff} and b_i as adjustable parameters, while the other parameters were all fixed to literature values. The best fit obtained by a nonlinear regression analysis[5,15] yielded the value χ_{eff} for the SBR-1/H-9 (70/30) blend at five different temperatures. The solid line in Figure 1 shows the best-fit theoretical curve to the data at 20 °C. A systematic undershoot of $S(q)$ at low q seen in Figure 1 is probably an artifact arising from the resolution limit associated with the beam stop. The zero wave vector scattering intensity, $S(q=0)$, and the correlation length, ξ, were also obtained as functions of temperature, according to[5,13,15-17]

$$S(q=0) = \frac{k_N}{\frac{2}{v_0}(\chi_s - \chi_{eff})} \qquad (4)$$

with

$$\chi_s = \frac{v_0}{2}\left(\frac{1}{v_A\phi_A\langle z_A\rangle_w} + \frac{1}{v_B\phi_B\langle z_B\rangle_w}\right) \qquad (5)$$

and

$$\xi^2 = \frac{v_0}{36(\chi_s - \chi_{eff})}\left(\frac{b_A^2}{v_A\phi_A}\frac{h_A + 2}{h_A + 1} + \frac{b_B^2}{v_B\phi_B}\frac{h_B + 2}{h_B + 1}\right) \qquad (6)$$

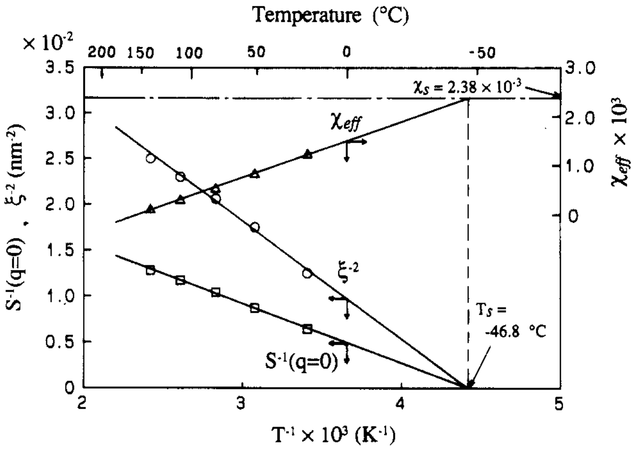

Figure 2. Plots of χ_{eff}, ξ^{-2}, and $S^{-1}(q=0)$ for SBR-1/H-9 (70/30) against reciprocal absolute temperature, T^{-1}. Dot-and-dashed line shows the level of χ_s.

χ_{eff}, ξ^{-2}, and $S^{-1}(q=0)$ for the SBR-1/H-9 (70/30) blend thus estimated were plotted against reciprocal absolute temperature (T^{-1}) in Figure 2. For each quantity the data points fall on a straight line over a temperature range of measurement and within experimental accuracy. The temperature dependence of χ_{eff} is given by

$$\chi_{eff} = -2.64 \times 10^{-3} + 1.14/T \qquad (7)$$

χ_{eff} increases and $S^{-1}(q=0)$ and ξ^{-2} decrease with decreasing temperature, suggesting that the SBR-1/H-9 blend is a UCST-type mixture. The dot-and-dashed line in Figure 2 shows the value χ_s (2.38×10^{-3}) for the SBR-1/H-9 (70/30) mixture given by eq 5. The *mean-field* spinodal temperature, T_s, is the temperature at which $\chi_{eff} = \chi_s$, $\xi^{-2} = 0$, and $S^{-1}(q=0) = 0$. As seen in Figure 2, within experimental accuracy, all the three extrapolated lines give consistently the same value of T_s, which is −46.8 °C for this particular mixture.

The SANS profile of the SBR-3/H-9 (50/50) blend was also obtained at 20 °C and analyzed by the same procedure, yielding effectively zero value for χ_{eff} at 20 °C (i.e., $\chi_{eff} = -8.2 \times 10^{-6} \pm 8.0 \times 10^{-5}$). Agreement of the experimental SANS profile with the theoretical one was again excellent, suggesting that the blend was in a single-phase state at 20 °C.

B. Interaction Parameter of SBR/PB Blends. B.1. Random Copolymer Theory. By following the original Flory–Huggins treatment, the expression for the change of the Gibbs free energy per lattice site upon mixing the two random copolymers, copolymer 1 $(A_xB_{1-x})_{N_1}$ and copolymer 2 $(C_yD_{1-y})_{N_2}$, was obtained.[9]

$$\frac{\Delta G}{kT} = \frac{\phi_1 \ln \phi_1}{N_1} + \frac{\phi_2 \ln \phi_2}{N_2} + \phi_1\phi_2\chi_{eff} \qquad (8)$$

with

$$\chi_{eff} = \chi_1 - \chi_2 \qquad (9)$$

where χ_1 is associated with *intermolecular* effective segmental interaction given by

$$\chi_1 = xy\chi_{AC} + (1-x)y\chi_{BC} + x(1-y)\chi_{AD} + (1-x)(1-y)\chi_{BD} \qquad (9a)$$

and χ_2 with *intramolecular* effective segmental interaction given by

$$\chi_2 = x(1-x)\chi_{AB} + y(1-y)\chi_{CD} \qquad (9b)$$

where x and y are the copolymer compositions in volume fraction, ϕ_1 and ϕ_2 are, respectively, the volume fractions of the copolymers 1 and 2 in the blend, and N_1 and N_2 are the degrees of polymerization of the copolymers 1 and 2, respectively. χ_{ij} $(i,j = \mathrm{A{-}D})$ is the fundamental segmental interaction parameter between i and j components. Similarly, we can write down χ_{eff} for a mixture of two three-component random copolymers, copolymer 1 $(\mathrm{A}_x\mathrm{B}_y\mathrm{C}_{1-x-y})_{N_1}$ and copolymer 2 $(\mathrm{D}_u\mathrm{E}_v\mathrm{F}_{1-u-v})_{N_2}$, as follows:

$$\chi_{\mathrm{eff}} = \chi_1 - \chi_2 \tag{10}$$

with

$$\chi_1 = xu\chi_{\mathrm{AD}} + xv\chi_{\mathrm{AE}} + x(1-u-v)\chi_{\mathrm{AF}} + yu\chi_{\mathrm{BD}} + yv\chi_{\mathrm{BE}} + y(1-u-v)\chi_{\mathrm{BF}} + (1-x-y)u\chi_{\mathrm{CD}} + (1-x-y)v\chi_{\mathrm{CE}} + (1-x-y)(1-u-v)\chi_{\mathrm{CF}} \tag{10a}$$

and

$$\chi_2 = xy\chi_{\mathrm{AB}} + x(1-x-y)\chi_{\mathrm{AC}} + y(1-x-y)\chi_{\mathrm{BC}} + uv\chi_{\mathrm{DE}} + u(1-u-v)\chi_{\mathrm{DF}} + v(1-u-v)\chi_{\mathrm{EF}} \tag{10b}$$

B.2. Assumptions. For polybutadienes, there are three kinds of repeating unit depending on the chemical linkages, i.e., the 1,2-, cis 1,4-, and trans 1,4-linkages. Since the chemical difference between the cis 1,4- and trans 1,4-linkages can be considered to be trivial compared with that between the 1,2- and 1,4-linkages, the repeating units of the cis 1,4- and trans 1,4-linkages are treated as the same units in this work. And a similar assumption is also applied to the deuterated and protonated butadiene segments.[18] These assumptions will be expressed by

$$\chi_{\mathrm{cBS}} = \chi_{\mathrm{tBS}} = \chi_{\mathrm{cDBS}} = \chi_{\mathrm{tDBS}} = \chi_{\mathrm{BS}}$$

$$\chi_{\mathrm{VcB}} = \chi_{\mathrm{VtB}} = \chi_{\mathrm{VcDB}} = \chi_{\mathrm{VtDB}} = \chi_{\mathrm{VB}}$$

$$\chi_{\mathrm{cBtB}} = \chi_{\mathrm{cBtDB}} = \chi_{\mathrm{cDBtB}} = \chi_{\mathrm{cDBtDB}} = 0$$

where the subscripts cB, tB, cDB, and tDB denote the protonated cis 1,4- and trans 1,4- and the deuterated cis 1,4- and trans 1,4-linkages, respectively. Therefore, in this work, polybutadiene is treated as a random copolymer comprising two kinds of repeating unit, i.e., the 1,2- (V) and 1,4-linkages (B). Similarly, SBR is treated as a three-component random copolymer comprising three kinds of repeating unit, i.e., styrene, V, and B. Equation 10 is utilized to express χ_{eff} for the SBR/PB blends, which are represented by $[\mathrm{S}_{\phi_\mathrm{S}}\mathrm{V}_{(1-\phi_\mathrm{S})x}\mathrm{B}_{(1-\phi_\mathrm{S})(1-x)}]_{N_1}/[\mathrm{V}_y\mathrm{B}_{1-y}]_{N_2}$, where ϕ_S, x, and y are the volume fractions of the styrene segment in SBR, the 1,2-linkage in the butadiene segment of SBR, and the 1,2-linkage in PB, respectively. Then eq 10 can be reduced to a simpler form as

$$\chi_{\mathrm{eff}} = k\phi_\mathrm{S}\chi_{\mathrm{VS}} + (\phi_\mathrm{S} - k)\phi_\mathrm{S}\chi_{\mathrm{BS}} - k(\phi_\mathrm{S} - k)\chi_{\mathrm{VB}} \tag{11}$$

with

$$k = y - x\,(1 - \phi_\mathrm{S}) \tag{11a}$$

It should be noted that χ_{eff} and therefore the miscibility are controlled by a subtle balance between the *intra-* and *inter*molecular segmental interactions. The fundamental interaction parameters for the SBR/PB blends are schematically shown in Figure 3. If the three segmental interaction parameters, χ_{VS}, χ_{BS}, and χ_{VB}, are known, χ_{eff} of the SBR/PB blends with any microstructure and copolymer composition can be calculated. In this study, three sets of temperature dependence of χ_{eff} will be used to obtain the three fundamental segmental interaction parameters. The discussion made hereto assumes that the measured χ_{eff} is independent of the blend composition ϕ_1 or ϕ_2. This leads to the conclusions that the fundamental χ's estimated from the measured χ_{eff}'s and the values χ_{eff}'s predicted from the fundamental χ's are also independent of ϕ_1. Our analysis is based on this assumption throughout this paper. In the case when the measured χ_{eff} strongly depends on ϕ_1, our analysis becomes very complex. Obviously a more elaborated approach is required to be developed in future.

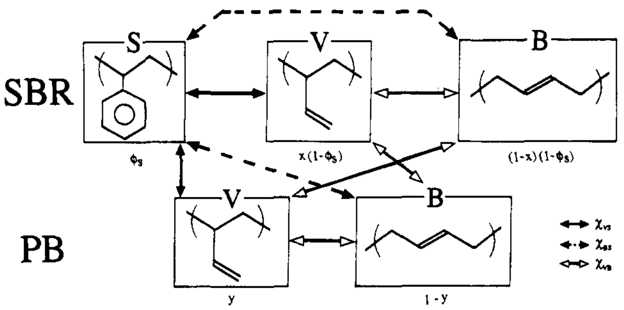

Figure 3. Schematic representation of fundamental interaction parameters for SBR/PB blends. ϕ_S, x, and y stand for fractions of the styrene segment in SBR, the 1,2-linkage in the butadiene segment of SBR, and the 1,2-linkage in PB, respectively.

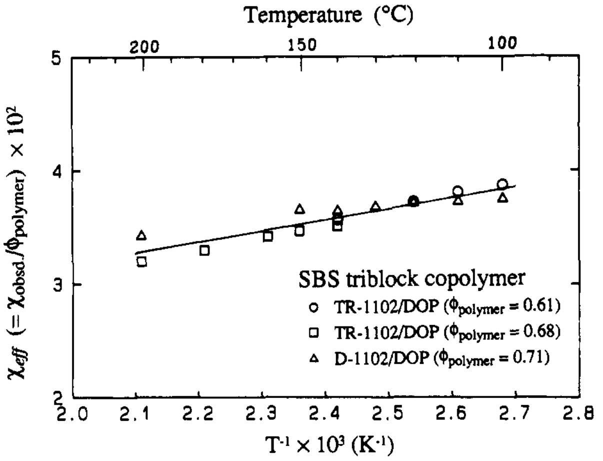

Figure 4. Effective interaction parameter, χ_{eff}, for the two SBS triblock copolymers plotted as a function of inverse of absolute temperature, T^{-1}. χ_{eff} is given by $\chi_{\mathrm{obsd}}/\phi_{\mathrm{polymer}}$, where the values χ_{obsd} were obtained by analyzing the SAXS profiles for dioctyl phthalate (DOP) solutions of these triblock copolymers in the disordered state with the RPA calculation for polydisperse, asymmetric triblock copolymer. ϕ_{polymer} is the volume fraction of polymers in the solution (see ref 20).

B.3. Determination of Fundamental χ's. The first set of data used is eq 7, which was obtained for the SBR/DPB blend (SBR-1/H-9, 70/30). Strictly speaking, we should note a difference between DPB and HPB because the isotope effect cannot be neglected in principle.[5,19] However, the repulsive interaction between the styrene and butadiene units is much larger than that between the deuterated and protonated butadiene units, as will be shown later. Therefore we will not distinguish between the deuterated and protonated butadiene units in this work, but we will still distinguish between the 1,2- and 1,4-linkages. The second set of data is temperature dependence of χ_{eff} for SBS triblock copolymers obtained by SAXS in the disordered state. In Figure 4, three sets of data on χ_{eff} are plotted as functions of inverse of absolute temperature, T^{-1}, where two of them are for Shell's Kraton TR-1102[20] and the other for Shell's Kraton D-1102.[20] Note that χ_{eff} given by $\chi_{\mathrm{obsd}}/\phi_{\mathrm{polymer}}$ is an effective segmental interaction parameter between PS and PB with the 1,2- and 1,4-linkages. Here the values χ_{obsd} were obtained by analyzing the SAXS profiles for dioctyl phthalate (DOP) solutions of these triblock copolymers in the disordered state, and ϕ_{polymer} is the volume fraction of the polymer in the DOP solution. The value χ_{obsd} was determined by comparing the measured SAXS profile with that calculated on the basis of the RPA theory, which is generalized to polydisperse and asymmetric triblock copolymers.[21] The values χ_{eff} for these two polymers are found to have essentially identical temperature dependence as

$$\chi_{\text{eff}} = 12.4 \times 10^{-3} + 9.69/T \qquad (12)$$

According to ^{13}C NMR analysis of TR-1102, the styrene content is 0.19 mol fraction, and the polybutadiene block chain comprises the 1,2-, cis 1,4-, and trans 1,4-linkages with 7.4, 55.6, and 37.0%, respectively. M_n and M_w/M_n were determined by osmometry and by GPC, respectively, to be 5.9×10^4 and 1.2 for TR-1102, and to be 5.7×10^4 and 1.2 for D-1102. For D-1102, the styrene content is 0.17 mol fraction and the PB block chain consists of the 1,2-, cis 1,4-, and trans 1,4-linkages with 9.8, 36.6, and 53.6%, respectively. Although these data on the microstructure show a difference between TR-1102 and D-1102, this difference may be negelected if the error involved in determining the microstructure is taken into account. Thus, we assume the PB block chain in SBS has 8.6%[21] 1,2-linkage (i.e., $y = 0.086$), an average of the two data. This value of χ_{eff} can be considered as that corresponding to one of the extreme cases of SBR/PB blends with zero butadiene content in SBR, in the context of the *mean-field* approximation. The third set of χ_{eff} is our previous result of χ_{VB}, which was obtained from the HPB/DPB blends.[5] This is another extreme case of SBR/PB with zero styrene content in SBR.

$$\chi_{\text{eff}} = 2.69 \times 10^{-3} + 1.87/T \; (=\chi_{\text{VB}}) \qquad (13)$$

We obtained the following solutions for the three simultaneous equations of eqs 7, 12, and 13:

$$\chi_{\text{VS}} = 56.5 \times 10^{-3} + 5.62/T \qquad (14)$$

$$\chi_{\text{BS}} = 8.43 \times 10^{-3} + 10.2/T \qquad (15)$$

$$\chi_{\text{VB}} = 2.69 \times 10^{-3} + 1.87/T \qquad (16)$$

These results are shown in Figure 5. All the segmental interaction parameters χ_{VS}, χ_{BS}, and χ_{VB} are positive within the experimental temperature range (20–140 °C) and have positive slopes in plots of χ vs reciprocal absolute temperature, suggesting UCST-type phase behavior. It is obvious from the results that the values χ_{VS} and χ_{BS} are found to be, respectively, 4.8 and 8.5 times larger than the value χ_{VB} at 30 °C shown in Figure 5. The slopes for χ_{VS} and χ_{BS} are also much larger than that for χ_{VB}.

Roe and Zin[22] were the first who elegantly determined the fundamental interaction parameter χ_{SB} between the styrene and butadiene units from the effective interaction parameters obtained for various polystyrene/SBR blends, on the basis of the copolymer effect, by considering SBR as a two-component random copolymer comprising the styrene and the butadiene units. However, they neglected the difference between the 1,2- and 1,4-linkages in the butadiene segment, which is shown to be not negligible according to our results.

C. Predicted Miscibility Behavior of SBR/PB Blends as a Function of Microstructure and Styrene Content. In order to examine the effect of the copolymer composition of SBR in terms of the styrene content (i.e., ϕ_S) and the microstructure of PB (i.e., the fraction of the 1,2-linkage in the butadiene segment of SBR, x, and that in PB, y) on χ_{eff} for the SBR/PB blends, χ_{eff} was calculated by use of eqs 11 and 14–16 as a function of x, y, and ϕ_S.

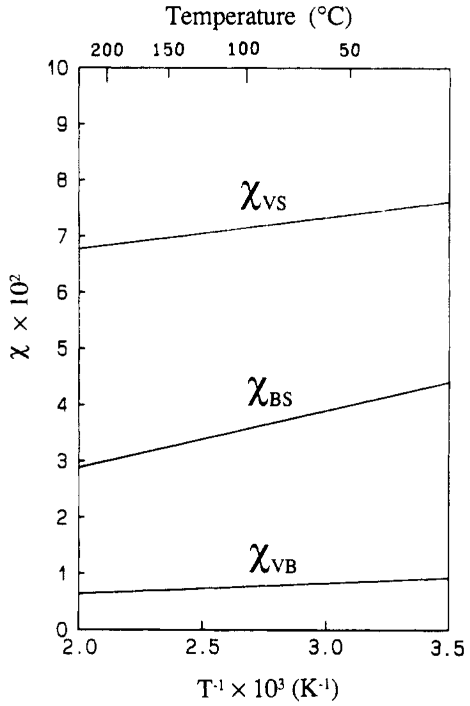

Figure 5. Plots of resulting three fundamental segmental interaction parameters χ_{VS}, χ_{BS}, and χ_{VB} against reciprocal absolute temperature.

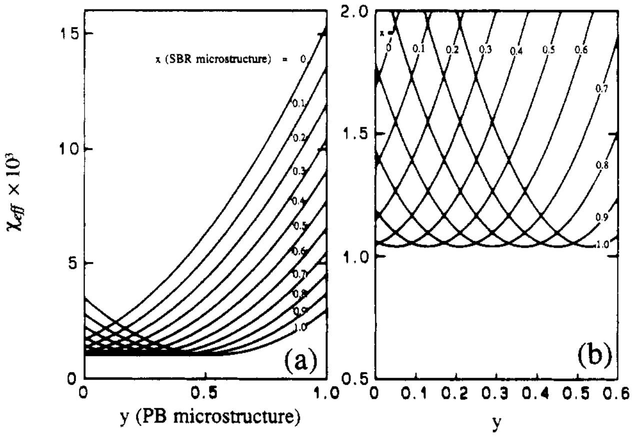

Figure 6. (a) Calculated χ_{eff} of SBR/PB blends at 30 °C plotted against the volume fraction of the 1,2-linkage in PB, y, for various volume fractions of the 1,2-linkage in the butadiene segment of SBR, x. The volume fraction of the styrene segment of SBR, ϕ_S, is fixed at 0.2. (b) Expanded view of (a) in the domain of $0.5 \times 10^{-3} \le \chi_{\text{eff}} \le 2 \times 10^{-3}$ and $0 \le y \le 0.6$.

C.1. Miscibility as a Function of *y* (PB Microstructure). Parts a and b of Figure 6 show examples of the copolymer effect on χ_{eff} at 30 °C where χ_{eff}'s were plotted against y for various values x, but for the fixed volume fraction of the styrene segment in SBR, i.e., $\phi_S = 0.2$. This value of ϕ_S is close to that for the SBR samples used in this study (see Table I). Figure 6b shows an expanded view of Figure 6a in the domain of $0.5 \times 10^{-3} \le \chi_{\text{eff}} \le 2 \times 10^{-3}$ and $0 \le y \le 0.6$. It highlights the value y (y_{min}) at which χ_{eff} becomes a minimum ($\chi_{\text{eff,min}}$). It also highlights that this value $\chi_{\text{eff,min}}$ is independent of x. These two factors are more clearly demonstrated in Figure 6b than in Figure 6a.

It is obvious from Figure 6a,b that there are two regimes in terms of x where χ_{eff} as a function of y behaves differently; i.e., (i) in the regime of $x \leq x_c$, χ_{eff} increases monotonically with y, and hence the miscibility is monotonically suppressed with increasing volume fraction of the 1,2-linkage in PB, and (ii) in the regime of $x > x_c$, χ_{eff} as a function of y shows a minimum at $y = y_{\text{min}}$, and hence the miscibility is first enhanced with increasing y and then suppressed with a further increase of y. The critical value x_c can be easily estimated as follows. From eq 11 it follows that

$$\partial\chi_{\text{eff}}/\partial y = \phi_S U + 2k\chi_{\text{VB}} \tag{17}$$

where

$$U \equiv \chi_{\text{VS}} - \chi_{\text{BS}} - \chi_{\text{VB}} \tag{18}$$

The value y_{min} is given by $\partial\chi_{\text{eff}}/\partial y = 0$, and hence

$$y_{\text{min}} = x(1 - \phi_S) - \phi_S U/2\chi_{\text{VB}} \tag{19}$$

The condition that $y_{\text{min}} = 0$ gives x_c:

$$x_c = \phi_S U/[2\chi_{\text{VB}}(1 - \phi_S)] \tag{20}$$

Using the given values for χ_{VS}, χ_{BS}, and χ_{VB} at 30 °C (eqs 14–16), $x_c = 0.338$ is obtained for $\phi_S = 0.2$.

C.2. Miscibility as a Function of x (PB Microstructure in SBR). In the regime of $x \leq x_c$, χ_{eff} decreases with increasing x, regardless of the values y, implying that the miscibility is enhanced with increasing volume fraction of the 1,2-linkage in the butadiene segment of SBR, regardless of the microstructure of PB. This general tendency may be surprising at first glance in view of the effect of increasing the 1,2-linkage in the butadiene segment of SBR and that in PB being *opposite* or *asymmetric*. However, one may realize that this is reasonable and is consistent with the concept of the copolymer effect. It can be seen from Figure 5 that χ_{VS} is about 1.8 times as large as χ_{BS} and that χ_{VB} is negligibly small compared with χ_{VS} and χ_{BS} at 30 °C. Thus increase of the 1,2-linkage in PB, i.e., increase of y, increases the most dominant interaction term χ_{VS} in eq 11 through increase of the *inter*molecular segmental interaction. On the other hand, increase of the 1,2-linkage in the butadiene segment of SBR, i.e., increase of x, decreases the most dominant interaction term χ_{VS} in eq 11 through increase of the *intra*molecular segmental interaction, i.e., $-x(1-\phi_S)\phi_S\chi_{\text{VS}}$. The maximum miscibility in the regime of $x \leq x_c$ is obtained when SBR with $x = x_c$ is blended with PB with 100% 1,4-linkage.

On the other hand, in the regime of $x > x_c$, there exists the minimum value of χ_{eff}, i.e., maximum miscibility at $y = y_{\text{min}}$. Upon substituting eq 19 into eq 11, we obtain the minimum:

$$\chi_{\text{eff,min}} = \frac{\phi_S^{\,2}}{4\chi_{\text{VB}}}(4\chi_{\text{VB}}\chi_{\text{BS}} - U^2) \tag{21}$$

At 30 °C and for $\phi_S = 0.2$, $\chi_{\text{eff,min}}$ is 1.04×10^{-3}, independent of the values x, i.e., the fraction of the 1,2-linkage in the butadiene segment of SBR. It should be noted that from eq 19 the maximum value of y_{min} is 0.53 at $x = 1.0$. The miscibility is always promoted with increasing x if $y \geq 0.53$, but it is first promoted with increasing x and then suppressed with further increasing x if $y < 0.53$. These trends indicate that the miscibility behavior can be altered by a subtle balance of the microstructure.

For better understanding of χ_{eff} as a function of x, it is useful to consider the case of $y = 0$, i.e., the blend of SBR and PB with 100% 1,4-linkage. In this case eq 11 is written as

$$\chi_{\text{eff}} = (1 - \phi_S)^2\chi_{\text{VB}}(x - x_c)^2 + \chi_{\text{eff,min}} \tag{22}$$

Hence χ_{eff} depends on $(x - x_c)^2$; i.e., χ_{eff} is symmetric in terms of $x = x_c$ (=0.338) for $y = 0$.

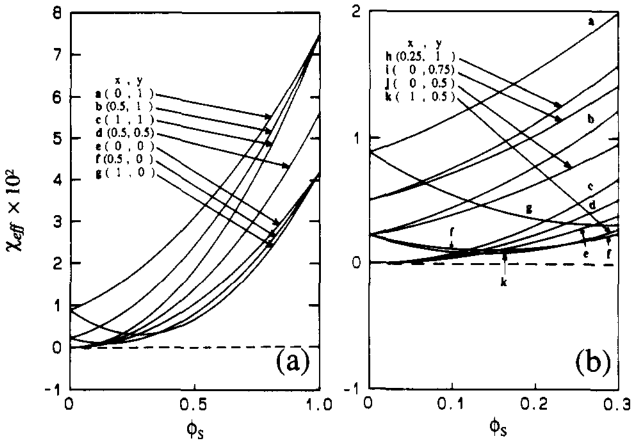

Figure 7. (a) Calculated χ_{eff} of SBR/PB blends at 30 °C plotted against the volume fraction of the styrene segment of SBR, ϕ_S, for various sets of (x, y) with x being the volume fraction of the 1,2-linkage in the butadiene segment of SBR and y being that in PB. (b) Expanded view of (a) in the domain of $-0.01 \leq \chi_{\text{eff}} \leq 0.02$ and $0 \leq \phi_S \leq 0.3$.

C.3. Miscibility as a Function of ϕ_S (PS Content in SBR). Parts a and b of Figure 7 show χ_{eff}'s as functions of ϕ_S for various pairs (x, y) at 30 °C. Figure 7b is an expanded view of Figure 7a in the domain of $-0.01 \leq \chi_{\text{eff}} \leq 0.02$ and $0 \leq \phi_S \leq 0.3$. In general, the miscibility of the blends increases with decreasing volume fraction of the styrene segment in SBR (i.e., decreasing ϕ_S). If we examine Figure 7b closely, each curve with $x > y$ (e.g., f, g, or k) shows a minimum in the regime of $0 \leq \phi_S \leq 0.3$. The larger the difference between x and y, the larger *the miscibility enhancement with an increase of* ϕ_S that can be expected. The maximum enhancement is obtained when $\phi_S = \phi_{S,\text{min}}$, at which χ_{eff} becomes minimum (see curves f, g, and k). This miscibility enhancement with the increase of ϕ_S may be again surprising at first glance but can be interpreted as follows. From eq 11

$$\frac{\partial\chi_{\text{eff}}}{\partial\phi_S} = 2\phi_S(xU + \chi_{\text{BS}} + x^2\chi_{\text{VB}}) + (y - x)(U + 2x\chi_{\text{VB}}) \tag{23}$$

where U is defined by eq 18. Thus $\phi_{S,\text{min}}$ is obtained by solving the equation $\partial\chi_{\text{eff}}/\partial\phi_S = 0$, which leads to

$$\phi_{S,\text{min}} = \frac{(x - y)(U + 2x\chi_{\text{VB}})}{2(xU + \chi_{\text{BS}} + x^2\chi_{\text{VB}})} \tag{24}$$

Since the result shown in Figure 5 indicates $\chi_{\text{VS}} > 0$, $\chi_{\text{BS}} > 0$, $\chi_{\text{VB}} > 0$ and also $U > 0$ at 30 °C, a condition for $0 < \phi_{S,\text{min}} < 1$ turns out to give $x > y$ from eq 24. In the case when $x = 1$ and $y = 0$, $\phi_{S,\text{min}}$ is 0.278 and $\chi_{\text{eff,min}}$ (the value χ_{eff} at $\phi_S = \phi_{S,\text{min}}$) is 3.07×10^{-3} (see curve g in Figure 7b). The miscibility enhancement with the increase of ϕ_S can be easily understood on the basis of the copolymer effect. It is useful to consider the special case of $x = 1$ and $y = 0$ to facilitate the interpretation. In this case the mixture corresponds to $S_{\phi_S}V_{1-\phi_S}/B$, and hence χ_{eff} is given by

$$\chi_{\text{eff}} = -\phi_S(1 - \phi_S)\chi_{\text{VS}} + \phi_S\chi_{\text{BS}} + (1 - \phi_S)\chi_{\text{VB}} \tag{25}$$

χ_{eff} decreases with the increase of ϕ_S when $\phi_S < \phi_{S,\text{min}}$ because the increase of the *intra*molecular repulsive interaction, $\phi_S(1 - \phi_S)\chi_{\text{VS}}$, dominantly contributes to the

Table III
Calculated χ_{eff} Values at 30 °C and χ_s for SBR/PB Blends

blend	compstn, wt	$10^3\chi_{eff}$ (30 °C)		$10^3\chi_s$
SBR-1/H-9	70/30	1.12	<	2.52
SBR-3/H-9	50/50	1.12	<	1.35
SBR-1/PB-1	50/50	1.04	>	0.782
SBR-1/PB-2	50/50	1.56	>	0.782
SBR-1/PB-3	50/50	4.58	>	0.666
SBR-2/PB-1	50/50	0.586	<	0.592
SBR-2/PB-2	50/50	1.24	>	0.590
SBR-2/PB-3	50/50	4.47	>	0.475

decrease of χ_{eff}, compared with the variations of the *inter*molecular repulsive interaction, $\phi_S\chi_{BS} + (1 - \phi_S)\chi_{VB}$. Similar arguments are applied to all the cases of $x > y$.

Now let us discuss the value χ_{eff} at $\phi_S = 0$. In this case the mixture corresponds to that of two polybutadienes with different microstructures, and then χ_{eff} is given by $\chi_{eff} = (x - y)^2\chi_{VB}$, as is obvious from eq 11. The larger the microstructure difference between the two polybutadienes, i.e., the larger the $|x - y|$, the larger the value χ_{eff} is, and hence the less miscible the mixture is.

Finally, for the case $\phi_S = 1.0$, the value χ_{eff} depends only on y, the fraction of the 1,2-linkage in PB. The mixture corresponds to S/V_yB_{1-y}, and hence χ_{eff} is given by

$$\chi_{eff} = -y(1 - y)\chi_{VB} + y\chi_{VS} + (1 - y)\chi_{BS} \qquad (26)$$

Since $\partial\chi_{eff}/\partial y = U + 2y\chi_{VB} > 0$ at 30 °C, the value χ_{eff} monotonically increases with y; i.e., the miscibility is suppressed with increasing fraction of the 1,2-linkage in PB.

D. Light Scattering Experiments. In this section we will show that the prediction of miscibility based on the copolymer effect is applicable to all the SBR/HPB and SBR/DPB blends studied by LS. In Table III the calculated χ_{eff} values at 30 °C by use of eq 11 with eqs 14–16 and χ_s values by use of eq 5 for all the blends are shown. The SBR-1/H-9, SBR-3/H-9, and SBR-2/PB-1 blends have χ_{eff} values at 30 °C smaller than their χ_s values, suggesting these blends should be miscible at 30 °C. These predictions are consistent with the preliminary results shown in Table II.

In order to judge the miscibility more rigorously, the LS profiles were measured for the as-cast blend films of the six SBR/HPB blends at 30 °C, which are shown in Figure 8. The intensity levels of the five blends other than the SBR-2/PB-1 (50/50) blend were very high, indicating that the specimens had already phase separated. Especially the profile of the SBR-1/PB-1 (50/50) blend and that of the SBR-2/PB-2 (50/50) blend show scattering maxima at $q \cong 1.46 \times 10^{-3}$ and $q \cong 7.77 \times 10^{-3}$ nm^{-1}, respectively, corresponding to the spinodal ring, which is due to the periodic concentration fluctuation developed by the spinodal decomposition during solvent evaporation.[23] On the other hand, only one blend (SBR-2/PB-1, 50/50) shows a profile that has the intensity level lower than the other five by a factor of 10^2, suggesting that this blend is a homogeneous mixture.

Since toluene used as a casting solvent is a neutral solvent for PB and SBR, the miscibility assessment made on the solvent-cast films should correctly reflect the miscibility of the two polymers in melt. However, it may still be impossible for us to rule out completely the solvent effect on the miscibility (such as solvent-induced phase separation[24] or homogenization) when the solvent-cast films are used for the assessment. In order to further check that the miscibilities on the solvent-cast films truly reflect the miscibilities in melt, we carried out the following experiments. The phase-separated mixtures obtained by the solvent-casting process were first homogenized into a single-phase state by mechanical mixing as previously reported in detail.[25,26] The homogenized films or melts were then subjected to phase separation study.

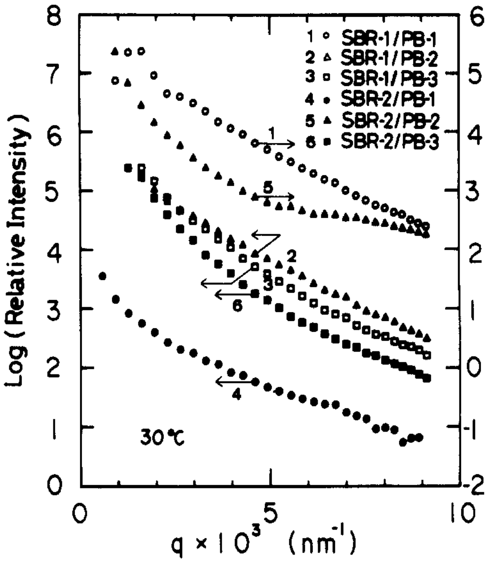

Figure 8. Light scattering profiles obtained for the as-cast blend films of SBR/HPB at 30 °C.

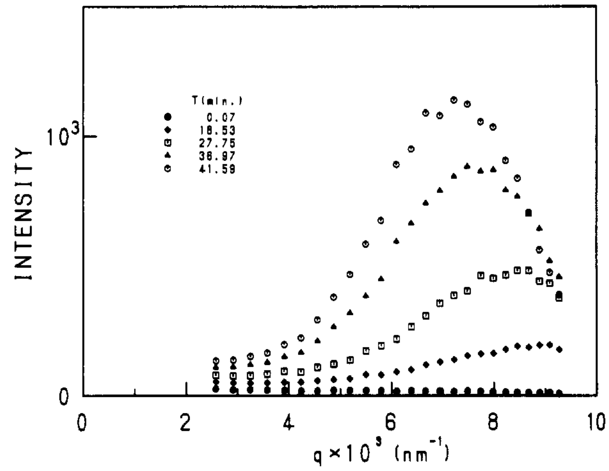

Figure 9. Time-resolved light scattering profiles at 60 °C for SBR-1/PB-2 blend. *T* (min) indicates time spent for the spinodal decomposition after homogenization by mechanically mixing the as-cast film.

Figure 9 shows an example of the time evolution of the LS profile at 60 °C for the SBR-1/PB-2 blend after homogenization by mechanically mixing the as-cast film.[25] It was observed that the scattering intensity at a given q in the small q regime covered in our experiment increased with time and that a scattering maximum appeared and shifted to the small q with time. This behavior is typical of spinodal decomposition.[26] This result confirms that the SBR-1/PB-2 blend is immiscible at 60 °C and hence at 30 °C because the SBR/PB blends are UCST-type mixtures.[26] It should be noted from this result that miscibility assessment of the various mixtures based upon the results shown in Table II and Figure 8 is free from the solvent effect encountered in the film-casting process (i.e., $\Delta\chi$ effect[24]) and is truly meaningful. All the LS results are consistent with the prediction based on the copolymer effect. In this way we could qualitatively predict the miscibility of SBR/PB blends by eq 11 together with the fundamental χ values given by eqs 14–16. The spinodal temperature can be also estimated by setting $\chi_{eff} = \chi_s$. For a better prediction, refinement of the equation in the determination of the fundamental χ values may be necessary; e.g., the difference between cis 1,4- and trans 1,4-linkages of the polybutadiene and that between DPB and HPB should be taken into account, and the dependence of χ_{eff} on the blend composition and on the molecular weight should also be accounted for.

IV. Conclusions

Miscibility behavior of the SBR/PB blend could be predicted on the basis of the copolymer blend theory by considering SBR and PB, respectively, a three-component random copolymer comprising repeating units of the styrene and the butadiene with 1,2- and 1,4-linkages, and a two-component random copolymer comprising those of the butadiene with 1,2- and 1,4-linkages. In this study the effective interaction parameter, χ_{eff}, of the blend was treated as a weighted sum of the three fundamental segmental interaction parameters χ_{VS}, χ_{BS}, and χ_{VB}, with knowledge of the copolymer compositions and the microstructures of the polybutadiene (Figure 3). From the experimental data on χ_{eff} obtained by SANS and SAXS, these fundamental χ's were evaluated as a function of temperature. For any given SBR/PB blend, the miscibility (more rigorously, the thermodynamic stability limit of the blend) could be predicted by comparing the value χ_{eff} given by eqs 11 and 14–16 and the value χ_s given by eq 5. The prediction of the blend miscibility was qualitatively confirmed by the light scattering experiments for various SBR/PB blends.

Acknowledgment. We are grateful to M. Takenaka for performing a time-resolved light scattering measurement. We are deeply grateful to Japan Synthetic Rubber Co. for providing the SBR and PB samples. This work was supported in part by a Grant-in-Aid for Scientific Research in Priority Areas "New Functionality Materials, Design, Preparation and Control" (02205066) from the Ministry of Education, Science and Culture, Japan, and by a scientific grant from Japan Synthetic Rubber Co.

References and Notes

(1) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.

(2) Matsuo, M.; Nozaki, C.; Jyo, Y. *Polym. Eng. Sci.* **1969**, *9*, 197.

(3) Bond, R.; Morton, G. F.; Krol, L. H. *Polymer* **1984**, *25*, 132.

(4) Kuntz, I. *J. Polym. Sci.* **1961**, *54*, 569.

(5) Sakurai, S.; Hasegawa, H.; Hashimoto, T.; Glen Hargis, I.; Aggarwal, S. L.; Han, C. C. *Macromolecules* **1990**, *23*, 451. Hasegawa, H.; Sakurai, S.; Takenaka, M.; Hashimoto, T.; Han, C. C. *Macromolecules* **1991**, *24*, 1813. Sakurai, S.; Jinnai, H.; Hasegawa, H.; Hashimoto, T.; Han, C. C. *Macromolecules* **1991**, *24*, 4839.

(6) Sato, H.; Takebayashi, K.; Tanaka, Y. *Macromolecules* **1987**, *20*, 2418.

(7) Sato, H.; Ono, A.; Tanaka, Y. *Polymer* **1977**, *18*, 580.

(8) Kawahara, S.; Akiyama, S.; Ueda, A. *Polym. J.* (*Tokyo*) **1989**, *21*, 221.

(9) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827. Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.

(10) Hasegawa, H.; Tanaka, H.; Hashimoto, T.; Han, C. C. *Macromolecules* **1987**, *20*, 2120.

(11) Morero, D.; Santambrigio, A.; Pori, L.; Ciampelli, E. *Chem. Ind.* (*Milan*) **1959**, *41*, 758.

(12) Glinka, C. J.; Rowe, J. M.; LaRock, J. G. *J. Appl. Crystallogr.* **1986**, *19*, 427.

(13) de Gennes, P.-G. *J. Phys.* **1970**, *31*, 235; *J. Chem. Phys.* **1980**, *72*, 4756.

(14) Mori, K.; Tanaka, H.; Hashimoto, T. *Macromolecules* **1987**, *20*, 381.

(15) Shibayama, M.; Yang, H.; Stein, R. S.; Han, C. C. *Macromolecules* **1985**, *18*, 2179.

(16) Joanny, J. F. *C. R. Acad. Sci., Paris* **1978**, *286B*, 89.

(17) Han, C. C.; Bauer, B. J.; Clark, J. C.; Muroga, Y.; Matsushita, M.; Okada, M.; Tran-Cong, Q.; Chang, T.; Sanchez, I. C. *Polymer* **1988**, *29*, 2002.

(18) From ref 5, the values of fundamental segmental interaction, χ, at 30 °C were estimated to be 8.86×10^{-3} and 1.46×10^{-3} for H1,2/H1,4 and H1,2/D1,2, respectively, for DPB/HPB blends. The former is approximately 6 times as large as the latter. This indicates the deuterium labeling effect on χ is comparably smaller than the interaction between the different microstructures. Although the value of $\chi_{\mathrm{H1,2/D1,2}}$ is larger than experimental accuracy (8.0×10^{-5}), we neglected the deuterium labeling effect on χ in order to reduce the unknown variables in the simultaneous equations.

(19) Bates, F. S.; Dierker, S. B.; Wignall, G. D. *Macromolecules* **1986**, *19*, 1938.

(20) Sakurai, S.; Mori, K.; Okawara, A.; Hashimoto, T., in preparation.

(21) This value is close to that reported by Gergen et al.: Gergen, W. P.; Lutz, R. G.; Davison, S. In *Thermoplastic Elastomers*; Legge, N. R., Holden, G., Schroeder, H. E., Eds.; Hanser: Munich, Vienna, New York, 1987; Chapter 14, p 507.

(22) Roe, R. J.; Zin, W. C. *Macromolecules* **1980**, *13*, 1221.

(23) Hashimoto, T.; Sasaki, K.; Kawai, H. *Macromolecules* **1984**, *17*, 2812. Sasaki, K.; Hashimoto, T. *Macromolecules* **1984**, *17*, 2818.

(24) Robard, A.; Patterson, D., Delmas, G. *Macromolecules* **1977**, *10*, 706.

(25) Hashimoto, T.; Izumitani, T.; Takenaka, M. *Macromolecules* **1989**, *22*, 2293.

(26) Izumitani, T.; Hashimoto, T. *J. Chem. Phys.* **1985**, *83*, 3694.