Small-Angle Neutron Scattering and Light Scattering Studies on the Miscibility of Protonated Polyisoprene/Deuterated Polybutadiene Blends†

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ABSTRACT: Binary mixtures of protonated polyisoprene and deuterated polybutadiene with particular microstructures exhibit an LCST-type phase behavior. Small-angle neutron scattering (SANS) and time-resolved small-angle light scattering (SALS) techniques were employed to study the static and dynamic phase behavior of the mixtures. From the static study by SANS, binary interaction parameters, χ, and the phase diagram were obtained. The spinodal temperature at the critical blend composition obtained by the analysis of SANS profiles from the single-phase state was in good agreement with that obtained by the time-resolved SALS measurements. The component polymers are prepared by living anionic polymerization and hence have well-defined molecular characteristics. Therefore, this system is considered to be an excellent polymer mixture system for the study of the relationships between static and dynamic phase behaviors of the polymer mixture and the molecular parameters such as molecular weight, polydispersity, microstructure, etc.

I. Introduction

It is extremely important to control the state of mixing and the phase-separated structure of polymer blends if it is expected for them to have superior properties to those of the individual constituent polymers. For this purpose, it is necessary to clarify the fundamental relationships between the molecular parameters of constituent polymers and the static and dynamic phase behaviors of polymer mixtures, e.g., miscibility, phase diagrams, critical phenomena, mechanism, and dynamics of phase transition, etc. This is also an extremely interesting problem from the fundamental point of view. The molecular parameters to be considered are the molecular weight (M), polydispersity (M_w/M_n) of polymers, molar volume of monomeric units (v), statistical segment length (b) related to the flexibility of the polymers, and the thermodynamic interaction parameter (χ) between two polymers. The other parameters such as copolymer composition, microstructure of polydienes, tacticity of vinyl polymers, and isotope effects can be taken into consideration in terms of the χ-parameter. Our aim is to clarify these relationships by a systematic scattering study using well-defined polymer systems.

Binary blends of rubbers (polydienes) are preferable systems for such studies because these polymers are usually in the liquid states above room temperature at which sample preparations and most experiments are conducted. This eliminates any complications caused by crystallization and vitrification of polymers. Moreover, it is especially important that various kinds of polydienes can be synthesized with very narrow molecular weight distributions ($M_w/M_n < 1.1$) by living anionic polymerization techniques. As an excellent example of such blend systems we found a rubber/rubber blend system with well-characterized molecular parameters that had a phase diagram of the lower critical solution temperature (LCST) type in the temperature range of practical measurements, i.e., above room temperature and below degradation temperature. It was a mixture of protonated polyisoprene (HPI) and deuterated polybutadiene (DPB).

Small-angle neutron scattering (SANS) is a powerful technique for the study of the miscibility and critical phenomena of polymer mixtures.[1] One of the great advantages of the SANS technique is that even when a polymer mixture is in the one-phase region one can measure the Flory–Huggins χ-parameter by analyzing the scattering profiles obtained for the one-phase mixture and can predict the type of the phase diagram and the spinodal temperature from the temperature dependence of the χ-parameter. Small-angle light scattering (SALS) is also an excellent technique for studying dynamic behaviors of polymer mixtures in phase transition.[2] In this paper we report the preliminary results on the SANS and SALS study of an HPI/DPB blend system and show how the HPI/DPB system and the scattering techniques are valid for the purpose mentioned above. In the subsequent papers on this system, we will discuss the microstructure effects on the miscibility and phase behavior[3] and dynamic behavior of the mixture in the course of phase separation.[4]

II. Experimental Section

1. Sample Preparation and Characterization. Two polymers used in this study were synthesized by living anionic polymerization at room temperature using *sec*-butyllithium as the initiator. One is a protonated polyisoprene (GL-4) synthesized in xylene, and the other is a perdeuterated polybutadiene (H-9) synthesized in benzene. The protonated polyisoprene sample was kindly supplied by Tosoh Co., Ltd., Japan.[5] The synthesis technique of the deuterated polybutadiene has been reported elsewhere.[6] The number-average molecular weight (M_n) of H-9

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Table I
Sample Characterization

sample code	polymer	M_n[c]	M_w/M_n[d]	microstructure,[e] %			
				cis-1,4	trans-1,4	1,2	3,4
GL-4	HPI[a]	1.00×10^5	1.01	70.0	23.0	0.0	7.0
H-9	DPB[b]	4.94×10^4	1.07	36.0	52.0	12.0	

[a] Protonated polyisoprene. [b] Perdeuterated polybutadiene. [c] Measured by GPC with low-angle light scattering (GL-4) and membrane osmometry (H-9). [d] Evaluated by GPC. [e] Obtained by ^{13}C NMR.

determined by membrane osmometry was 4.94×10^4, and the M_n of GL-4 determined by size-exclusion chromatography with light scattering was 1.00×10^5. The polydispersity indices (M_w/M_n) estimated by size-exclusion chromatography were 1.07 for H-9 and 1.01 for GL-4. The microstructure obtained by ^{13}C NMR was 36% cis-1,4, 52% trans-1,4, and 12% 1,2 linkages for H-9 and 70% cis-1,4, 23% trans-1,4, 7% 3,4, and an undetectable amount of 1,2 linkages for GL-4. The microstructure of GL-4 was also obtained by ^1H NMR and was 93% 1,4, 7% 3,4, and an undetectable amount of 1,2 linkages, which agreed very well with the results by ^{13}C NMR. The results of sample characterization are summarized in Table I.

Blend samples of GL-4/H-9 were prepared with four compositions: 70/30, 60/40, 50/50, and 30/70 wt %, and these numbers are used as the sample codes hereafter. Film specimens of the blends were obtained by slowly casting from ca. 5 wt % solutions in toluene in a vessel placed in a water bath controlled at 30 °C. No antioxidant was added to the film specimens. The film specimens were further dried at room temperature under vacuum for about 1 week. All the as-cast film specimens were clear and homogeneous, suggesting that the specimens were in the single-phase state.

2. SANS Experiments. The SANS experiments and the data analyses were performed by using the NIST SANS instrument[7] and computers. The monochromatized neutron beam with a wavelength $\lambda = 6.0$ Å ($\Delta\lambda/\lambda \cong 0.25$), a focusing collimation with 12 apertures, each having seven pinholes and 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 in this study. The scattering intensity data were corrected for the electronic noise, sample transmittance, empty sample cell, and room background, converted to the absolute scale with dried silica gel as a secondary standard, and circularly averaged to obtain the dependence of scattering intensity on q ($=4\pi \sin\theta/\lambda$, 2θ = scattering angle). The scattering intensity distribution data were obtained in the q-range between 0.0097 and 0.115 Å^{-1}.

Three blend samples, 30/70, 50/50, and 70/30, were used in the SANS experiments. The film specimens were mounted in the heat-conducting and air-sealed sample cells consisting of copper windows of 99.99% purity and 0.2-mm thickness and a brass cylinder with a pair of ring-shaped screws to hold the sample specimen between them. The thickness of the specimens was kept constant at 1.0 mm with a ring-shaped spacer. The sample cell with a specimen was placed in a vacuum oven before sealing, and air bubbles in the film specimens were carefully removed to avoid the change of the irradiated sample volume on heating during the measurements. To measure the temperature dependence of the scattering profile, the sample cells were placed in a copper heating block attached to the sample stage of the SANS instrument. The temperature was controlled within ±0.2 °C and raised stepwise from room temperature up to 130 °C depending on the blends.

3. Light Scattering Experiments. The cloud points of GL-4/H-9 blends of four compositions (30/70, 50/50, 60/40, and 70/30) were obtained by measuring the laser light ($\lambda = 6328$ Å) scattering intensity at a fixed scattering angle ($2\theta = 15°$) with increasing temperature at constant heating rates (0.3, 0.5, and 0.7 °C/min).[8] The scattering intensity significantly increases when the cloud point is passed; i.e., the rate of increase in the scattering intensity with temperature changes abruptly at the cloud point. The cloud point at each heating rate was obtained from the intersection of two straight lines with different slopes. The cloud point at zero heating rate was determined by an extrapolation of the cloud-point data obtained at three different heating rates.

A time-resolved small-angle light scattering (SALS) experiment was performed on the 50/50 mixture. The apparatus and the technique have been reported elsewhere.[9] A He–Ne laser with a wavelength $\lambda = 6328$ Å was used, and the scattered intensity in the range of $3.2 \times 10^{-4} < q < 9.3 \times 10^{-4}$ Å^{-1} was measured as a function of time after the temperature jump (T-jump) from 80 °C to six different temperatures (91.0, 92.0, 93.0, 97.0, 98.0, and 101.0 °C).

III. Results and Discussion

The as-cast films of GL-4/H-9 blends were all clear and homogeneous at room temperature, suggesting that GL-4 and H-9 were miscible and in the single-phase state at room temperature. Since the glass transition temperatures of polyisoprene and polybutadiene with a low content of 1,2 and 3,4 linkages such as GL-4 and H-9 are much lower than room temperature, these polymers have large mobility at room temperature. If these polymers had been immiscible, those films should have been phase-separated and should have appeared turbid. The refractive indices n measured by an Abbe refractometer were 1.517 for GL-4 and 1.512 for H-9, the difference of which is not as large as for the case of polystyrene (PS; $n = 1.59$)[10] and poly(vinyl methyl ether) (PVME; $n = 1.467$)[10] but is large enough to cause significant scattering of visible light as shown below.

1. Analysis of SANS Profiles. Figure 1 shows the temperature dependence of the SANS intensity distribution profiles for (a) 70/30, (b) 50/50, and (c) 30/70 blends of GL-4/H-9. The volume fractions of deuterated polybutadiene (ϕ_{DPB}) are 0.279, 0.475, and 0.679, respectively. For each blend the profiles were obtained at various temperatures above room temperature, at which the samples are in the liquid state. All profiles show that the intensity decreases monotonously with q. In Figure 2 the scattering intensities at $q = 0.0093$ Å^{-1} (open circles), 0.0108 Å^{-1} (open triangles), and 0.0122 Å^{-1} (open squares) are plotted against temperature for (a) 70/30, (b) 50/50, and (c) 30/70 blends. For each blend the scattering intensity at fixed q first increases gradually and then decreases with increasing temperature. Considering that all the blend specimens were homogeneous mixtures at room temperature, the first increase in the scattering intensity with temperature suggests the LCST nature of this blend system; i.e., the thermal concentration fluctuation and, therefore, the scattering intensity increase as the system approaches closer to the critical temperature.

The subsequent decrease in the scattering intensity suggests that the system has undergone phase separation because the total intensity of the critical scattering due to the local composition fluctuations inside each phase-separating domain should be smaller than that from a homogeneous mixture before phase separation[4] and because in the time and q domains covered in this experiment we can observe only the critical scattering. The scattering contribution due to the growing domains at the time scale of our observation should appear at q much lower than the experimentally accessible q-window. It should be noted, however, that the increase of the intensity was

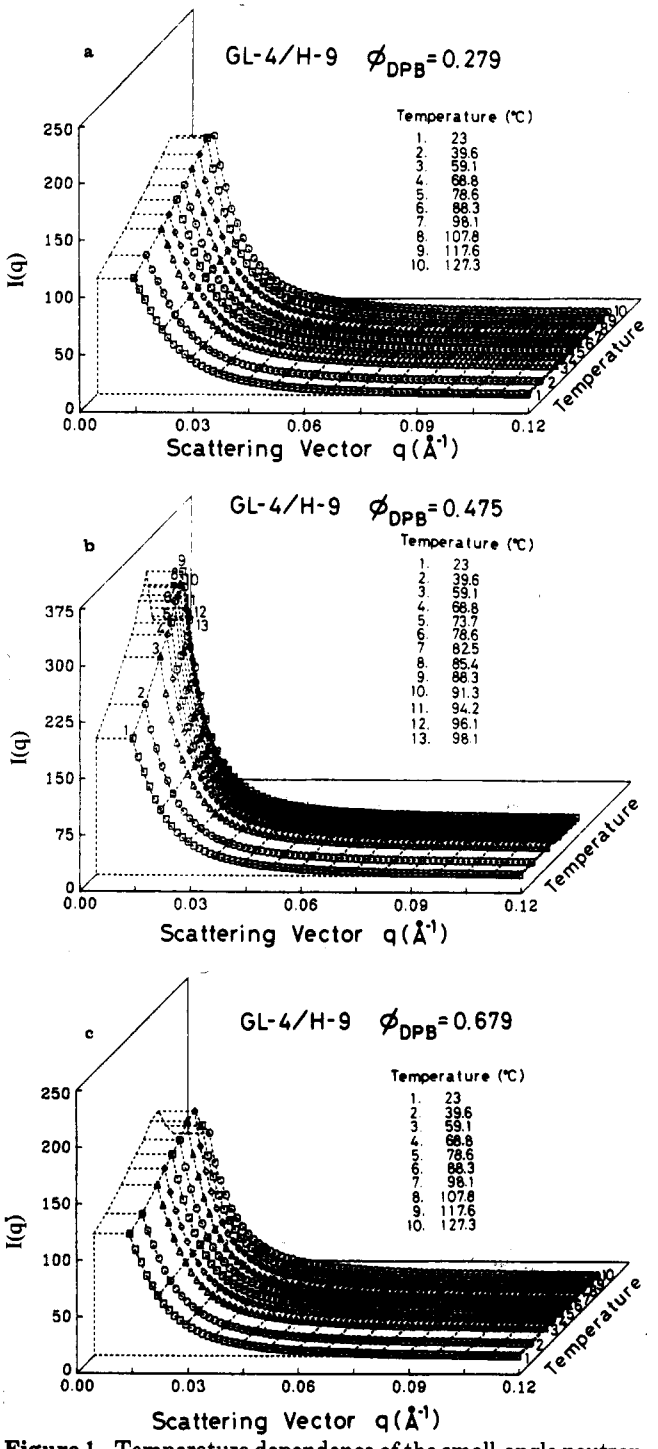

Figure 1. Temperature dependence of the small-angle neutron scattering profiles ($I(q)$ vs q plots) obtained for GL-4/H-9 blends: (a) 70/30 (ϕ_{DPB} = 0.279), (b) 50/50 (ϕ_{DPB} = 0.475), (c) 30/70 (ϕ_{DPB} = 0.679).

instantaneously observed after T-jump at a lower q-region by a separate measurement,[4] which is believed to arise from the scattering due to the growing domains. Again in Figures 1 and 2 there is no such observation that the intensity increases at phase separation because the scattering intensity due to the domain is expected to occur at a much lower q-region than our observation after preheating the sample at the measuring temperature for at least 30 min. Therefore, this crossover temperature at which the scattering intensity began to decrease is considered as the cloud point $T_{c,SANS}$ of the blend measured by SANS. It is located between 117.6 and 127.3 °C for 70/30, between 88.3 and 91.3 °C for 50/50, and between 107.8 and 117.6 °C for 30/70. These are plotted by

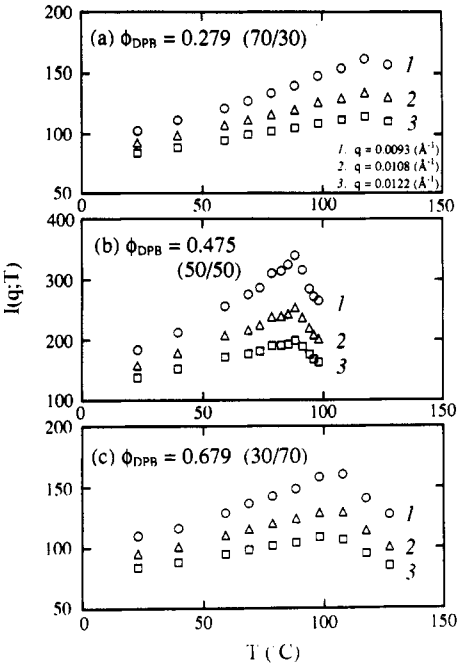

Figure 2. Temperature dependence of the small-angle neutron scattering intensities at fixed q (open circles, q = 0.0093 Å^{-1}; open triangles, q = 0.0108 Å^{-1}; open squares, q = 0.0122 Å^{-1}) obtained for GL-4/H-9 blends: (a) 70/30 (ϕ_{DPB} = 0.279), (b) 50/50 (ϕ_{DPB} = 0.475), (c) 30/70 (ϕ_{DPB} = 0.679).

triangles with error bars in the phase diagram in Figure 7, which will be discussed later. According to this consideration, the scattering curves obtained at the temperatures below the crossover temperatures were analyzed on the basis of the scattering theory from a single-phase mixture.

de Gennes[11] has shown the structure factor $S(q)$ of a binary polymeric mixture in the single-phase state for all q-region based on the random-phase approximation (RPA) in the context of the mean-field model. For the asymmetric polymer pairs it is given by[1,12]

$$\frac{k_N}{S(q)} = \frac{1}{\phi_1 z_{n1} v_1 S_1(q)} + \frac{1}{\phi_2 z_{n2} v_2 S_2(q)} - \frac{2\chi}{v_0} \quad (1)$$

$$k_N = N_A\left(\frac{a_1}{v_1} - \frac{a_2}{v_2}\right)^2 \quad (2)$$

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

$$x_i \equiv q^2\langle R_0^2\rangle = \frac{q^2 z_{ni} b_i^2}{6}$$

$$h_i \equiv ((M_w/M_n)_i - 1)^{-1} \quad (i = 1 \text{ or } 2)$$

where subscripts 1 and 2 denote the quantities for the 1 and 2 components, respectively, a_i is the scattering length per mole of monomer units for neutrons (2.03×10^{11} cm/mol for HPI and 4.01×10^{12} cm/mol for DPB),[13] v_i is the molar volume (75.6 cm^3/mol for HPI and 60.4 cm^3/mol for DPB),[14] ϕ_i is the volume fraction, z_{ni} is the number-average degree of polymerization (1471 for GL-4 and 823.3 for H-9), b_i is the statistical segment length, N_A is Avogadro's number, χ is the binary interaction parameter per monomeric unit, v_0 is the molar volume of the reference cell, and $(M_w/M_n)_i$ is the heterogeneity index. $S_i(q)$ is the

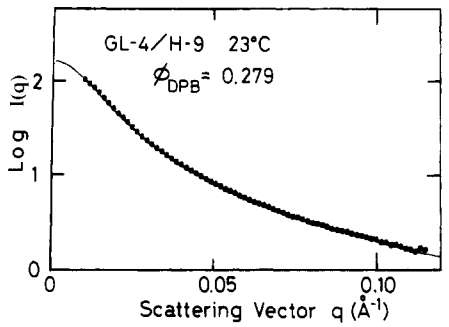

Figure 3. Example of nonlinear regression curve fitting of the experimental SANS profile (data points) for a GL-4/H-9 blend (70/30 (ϕ_{DPB} = 0.279) at 23 °C) and the theoretical scattering curve by eq 4 (solid line) in the single-phase state.

Debye function for the ith component, taking the polydispersity of the component polymer into account when the Schultz–Zimm distribution is assumed.[15] Since there is a large difference between the scattering lengths of the deuterated and protonated polymers, the neutron scattering intensity $I(q)$ from the mixtures is strong enough to hold statistical accuracy for the analysis by a nonlinear regression curve fitting with eq 4.

$$I(q) = S(q) + I_{inc} = k_N/\left[\frac{1}{\phi_1 z_{n1} v_1 S_1(q)} + \frac{1}{\phi_2 z_{n2} v_2 S_2(q)} - \frac{2\chi}{v_0}\right] + I_{inc} \quad (4)$$

In eq 4, the parameters except b_{HPI}, χ/v_0, and I_{inc} were fixed to the constant values obtained from measurements or literatures. I_{inc} was determined by curve fitting rather than evaluation from the measurements of the SANS intensity of the neat constituent polymers at each temperature, which would require unadmissibly long beam time. b_{DPB}/b_{HPI} was fixed to unity, which is a resonable assumption because the literature values of b for polyisoprenes[16] and polybutadienes[17] are within the range of 7 ± 1 Å.

Figure 3 shows an example of the curve-fitting analysis for a single-phase-state mixture, 70/30 at 23 °C. The agreement between the data points and the theoretical scattering curve (solid line) is excellent. For the scattering profiles obtained at the temperatures above the cloud-point temperature $T_{c,SANS}$ the agreement between the data points and the theoretical scattering curve became poor, which again suggests the phase separation. Thus, the value of χ/v_0 for each blend and at each temperature was uniquely determined by the curve-fitting method. To calculate χ from χ/v_0 data, the value of v_0 is necessary, and it was calculated by using the following equation.

$$v_0 = \left(\frac{\phi_1}{v_1} + \frac{\phi_2}{v_2}\right)^{-1} \quad (5)$$

Thus determined χ is denoted as χ_{eff} hereafter. χ_{eff} expresses the mean interaction per monomeric unit between the two particular polymers with given microstructures.

The scattering intensity at $q = 0$, $S(q=0)$, as well as the correlation length ξ of the concentration fluctuation in the single-phase state given by the following equation was also obtained

$$\xi^2 = \frac{v_0}{36(\chi_s - \chi)}\left[\frac{b_1^2 z_{z1}}{v_1 \phi_1 z_{w1}} + \frac{b_2^2 z_{z2}}{v_2 \phi_2 z_{w2}}\right] \quad (6)$$

$$\chi_s = \frac{v_0}{2}\left(\frac{1}{\phi_1 z_{w1} v_1} + \frac{1}{\phi_2 z_{w2} v_2}\right) \quad (7)$$

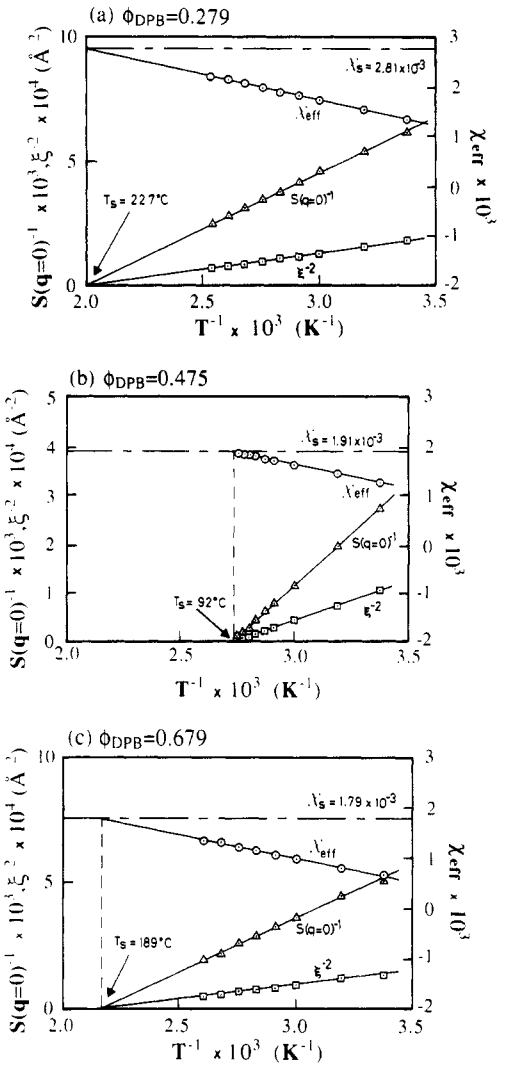

Figure 4. Reciprocal temperature (T^{-1}) dependences of the reciprocal zero-angle coherent scattering intensity, $S(q=0)^{-1}$ (triangles), the reciprocal square of correlation length, ξ^{-2} (squares), and the effective binary interaction parameter, χ_{eff} (circles) for GL-4/H-9 blends: (a) 70/30 (ϕ_{DPB} = 0.279), (b) 50/50 (ϕ_{DPB} = 0.475), (c) 30/70 (ϕ_{DPB} = 0.679). The calculated values of interaction parameters at spinodal temperatures, χ_s, are shown by dash-and-dot lines.

where z_{wi} and z_{zi} are, respectively, the weight-average and z-average degrees of polymerization of polymer i. Here χ_s corresponds to χ at the spinodal temperature and is calculated to be 2.81 × 10^{-3}, 1.91 × 10^{-3}, and 1.79 × 10^{-3} for ϕ_{DPB} = 0.279, 0.475, and 0.679, respectively.

The values of χ_{eff}, $S(q=0)^{-1}$, and ξ^{-2} thus obtained were plotted against reciprocal temperature ($1/T$) in Figure 4 for (a) ϕ_{DPB} = 0.279, (b) ϕ_{DPB} = 0.475, and (c) ϕ_{DPB} = 0.679, together with the level of χ_s indicated by a dash-and-dot line. $S(q=0)^{-1}$ and ξ^{-2} change linearly with $1/T$ in the mean-field regime, if χ_{eff} also changes linearly with $1/T$ as found experimentally

$$\chi_{eff} = A + B/T \quad (8)$$

since

$$S(q=0)^{-1} \sim \xi^{-2} \sim (\chi_s - \chi_{eff}) \quad (9)$$

The "mean-field spinodal temperature" T_s is determined at such a temperature that (i) χ_{eff} reaches χ_s, (ii) the scattering intensity at $q = 0$ becomes infinite or $S(q=0)^{-1}$ becomes zero, and (iii) the correlation length becomes infinite or ξ^{-2} becomes zero. In fact, the data points of χ_{eff}, $S(q=0)^{-1}$, and ξ^{-2} all exhibit reasonably linear rela-

Table II
Dependences of A and B Values in $\chi_{eff} = A + B/T$ on the Composition of GL-4/H-9 Blends

blend samples[a]	ϕ_{DPB}	$A \times 10^3$	B
30/70	0.679	3.84 ± 0.02	−0.95 ± 0.01
50/50	0.475	4.68 ± 0.02	−1.01 ± 0.01
70/30	0.279	4.99 ± 0.02	−1.09 ± 0.01

[a] GL-4/H-9 blends with compositions indicated by wt %/wt %.

tionships with $1/T$. T_s's obtained from the points where the extrapolation of χ_{eff} reaches χ_s are 227, 92, and 189 °C for 70/30, 50/50, and 30/70 mixtures, respectively. These values are plotted by squares in the phase diagram in Figure 7. The extrapolations of $S(q=0)^{-1}$ and ξ^{-2} data to 0 give a single T_s value that also agrees with the T_s value obtained from χ_{eff} data and χ_s. The critical composition of the mixture ϕ_{c1} (volume fraction of polymer 1 in the critical mixture) is given by[18]

$$\phi_{c1} = \frac{Z_{w2}Z_{z2}^{-1/2}v_2^{1/2}}{Z_{w1}Z_{z1}^{-1/2}v_1^{1/2} + Z_{w2}Z_{z2}^{-1/2}v_2^{1/2}} \quad (10)$$

The calculated value of $\phi_{c,DPB}$ for GL-4/H-9 mixture assuming a Shultz–Zimm distribution for molecular weight is 0.598. Since the 50/50 specimen ($\phi_{DPB} = 0.475$) is close to the critical mixture, the T_s for this mixture was accurately determined by the method as described above, i.e., extrapolating the data points at the temperatures very close to the T_s. However, the 70/30 specimen ($\phi_{DPB} = 0.279$) is a distance away from the critical composition, and the extrapolation had to be made from the temperatures far from the T_s. Therefore, the T_s determined is less reliable than that for the critical mixture. Time-resolved SALS measurements may be useful for the determination of T_s accurately as shown for critical and off-critical mixtures of a PS/PVME system.[8] In this case, the spinodal point can be determined as the crossover temperature of the following two behaviors.[2,8] In the early stage of unmixing after a T-jump to the phase-separation temperature T_x above the cloud point T_c, the scattered intensity at a given q increases exponentially with time if $T_x > T_s$. On the other hand, the intensity should not increase exponentially but rather according to the power law if $T_c < T_x < T_s$.[2,8] However, such an experiment for this particular mixture of DPB/HPI was left for future work.

Figure 4 shows that for each blend χ_{eff} data fall on a straight line, with a negative slope expressed by eq 8 within the temperature range of the measurement. The values of A and B depend on the blend composition as indicated in Table II. Since B values are negative, i.e., χ_{eff} increases with increasing temperature, it is suggested again that the GL-4/H-9 system has an LCST-type phase diagram.[19] It should be noted that B values are almost constant with the composition, but the A value increases with decreasing ϕ_{DPB}. This observation is in contrast with the results of deuterated PS/protonated PVME mixtures reported by Shibayama et al.,[1] who observed that both A and B change with composition. The composition (ϕ_{DPB}) dependence of χ_{eff} is shown in Figure 5 for six different temperatures. χ_{eff} tends to decrease with increasing ϕ_{DPB}.[20] The composition dependence of χ_{eff} means the breakdown of Flory–Huggins lattice theory. Thus, either the blend compressibility[21-23] or the packing entropy effect[24-30] must be taken into account. However, we leave it to future work, and it is not discussed further in this paper.

2. Phase Diagram. Cloud-point temperatures T_c of GL-4/H-9 mixtures were obtained from light scattering measurements for four different compositions. Figure 6

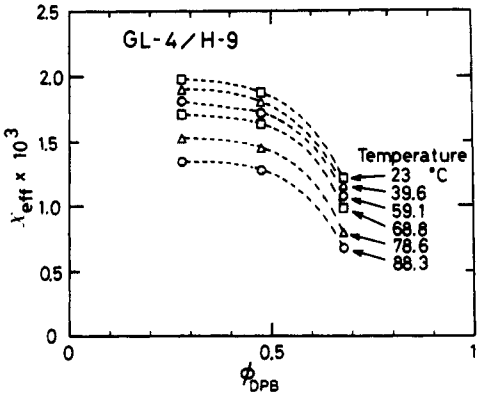

Figure 5. Composition dependence of the effective binary interaction parameter, χ_{eff}, plotted for six different temperatures as indicated in the figure.

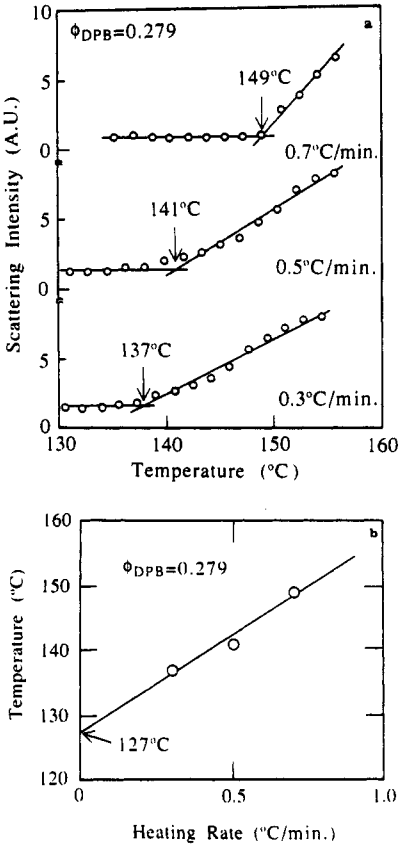

Figure 6. Example of cloud-point measurements by light scattering for 70/30 ($\phi_{DPB} = 0.279$). (a) The scattering intensity at $2\theta = 15°$ is plotted against the temperature for the heating rates of 0.7, 0.5, and 0.3 °C/min. The crossover temperatures are indicated by arrows. (b) The crossover temperature obtained in (a) is plotted against the heating rate. The extrapolation is to obtain the cloud point at zero heating rate.

shows an example of the cloud-point determination by light scattering. In Figure 6a the scattering intensity at $2\theta = 15°$ was plotted against temperature for three different heating rates for the 70/30 specimen. The temperature dependence of the scattering intensity can be divided into two regions. The low-temperature region with a constant value or a very small increase of scattering intensity with increasing T corresponds to the single-phase state. The subsequent steeper increase in scattering intensity suggests the phase separation by nucleation and growth for this off-critical mixture. Therefore, the crossover temperature corresponds to the phase-separation temperature for a given heating rate. Since the growth rate of domains is much slower for the nucleation-and-growth mechanism

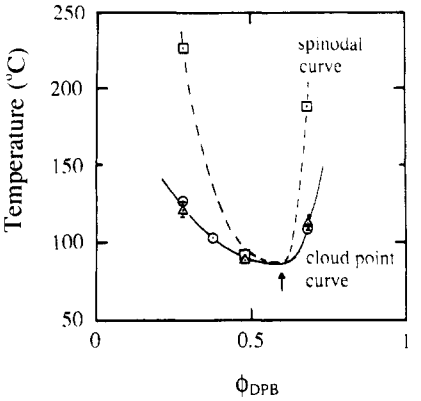

Figure 7. Phase diagram of the GL-4/H-9 blend system. Spinodal temperatures determined by the analysis of the SANS data are shown by squares, and cloud points measured by light scattering experiments and those determined from the SANS profiles were shown by circles and triangles with error bars, respectively. The critical composition ϕ_{DPB} calculated by eq 10 is 0.598 (indicated by an arrow).

than for the spinodal decomposition, the crossover temperature depends on the heating rate. To eliminate the effect of time lag of the phase separation, the crossover temperature was plotted against the heating rate as shown in Figure 6b, and the crossover temperature at zero heating rate was obtained by linear extrapolation. Thus obtained cloud points by light scattering $T_{c,LS}$ were 109 °C for 30/70, 92 °C for 50/50, 103 °C for 60/40, and 127 °C for 70/30 blends.

Figure 7 shows the phase diagram of the GL-4/H-9 system constructed with the SANS and light scattering data. The open circles (solid line) are $T_{c,LS}$ obtained by light scattering. The temperatures above which SANS intensity began to decrease, $T_{c,SANS}$, were indicated by open triangles and error bars, and agreed very well with the $T_{c,LS}$ values within the error bars. The open squares (broken line) are T_s obtained by SANS. The phase diagram is obviously that of an LCST system and has much more symmetrical shape with composition than mixtures of PS and PVME,[1,8,9,31] for which asymmetric phase diagrams were attributed to the composition dependence of the free-volume change upon mixing. The DPB/HPI system can be prepared with extremely monodispersed and well-defined polymers, which eliminates the problems of contamination with low molecular weight polymer[31] or which enables us to examine easily the effect of mixing a small amount of low molecular weight species into the system.

An LCST-type cloud-point curve determined by DSC measurements has been reported by Kawahara et al.[32] for an HPB/HPI mixture where HPB, protonated polybutadiene, has the microstructure with 32.3% 1,2 linkages and the microstructure of HPI is not mentioned. Nevertheless, it is consistent with our observation. They also examined the effect of microstructure (content of 1,2 linkages) of HPB on the miscibility of HPB and HPI by fixing HPI to the same sample and concluded that HPB and HPI were miscible in the temperature range between −25 and 200 °C when the content of 1,2 linkages in HPB was equal to or more than 32.3% and immiscible when it was less than 24.3%. This conclusion is not consistent with our result. Although our DPB (H-9) contains only 12% 1,2 linkages, it is miscible with HPI (GL-4). It may be attributed to the isotope effect[33] that deuteration enhances the miscibility. However, a much more important aspect is that the miscibility of HPB/HPI also depends on the microstructure of HPI and the molecular

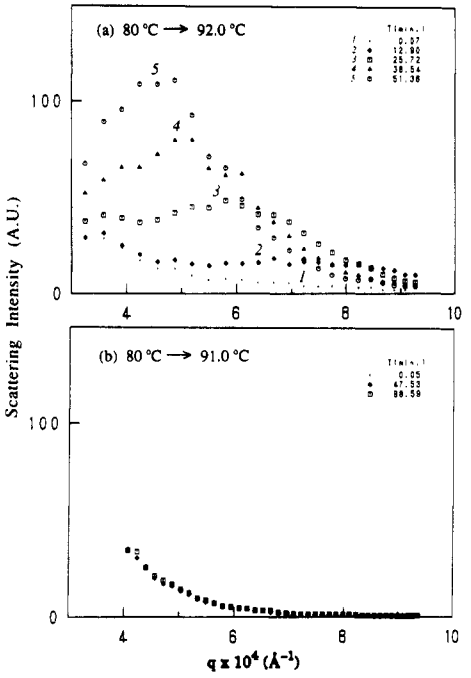

Figure 8. Time-resolved small-angle light scattering profiles for the GL-4/H-9 50/50 mixture (ϕ_{DPB} = 0.475) after a T-jump from 80 °C to (a) 92 °C and (b) 91.0 °C.

weights of HPB and HPI, and these effects are much more important than the isotope effects. The effects of molecular weight, microstructure, and composition on the miscibility of such polymer blends should be decoupled in order to understand the nature of miscibility. This is possible only when χ_{eff} is measured as a function of microstructure and composition. Therefore, their conclusion lacks generality, and their data are not necessarily inconsistent with our results.

One of the great advantages of the DPB/HPI system is that χ-values can be directly measured by SANS as a function of those variables as described above and that the miscibility of DPB/HPI with any combination of their degrees of polymerization can be estimated in the context of the mean-field theory; i.e., the mixture is miscible at the temperatures where the χ-values are less than χ_s, which is a function of the degree of polymerization as given by eq 7. Moreover, we have shown that the effect of the microstructure of polydienes on the miscibility is successfully treated by the random copolymer effects.[15,34] Therefore, the miscibility of DPB/HPI with any microstructure can be estimated in terms of segmental interaction parameters in the context of the random copolymer effects,[34] full discussions of which will be shown elsewhere.[3]

3. Time-Resolved SALS. To confirm the validity of the T_s values determined by SANS, time evolution of the light scattering intensity distribution curve after the T-jumps from 80 °C to six different temperatures around T_s was investigated by time-resolved SALS.[8,9] Figure 8 shows the scattering profiles of the 50/50 specimen after the T-jumps to 92.0 (a) and 91.0 °C (b) whereas T_s of this blend determined by SANS is 92 °C. An intensity maximum in the scattering profile appeared shortly after the T-jump to 92.0 °C in Figure 8a. The data show that the DPB/HPI system has enough scattering power for the SALS study. The peak position moved toward smaller q, and the peak intensity increased with time within the time interval of ca. 50 min. This behavior is typical of spinodal decomposition.[2,8,9] The similar behavior of the scattering profiles was observed for the T-jumps to the temperatures higher than 92.0 °C. On the other hand, the

scattering profile at a long time scale (longer than the relaxation time for the concentration fluctuations in the single-phase state) did not change even after ca. 100 min from the T-jump to 91.0 °C, suggesting that the mixture was in the single-phase state at this temperature. Therefore, the T_s of the 50/50 mixture obtained by the time-resolved SALS measurement was between 91.0 and 92.0 °C and in good agreement with T_s obtained by SANS. Thus it was confirmed by the preliminary result from the time-resolved SALS study on the GL-4/H-9 mixture that the analysis of SANS profiles in a single-phase state enables us to determine the T_s of the mixture with reasonable accuracy. Further analyses of the data from the time-resolved SALS study on DPB/HPI mixtures are now in progress.[35]

IV. Conclusions

A novel polymer mixture system with a relatively symmetrical LCST-type phase diagram was found. The constituent polymers (protonated polyisoprene and deuterated polybutadiene) can be synthesized by anionic polymerization techniques to have very narrow molecular weight distribution and various molecular weights and microstructures, and hence their molecular parameters are well-defined. Therefore, very precise studies on the relationships between the molecular parameters and static and dynamic behaviors of the polymer mixtures are possible by means of scattering techniques. Both SANS and SALS techniques can be used for this purpose because there are enough differences in scattering length and refractive index between the two polymers. χ_{eff} and T_s of the mixtures can be determined by the analysis of SANS profiles obtained for the single-phase states.

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