Inversion of the Phase Diagram from UCST to LCST in Deuterated Polybutadiene and Protonated Polybutadiene Blends

Hiroshi Jinnai, Hirokazu Hasegawa, and Takeji Hashimoto*

Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan

Charles C. Han

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

Recently, the miscibility of amorphous mixtures of normal (protonated) and perdeuterated polybutadiene (hereafter referred to as HPB and DPB, respectively) has been extensively studied and was characterized to have a phase diagram with an upper critical solution temperature (UCST).[1-3] Bates et al.[2,3] studied such an isotope polymer blend and explained the origin of partial miscibility in terms of the reduction in carbon–hydrogen bond length resulting from substituting deuterium for hydrogen (isotope effect). For the DPB/HPB blend, however, since polybutadiene consists of 1,2-units (vinyl) and 1,4-units, the microstructure in the blend should be another important factor affecting the miscibility of the blend. Sakurai et al.[1] separated out the isotope effect and the microstructure effect through a systematic small-angle neutron scattering (SANS) study on DPB/HPB blends with various vinyl contents on the basis of the theory of random copolymer mixtures.[4-6] Sakurai et al.[1] regarded the DPB/HPB blend as a blend of A–B random copolymer (A and B are the 1,2-unit and the 1,4-unit for DPB, respectively) and C–D random copolymer (C and D are the 1,2-unit and the 1,4-unit for HPB, respectively) and showed that the main contribution to miscibility for the blend is due to the intramolecular pairs of A/B and C/D rather than the isotope pairs of A/C and B/D. These intramolecular interactions account for their observation of negative χ's (χ is the binary interaction parameter) for one of their DPB/HPB blend pairs, while only positive χ's are expected for the isotope effect. Therefore, it is extremely important to clarify the effect of the microstructure on the miscibility of the DPB/HPB blends.

In this paper we present experimental evidence of an inversion of the phase diagram from UCST to LCST (lower critical solution temperature) with an increase of the vinyl content of HPB, while that of DPB is held constant. Again this type of phenomenon can never be predicted by merely taking the isotope effect into consideration, implying the importance of the microstructure effect in understanding the miscibility of the DPB/HPB blends.

One perdeuterated polybutadiene sample (DPB) (coded as H20) and five protonated polybutadiene samples (HPB) were synthesized by living anionic polymerization. Table I summarizes the detailed polymer characteristics. In Table I, the sample code (e.g., 17PB91) comprises the vinyl content in % (first number 17 in this case), polybutadiene (PB), and the weight-average molecular weight, M_w, in units of 1000 (the second number 91 in this case).

Blend specimens were prepared by dissolving the polymer mixtures with a composition of 30 wt % DPB and 70 wt % HPB in toluene and then casting into films. Five blend specimens with different compositions were prepared in order to examine the phase diagram for the

Table I
Sample Characteristics

sample code	microstructure (%)			z_n	z_w/z_n
	1,2	cis-1,4	trans-1,4		
H20 (DPB)	15.6	37.9	46.5	950	1.07
17PB91 (HPB)	17	28	55	1294	1.3
39PB91 (HPB)	39	24	37	1053	1.6
52PB215 (HPB)	52.2	15.8	32.0	3974	1.11
65PB104 (HPB)	64.9	11.0	24.1	1922	1.03
80PB110 (HPB)	80.4	5.4	14.2	2033	1.02

H20/80PB110 system. The as-cast films thus obtained were further dried under vacuum at room temperature until constant weight was attained. The thin as-cast films were pressed into a cell and then carefully degassed in order to avoid bubble formation during heating experiments. The specimens were sandwiched between two oxygen-free copper disks and mounted in a heating block. Small-angle neutron scattering (SANS) experiments were carried out using the 8-m SANS instrument at the NIST Cold Neutron Research Facility.[7] In this study, pinhole collimation was used with a 9-Å neutron wavelength (λ). The absolute scattering intensity for each specimen was obtained as a function of the wave vector q ($q = (4\pi/\lambda) \sin (\theta/2)$, θ being the scattering angle) by use of a dry silica gel as a secondary standard.[8] A copper heating block was used to control the specimen within ± 0.2 °C of the desired temperature.

de Gennes has calculated the structure factor, $S(q)$, for a binary polymeric blend in the single-phase state, in the context of the mean-field model and the random-phase approximation (RPA).[9] We used the extended version of the RPA calculation of de Gennes for a system having a molecular weight polydispersity given by the Schultz–Zimm distribution.[1] The structure factor, $S(q)$, of this version is given by

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

with

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

and

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

where

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

and

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

$\langle z_i \rangle_w$ and $\langle z_i \rangle_n$ denote respectively the number- and weight-average degree of polymerization for the ith component (i = A or B), and ϕ_i is the volume fraction of the ith component with molar volume v_i, Kuhn statistical segment length b_i, and neutron scattering length of one monomer unit a_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 $v_0 = (\phi_A/v_A + \phi_B/v_B)^{-1}$. The thermal expansion coefficient in the literature[11] $V^{-1} \partial V/\partial T = 7.5 \times 10^{-4}$ K^{-1} was used to estimate the molar volume of DPB and HPB at each measurement temperature. All SANS data were fitted with eq 1 in order to determine χ parameters as a function
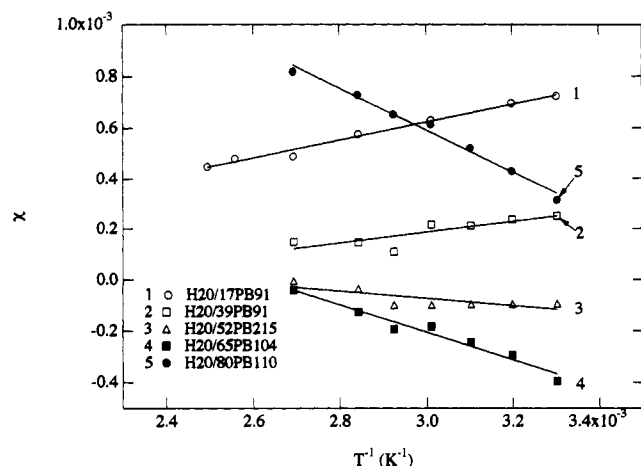
Figure 1. Plots of binary interaction parameters, χ, against reciprocal absolute temperature, T^{-1}, for five different DPB/HPB blends.
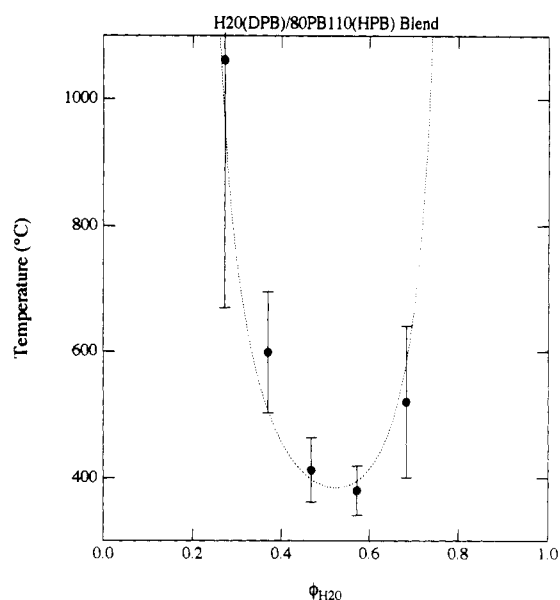

Figure 2. Phase diagram for a H20/80PB110 blend. Spinodal temperatures determined by SANS are shown by filled circles along with error bars. The dashed line in the figure is a visual guide.

of temperature (T) for each blend. The detailed fitting procedure can be found elsewhere.[1,10] The error for χ was estimated by fitting eq 1 to the data while varying the molecular weight of DPB and HPB in the range of $\pm 5\%$, which is an estimated error in the molecular weight measurement. The error for χ thus determined was approximately $\pm 1 \times 10^{-4}$ for each measurement.

In Figure 1, χ parameters for five DPB/HPB blends (30/70 wt %/wt %) with different vinyl contents of HPB are plotted against the reciprocal absolute temperature (T^{-1}). χ decreases with increasing temperature for the H20/17PB91 blend, suggesting that this blend is a UCST-type mixture. χ also decreases as temperature increases for the H20/39PB91 blend, although the absolute values of the χ parameters are smaller than that for H20/17PB91. It should also be noted that the temperature dependence of χ is weaker for H20/39PB91 than for H20/17PB91. Almost no temperature dependence was observed for the H20/52PB215 blend. We should point out that the χ values of this blend are negative in the temperature range of the experiment. Surprisingly, the temperature dependence of χ is inverted (i.e., χ increases with increasing temperature) for the H20/65PB104 and H20/80PB110 blends, suggesting that these two blends are LCST-type mixtures. It is interesting that the values of χ parameters suddenly become positive again as the vinyl fraction of HPB in DPB/HPB blends increases from 65% to 80%. It should also be emphasized that the temperature dependence of χ for the H20/80PB110 blend is larger than that for the H20/65PB104 blend. This series of χ data for DPB/HPB (30/70 wt %/wt %) blends with a wide range of vinyl content from 17% to 80% in HPB clearly demonstrates the inversion of the phase diagram. To our knowledge, such an inversion of the phase diagram has never been observed. This phenomenon is interesting because one can control not only the extent of miscibility but also the phase-separation behavior of DPB/HPB blends by changing the vinyl content of the constituent polymers.

SANS measurements were also carried out for the H20/80PB110 blends with five different volume fractions of H20 (DPB) (i.e., ϕ_{H20} = 0.272, 0.370, 0.468, 0.572, and 0.683). χ parameters were determined for all compositions as a function of temperature by the same procedure used above. Although the temperature dependence of χ for H20/80PB110 blends with five different compositions will not be presented in this paper (besides the 30/70 wt %/wt % blend which is shown in Figure 1), it is worth noting that these blends have exactly the same features as H20/80PB110 (30/70 wt %/wt %); i.e., χ increases as the

temperature increases. The mean-field spinodal temperature, T_s, is obtained by extrapolating χ to its value at the spinodal point, which is given by

$$\chi_s = \frac{v_0}{2}\left(\frac{1}{v_A\phi_A\langle z_A\rangle_w} + \frac{1}{v_B\phi_B\langle z_B\rangle_w}\right) \qquad (4)$$

T_s's at different compositions are plotted against ϕ_{H20} in Figure 2. Although the error bars due to the uncertainty of extrapolation in χ are significant, it is obvious that the H20/80PB110 has an LCST-type phase diagram.

The experimental observation of the inversion of the phase diagram in the DPB/HPB blends can be explained on the basis of the random copolymer theory by ten Brinke et al.[4] This analysis is now underway and will be presented in a future publication.

Balazs et al.[12] discussed the effect of sequence distribution on the miscibility of copolymer/copolymer blends. In their model a parameter was introduced to describe a block, random, or alternating copolymer. In the context of this model one can discuss a mixture of two random copolymers, which could be a possible way to explain our data.

References and Notes

(1) Sakurai, S.; Hasegawa, H.; Hashimoto, T.; Glen Hargis, I.; Aggarwal, S. L.; Han, C. C. *Macromolecules* **1990**, *23*, 451.
(2) Bates, F. S.; Wignall, G. D.; Koehler, W. C. *Phys. Rev. Lett.* **1985**, *55*, 2425.
(3) Bates, F. S.; Dierker, S. B.; Wignall, G. D. *Macromolecules* **1986**, *19*, 1938.
(4) ten Brinke, G.; Karasz, F. E.; Macknight, W. J. *Macromolecules* **1983**, *16*, 1827.
(5) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1986**, *19*, 1938.
(6) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.

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

(8) Glinka, C. J.; Krueger, S. NBS Memorandum for SANS Users, Dec 29, 1986.

(9) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979. de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.

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

(11) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*; Wiley: New York, 1989.

(12) Balazs, A. C.; Karasz, F. E.; MacKnight, W. J.; Ueda, H.; Sanchez, I. C. *Macromolecules* **1985**, *18*, 2784. Balasz, A. C.; DeMeuse, M. T. *Macromolecules* **1989**, *22*, 4260.