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# Phase Behavior and Flory–Huggins Interaction Parameter of Binary Polybutadiene Copolymer Mixtures with Different Vinyl Content and Molar Volume

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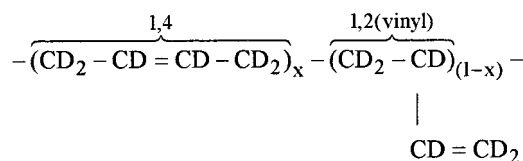
**ABSTRACT:** Binary blends of statistical polybutadiene copolymers of different vinyl content were explored by small-angle neutron scattering. These samples represent the simplest class of statistical copolymer mixtures. In spite of this simplicity, strong changes of phase behavior were observed with varying vinyl content, molar volume, and deuteration; the temperatures of phase separation are found between  $-230$  °C and more than  $200$  °C and phase separation can even reverse from an enthalpically driven one at low temperatures (UCST) to an entropically driven one at high temperatures (LCST). The experimentally determined entropic and enthalpic terms of the Flory–Huggins parameter are in excellent agreement with lattice cluster theory calculations by Dudowicz and Freed.

## I. Introduction

Chemically different homopolymers of reasonable high molecular weight show only a weak tendency of mixing. This behavior is mainly caused by the low entropy of mixing being inversely proportional to the molecular weight.<sup>1–3</sup> A better compatibility is often achieved for statistical copolymers; if one compares polymers of similar length one often finds that a “C” homopolymer is miscible with an “A–B” statistical copolymer even though “A, B, and C” homopolymers (A, B, C are types of monomer) are not miscible with each other. This phenomenon is interpreted by the interplay of the intermolecular interactions between the A–C and B–C monomers and the intramolecular interaction between the A–B monomers reducing the total enthalpy of mixing.<sup>4–7</sup> While this explanation seems to be sufficient to interpret the enhanced compatibility determined from cloud point experiments, it completely failed to correctly describe recent small-angle neutron (SANS) experiments on binary blends of polystyrene (PS) and polybutadiene (PB) of different vinyl content.<sup>8</sup> In these experiments, strong discrepancies were observed for the interaction energy between PB(1,4) and (1,2) monomers depending on whether the interaction energy was determined from the PB(1,2)/PB(1,4) or PS/PB blend as an intermolecular or intramolecular interaction energy, respectively. This discrepancy would not have been visible from the phase boundaries alone as the critical temperature of the blend with the copolymer PB(1,2;1,4) is well between those with PB(1,4) and PB(1,2) (see Figure 7 in ref 8). The reason using the phase boundary alone is insufficient is because the full Flory–Huggins (FH) parameter is the noncombinatorial part of a *free energy* of mixing consisting of an enthalpic and entropic term which cannot be determined from the phase boundary alone.

It is the aim of the present work to test the theory of the thermodynamics of statistical copolymers. We therefore started new SANS experiments on binary statistical copolymer blends which from the theoretical point of view represent the simplest possible model systems. We

Table 1. Polymer Chain Characteristics



polymer	polybutadiene			
	dPB (C <sub>4</sub> D <sub>6</sub> )		hPB(C <sub>4</sub> H <sub>6</sub> )	
vinyl content, % <sup>a</sup>	7	54	91	91
	dPB(1,4)	dPB(1,2;1,4)	dPB(1,2)	hPB(1,2)
Ω, cm <sup>3</sup> /mol <sup>b</sup>	60.4	60.4	60.4	60.4
ρ, 10 <sup>10</sup> cm <sup>-2</sup> <sup>c</sup>	6.76	6.76	6.76	0.416

<sup>a</sup> By <sup>13</sup>C NMR in CDCl<sub>3</sub>, <sup>1</sup>H NMR for hPB(1,2). <sup>b</sup> Monomer volume; densities: dPB = 1 g/cm<sup>3</sup>; hPB = 0.9 g/cm<sup>3</sup>. <sup>c</sup> Coherent scattering length density of the polymers determining the neutron scattering contrast.

have chosen blends of polybutadiene (PB) statistical copolymers with three different contents of (1,2) vinyl units, namely PB(1,4), PB(1,2;1,4), and PB(1,2) with, respectively, 7%, 54%, and 91% vinyl content and molar volumes between 2K and 20K in units of cm<sup>3</sup>/mol ( $K \equiv 10^3$ ) (see Tables 1 and 2). Two of these polymers were always mixed in 50% portions ( $\Phi = 0.5$ ), one component perdeuterated (C<sub>4</sub>D<sub>6</sub>) and the other one protonated (C<sub>4</sub>H<sub>6</sub>) in order to get a sufficiently good scattering contrast. Using SANS, thermal composition fluctuations and thereby the structure factor  $S(Q)$  ( $Q$  is the wave-number) were measured as a function of temperature within the homogeneously mixed sample. The phase transition temperature and the FH parameter were then derived from  $S(Q)$  and compared with a recently published theoretical expressions from lattice cluster theory (LCT) calculations by Dudowicz and Freed.<sup>9–11</sup> The LCT represents an extension of the FH theory insofar as each monomer is assigned a structure that covers several lattice sites. In this way, excess free volume and an entropic contribution to the Flory–Huggins interaction parameter were introduced.

The PB copolymer mixtures of different vinyl content show a surprisingly rich phase behavior. This aspect

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will later be explained by the weak interactions assigned to the different microstructures of the otherwise chemically identical monomers; those systems should sensitively depend on chain ends, flexibility, monomer sequence distribution, and deuteration. It is found that the FH parameter strongly depends on molar volume ( $V$ ) and is, to a good approximation, proportional to  $1/V$  in accordance with expectations from chain-end effects.<sup>12</sup> Copolymer theory from the LC theory<sup>9,10</sup> gives a consistent interpretation for extrapolation to infinite molar volume ( $1/V = 0$ ) of the FH parameters and shows that deuteration has a strong effect on the enthalpic FH parameter. Furthermore, the enthalpic FH parameter of dPB(1,4)/PB(1,2; $y$ ;1,4 $_{(1-y)}$ ) is sufficiently reduced (i.e., attractive) by deuteration so that phase decomposition is proposed to occur at high temperature (LCST behavior) for a vinyl content between  $0.15 < y < 0.7$  in agreement with experimental findings by Jinnai et al.<sup>13</sup> UCST behavior (phase decomposition occurring at low temperatures) is exclusively predicted in fully protonated PB copolymer mixtures in agreement with observations.<sup>14</sup> So, a first conclusion might be, that in weakly interacting polymer blends, as in (1,2) and (1,4) PB, additional dependences of the FH parameter appear and lead to a rather complex phase diagram and very different critical temperatures. In the following we will first give a short description of the theoretical background, then explain the experiments, and finally give an interpretation of the SANS results in terms of the presently available theory.

## II. Theoretical Background

Within a mean field approximation the equilibrium thermodynamic properties of polymer blends are described by the Flory–Huggins (FH) interaction parameter  $\Gamma = \Gamma_h/T - \Gamma_\sigma$ , which is a phenomenological parameter and which represents the noncombinatorial part of the free energy of mixing with the, respectively, enthalpic and entropic contributions  $\Gamma_h$  and  $\Gamma_\sigma$ . This  $\Gamma$  parameter is determined from the SANS structure factor  $S(Q)$  at scattering vector  $Q = 0$  and formally represents a thermodynamic susceptibility. Theoretical approaches for calculating  $\Gamma$  for copolymers, chain-end effects, and the relationships between susceptibility  $S(0)$  and  $\Gamma$  will be discussed next.

**A. Theory of Statistical Copolymers.** Quite recently, Dudowicz and Freed formulated an expression for the FH-parameter for statistical copolymers of the general type  $A_x B_{(1-x)} / C_y D_{(1-y)}$  within their “Lattice Cluster Theory for Pedestrians” (see eq 13 in ref 9 or eq 1 in ref 10). This expression leads to the “old theory” according to

$$\Gamma \equiv \Gamma_h = \Gamma_h(AC)xy + \Gamma_h(BC)(1-x)y + \Gamma_h(AD)x(1-y) + \Gamma_h(BD)(1-x)(1-y) - \Gamma_h(AB)x(1-x) - y(1-y)\Gamma_h(CD) \quad (1)$$

if  $\Gamma_\sigma$  is neglected and the monomers are taken to occupy single lattice sites.<sup>4–7</sup> The symbols A, B, C, and D represent the monomers and  $x$  and  $y$  the A and D monomer volume fractions of the copolymers, respectively. In the case of a positive intramolecular  $\Gamma_h(AB)$  and  $\Gamma_h(CD)$ , the overall enthalpic term in eq 1 is reduced resulting in a better compatibility between the polymers in the blend. The enthalpic term, representing the intramolecular interaction such as between C and D monomers, is determined by the van der Waals ex-

change energy  $\epsilon = \epsilon_{CC} + \epsilon_{DD} - 2\epsilon_{CD}$  in accordance with  $\Gamma_h(CD) = (2z/\Omega)\epsilon$ .

In the investigated blends of the perdeuterated dPB(1,2) $_x$ dPB(1,4) $_{(1-x)}$  and protonated PB(1,2) $_y$ PB(1,4) $_{(1-y)}$  statistical copolymer chains, the energies  $\epsilon_{CC}$ ,  $\epsilon_{DD}$ , and  $\epsilon_{CD}$  describe the interaction between the protonated 1,2–1,2, 1,4–1,4, and 1,2–1,4 pairs of monomer, respectively,  $z$  is the number of nearest neighbors (theoretical number is  $z = 6$ ), and  $\Omega$  is the monomer volume ( $\Omega = 60.4 \text{ cm}^3/\text{mol}$  for PB). A further simplification is achieved if the interaction energy of perdeuterated monomers is described by the polarizability model of Bates et al. and which leads to  $\epsilon_{AA} = \gamma^2\epsilon_{CC}$ ,  $\epsilon_{BB} = \gamma^2\epsilon_{DD}$ ,  $\epsilon_{AB} = \gamma^2\epsilon_{CD}$ ,  $\epsilon_{AC} = \gamma\epsilon_{CC}$ ,  $\epsilon_{BD} = \gamma\epsilon_{DD}$ ,  $\epsilon_{AD} = \epsilon_{BC} = \gamma\epsilon_{CD}$ .<sup>15</sup> The value of  $\gamma$  is slightly less than one because of the smaller interaction between perdeuterated monomers in comparison with the corresponding protonated ones. In case of a symmetric blend ( $\Phi_C = 0.5$ ), one gets from the LCT expression

$$\Gamma_h = (2z/\Omega)\{\epsilon_{CC}(\gamma x - y)^2 + \epsilon_{DD}[\gamma(1-x) - (1-y)]^2 - 2\epsilon_{CD}(y - \gamma x)[\gamma(1-x) - (1-y)]\} \quad (2)$$

(see eqs 1 and 11 in ref 10).<sup>9,10</sup> In case of a fully protonated blend with  $\gamma = 1$ ,  $\Gamma_h$  becomes

$$\Gamma_h = (2z/\Omega)(\epsilon_{CC} + \epsilon_{DD} - 2\epsilon_{CD})[x - y]^2 \quad (3)$$

and for the PB(1,4)/PB(1,2) homopolymer blend eq 3 reduces to

$$\Gamma_h = (2z/\Omega)(\epsilon_{CC} + \epsilon_{DD} - 2\epsilon_{CD}) \quad (4)$$

In the case of the blends with dPB(1,4)/PB(1,2) ( $x = 0$ ;  $y = 1$ ) and with dPB(1,2)/PB(1,4) ( $x = 1$ ;  $y = 0$ ) where one component is the deuterated one, respectively, eq 3 gives

$$\Gamma_h = (2z/\Omega)(\epsilon_{CC} + \gamma^2\epsilon_{DD} - 2\gamma\epsilon_{CD}) \quad \text{and} \quad \Gamma_h = (2z/\Omega)(\gamma^2\epsilon_{CC} + \epsilon_{DD} - 2\gamma\epsilon_{CD}) \quad (5)$$

which represents a different  $\Gamma_h$  in case of different van der Waals energies  $\epsilon_{DD}$  and  $\epsilon_{CC}$ .

In older theories the thermodynamics of statistical polymers is solely described by the enthalpic term as in eq 1.<sup>4–7</sup> Lattice cluster theory gives in addition an entropic term which for the PB copolymer blends reads<sup>9–11</sup>

$$\Gamma_\sigma = -(x - y)^2/(4z^2\Omega) \quad (6)$$

This negative entropic  $\Gamma_\sigma$  is related to the number of lattice sides per monomer that are occupied by tri- and tetrafunctional united atomic units of the (1,2) and (1,4) monomers; compressibility and chain-end effects are not considered.<sup>9,11</sup> The FH terms in eqs 1–6 are related to those of refs 9–11 by scaling factors  $\Gamma_\sigma = -(4/\Omega)\chi_{\text{site},\sigma}$  and  $\Gamma_h = (4/\Omega)\chi_{\text{site},h}$ .

**B. Chain-End Effects and Critical Temperature.** Chain-end effects of the FH parameter are described by the relations

$$\Gamma_h(V) = \Gamma_h + A_h/V; \quad \Gamma_\sigma(V) = \Gamma_\sigma + A_\sigma/V \quad (7)$$

with the coefficients  $A_h$  and  $A_\sigma$  for the enthalpic and entropic terms, respectively.<sup>12</sup> Such behavior was recently observed in several small angle neutron scatter-

ing experiments.<sup>16,17</sup> From eq 7 and the critical FH parameter  $\Gamma_C = 2/V$  for symmetric blends, one evaluates the critical temperature as

$$T_C = \Gamma_h(V)/[\Gamma_C + \Gamma_o(V)] = (\Gamma_h V + A_h)/[\Gamma_o V + 2 + A_o] \quad (8)$$

Symmetric blends are mixtures with components having the same molar volume ( $V = V_A = V_B$ ); they have a critical composition of  $\Phi_C = 0.5$ , and  $\Gamma_C$  is evaluated from the averaged molar volume as  $2/\langle V \rangle$ .<sup>1-3</sup>

**C. Structure Factor and Susceptibility of Binary Polymer Blends.** In order to determine the FH parameter, thermal composition fluctuations have to be measured in the homogeneously mixed state of the polymer blend. Neutron diffraction is caused by thermal composition fluctuations and is expressed in terms of the structure factor  $S(Q)$  which is a function of the momentum transfer  $Q$ . The value of  $Q$  is determined by the scattering angle  $\Theta$  and neutron wavelength  $\lambda$  according to  $Q = (4\pi/\lambda) \sin \Theta/2$ . At sufficiently small  $Q$ , the structure factor can be approximated by the Zimm approximation<sup>18</sup>

$$S^{-1}(Q) = S^{-1}(0) + L_2 Q^2 \quad (9)$$

The extrapolated  $S(0)$  represents a thermodynamic susceptibility, and  $L_2$  is related to the correlation length  $\xi$  of the thermal fluctuations according to  $L_2 = \xi^2/S(0)$ .<sup>1-3</sup> The relevant thermodynamic information is derived from the susceptibility  $S(0)$ , which is the average of a property over a macroscopic volume due to the inverse relationship between the length scales in real space and the reciprocal  $Q$ -space. The susceptibility  $S(0)$  is related by the fluctuation–dissipation theorem with the second derivative of the Gibbs free energy of mixing with respect to composition according to  $S^{-1}(0) = \partial^2(G_m/RT)/\partial\Phi^2$  ( $R$  is the gas constant;  $\Phi$  is the volume fraction of one component).<sup>1,2</sup>

The degree of thermal composition fluctuations and thereby  $S(Q)$  sensitively depends on temperature. At sufficiently high temperature above the critical temperature, thermal fluctuations become weak so that they can be described within the Gaussian approximation of noninteracting fluctuation modes; in this state the system is well described by the mean field approximation. Within the FH model the susceptibility is given as

$$S^{-1}(0) = 2[\Gamma_C - \Gamma] \quad (10)$$

with the FH parameter  $\Gamma$  and with  $\Gamma_C$  representing  $\Gamma$  at the critical temperature  $T_C$ .

On the other hand, near the phase boundary and especially near the critical temperature thermal fluctuations become very strong; under these conditions the interaction of different fluctuation modes leads to nonlinear effects. These nonlinear effects are measured by the susceptibility which then exhibits a crossover from mean field to 3D Ising critical behavior as described by scaling laws as  $S(0) = C\tau^{-\gamma}$  where the reduced temperature is  $\tau = |T_C - T|/T$  and the critical exponent  $\gamma$  equals 1 and 1.239 in case of mean field and 3D Ising behavior, respectively.<sup>1-3</sup> Generally, the susceptibility  $S(0)$  above the critical temperature is described by a crossover function; we applied the asymptotic crossover model by Belyakov and Kiselev<sup>19,20</sup>

$$\hat{\tau} = (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{(\gamma-1)/\Delta} [\hat{S}^{-1}(0) + (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{-\gamma/\Delta}] \quad (11)$$

with the exponents  $\gamma$  and  $\Delta$  ( $=0.5$ ) of the 3D Ising model. The rescaled reduced temperature  $\hat{\tau} = \tau/G_i$  ( $\tau = |T_C - T|/T$ ) is formulated as a function of the rescaled susceptibility  $\hat{S}(0) = S(0)G_i/C_{MF}$ . The parameters  $G_i$ ,  $C_{MF}$ , and  $T_C$  are extracted directly from the experimental results and characterize the system;  $G_i$  and  $C_{MF}$  are the Ginzburg number and the mean field critical amplitude of  $S(0)$ , respectively. This crossover function was already applied by us to other blend samples in several earlier SANS work.<sup>3,19</sup>

The Ginzburg number  $G_i$  represents an estimation of the reduced temperature  $\tau$  where the crossover occurs between the two universality classes of mean field and 3D Ising behavior. The mean field critical amplitude is related to the FH parameters by

$$C_{MF} = 1/2[\Gamma_S + \Gamma_o] = T_C^{MF}/2\Gamma_h \quad (12)$$

with the corresponding enthalpic and entropic parts of  $\Gamma$ .<sup>3,19</sup> Equation 12 is the analogue of eq 10 in the case of strong fluctuations and gives us the Flory–Huggins mean field parameters even though the experiments were performed in a region where the mean field approximation and thereby Flory–Huggins theory is not valid.

### III. Experimental Section

The scattering experiments were performed at the SANS diffractometer KWS1 at the FRJ2 reactor of the "Forschungszentrum Jülich".<sup>22</sup> For these studies a temperature cell was used which allows an in-situ change of temperature, with a temperature control better than 0.01 K. This cell was developed in our laboratory. The sample thickness and its neutron-irradiated diameter were 0.1 and 0.7 cm, respectively. The temperature of the sample could be rather accurately determined from the thermocouple and the always existing temperature gradient between sample and position of the thermocouple. The temperature gradient was determined in a separate measurement under identical conditions with an additional thermocouple at the sample position. The scattering data were corrected for background, detection efficiency of the single detector cells, radial averaged, and calibrated in absolute units by a Lupolen secondary standard. The resulting absolute macroscopic cross section  $d\Sigma/d\Omega(Q)$  in units of 1/cm is related to the structure factor  $S(Q)$  according to  $d\Sigma/d\Omega(Q) = S(Q)\Delta\rho^2/N_A$ , where  $\Delta\rho$  is the difference of the coherent scattering length densities of the polymer components  $\sum c_i b_i/\Omega_i$  (numerical values are given in Table 1) and the Avogadro number is  $N_A$ . The scattering experiments were performed in the momentum transfer range of  $0.007 \leq Q (\text{\AA}^{-1}) \leq 0.05$  using the settings of 7 Å for the neutron wavelength and the detector to sample distances of 4 and 8 m.

The polymers were synthesized by anionic polymerization using high vacuum and break seal techniques as has been described in more detail in ref 8. *sec*-Butyllithium was used as initiator for all polymerizations. The purification of solvents and monomers was performed according to the standards required for anionic polymerization.<sup>23</sup> Protonated and perdeuterated polybutadiene with 1,4 microstructure were polymerized in benzene. The preparation of polybutadienes with an increased 1,2 content demands the addition of polar cosolvents: Tetrahydrofuran (THF) and diethyl ether were respectively used as cosolvents for polymers with high vinyl content (h-dPB(1,2)) and for generating an almost equal distribution of the 1,4 and 1,2 units in dPB(1,2;1,4).

The polydispersity,  $M_w/M_n$ , of the polymers was determined by size exclusion chromatography using a Waters 150C instru-



Table 2. All Samples Investigated<sup>a</sup>

sample	deuterated polybutadiene	$V$	protonated polybutadiene	$V$	$\Gamma_C$	$\langle V \rangle$
1	dPB(1,4)	28	PB(1,4)	27.5	7.21	27.7
2 <sup>b</sup>	dPB(1,2)	20.5	PB(1,4)	27.5	8.4	23.8
3	dPB(1,2)	20.5	PB(1,2;1,4)	20.6	9.73	20.6
4	dPB(1,4)	28	PB(1,2;1,4)	20.6	8.43	23.7
5	dPB(1,4)	14.5	PB(1,2)	14.17	13.9	14.4
6	dPB(1,4)	8	PB(1,2)	10.3	22.2	9
7	dPB(1,2;1,4)	2.05	PB(1,4)	2.92	83	2.4
8	dPB(1,2;1,4)	2.05	PB(1,2)	2.29	92.4	2.2
9	dPB(1,4)	2.21	PB(1,2)	2.29	89.9	2.2
10	dPB(1,2)	2.06	PB(1,4)	2.92	82.8	2.4
11	dPB(1,2)	2.06	PB(1,2)	2.29	92.2	2.2

<sup>a</sup> The composition was always  $\Phi = 0.5$ ; the molar volume  $V$  and the critical FH parameter  $\Gamma_C = 2/\langle V \rangle$  is given in units of  $10^3 \text{ cm}^3/\text{mol}$  and  $10^{-5} \text{ mol/cm}^3$ , respectively. <sup>b</sup> SANS experiments showed that this sample was not miscible below 200 °C.

ment. This instrument was equipped with four  $\mu$ -Styragel columns with a porosity range of  $10^5$ –500 Å and one ultra-Styragel column of continuous porosity in combination with a refractive index detector. The eluent was THF at a flow rate of 1 mL/min and PS standards were used for calibration. In all cases  $M_w/M_n$  values were smaller than 1.1. The number average molecular weight of the polymers,  $M_n$ , was measured with a Knauer vapor pressure osmometer at 45 °C in benzene. The  $M_n$  values were obtained using a calibration function of the type  $(\Delta V/c)_{c \rightarrow 0} = KM_n^\alpha$ , where  $\Delta V$  is the change of the thermistors in voltage and  $c$  is the concentration.<sup>24</sup> The calibration constants  $K$  and  $\alpha$  were determined with benzene and PS standards of  $440 \leq M_n \leq 9600$  with an accuracy of about  $\pm 5\%$ . The 1,2/1,4 composition of the d-polybutadienes was determined by  $^{13}\text{C}$  NMR spectroscopy with a Bruker 300 MHz spectrometer. For the hPB(1,2) polymer the composition was additionally determined by  $^1\text{H}$  NMR. The cis/trans ratio of the 1,4-microstructure was determined to be 0.8 in all polymers independently of their vinyl content. The characteristic parameters of the polymers are summarized in Table 1.

The polymer blends were prepared by dissolving in and freeze-drying from benzene solutions. Since we had a mixture of symmetric polymers of nearly equal molar volume, we mixed the components always in volume fractions of  $\Phi = 0.5$  which should be near the critical composition. The thermal stability of the samples was improved by addition of 0.1% 2,6 di-*tert*-butyl-4-methylphenol and by filling them in an argon box into a leak-proof sample holder. In this way the blends were protected from degradation and cross-linking at the experimental temperatures as cross checked by SEC measurements after the SANS experiments.

#### IV. Experimental Results and Discussion

**A. Structure Factor and Susceptibility.** The structure factor measured at three temperatures in dPB(1,2)/PB(1,2;1,4) and dPB(1,4)/PB(1,2;1,4) (details of the corresponding samples 3 and 4 are given in Table 2) have been plotted in Figure 1 in a Zimm representation. The scattering data are well described by straight lines in accordance with eq 9. The scattering from both samples is very different in spite of their similar molar volumes of 20.6K and 23.7K; the sample with dPB(1,2) shows an order of magnitude stronger scattering and a visible change with temperature in contrast to the sample with dPB(1,4).

Figure 2 plots the susceptibilities  $S(0)$  of these two samples (3 and 4) together with the isotopic mixture of two PB(1,4) polymers (sample 1 in Table 2) versus the inverse temperature. The mixture of nearly pure dPB(1,2) and PB(1,4) (sample 2 in Table 2) was not miscible below 200 °C and could therefore not be plotted. The blend containing the dPB(1,2) and PB(1,2;1,4)

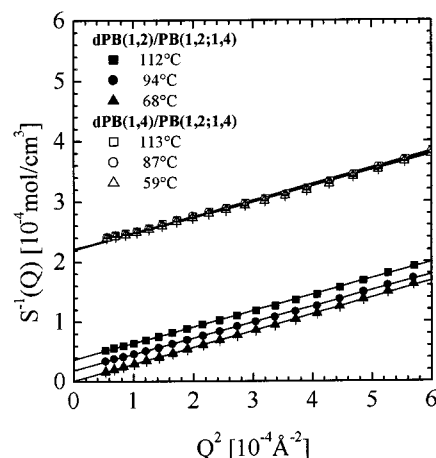
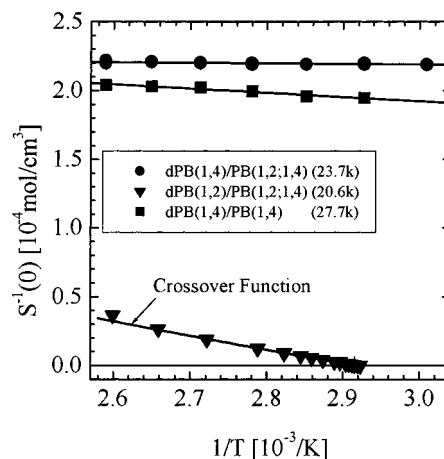
Figure 1. Structure factor  $S(Q)$  in a Zimm representation.

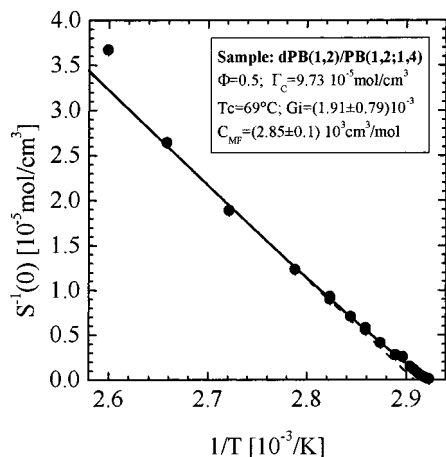
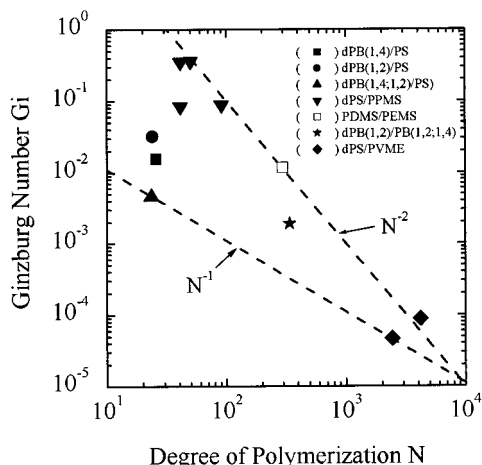
Figure 2. Inverse susceptibility versus inverse temperature for three PB mixtures of different microstructures.

components (sample 3) shows a large susceptibility which becomes infinite, e.g.,  $S^{-1}(0) = 0$ , at the critical temperature of phase separation at  $T_C = 69$  °C. The isotopic PB(1,4) blend shows only weak scattering and a weak temperature dependence, as expected. The susceptibilities of the blends with samples 1 and 4 were fitted by a straight line in accordance with eq 10 while for the strong scattering blend containing sample 3 the more sophisticated crossover theory in eq 11 had to be applied. At first glance, the strong difference between sample 3 and 4 is very surprising as the corresponding fully protonated mixtures ( $\gamma = 1$ ) with a vinyl content of  $|x - y| \approx 0.5$  would lead according to eq 2 to the same FH parameter and therefore to the same scattering. These differences will be explained later quite naturally from the effect of deuteration when  $\gamma \neq 1$ .

The susceptibility of the dPB(1,2)/PB(1,2;1,4) blend shows a crossover behavior according to eq 11 and which for clarity is plotted separately in Figure 3. The fit of the crossover function is represented by the solid line; the corresponding parameters are given in the inset of the figure and in Table 3. The FH parameter was evaluated from the mean field critical amplitude  $C_{MF}$  and the critical temperature  $T_C^{MF}$  using eq 12, while  $T_C^{MF}$  was determined from the linear extrapolation to  $S^{-1}(0) = 0$  as shown by the dashed line in Figure 3 (see eq 10). The deviation from mean field behavior is shown by the difference of the solid line from the dashed line near  $T_C$  which represents the corresponding mean field

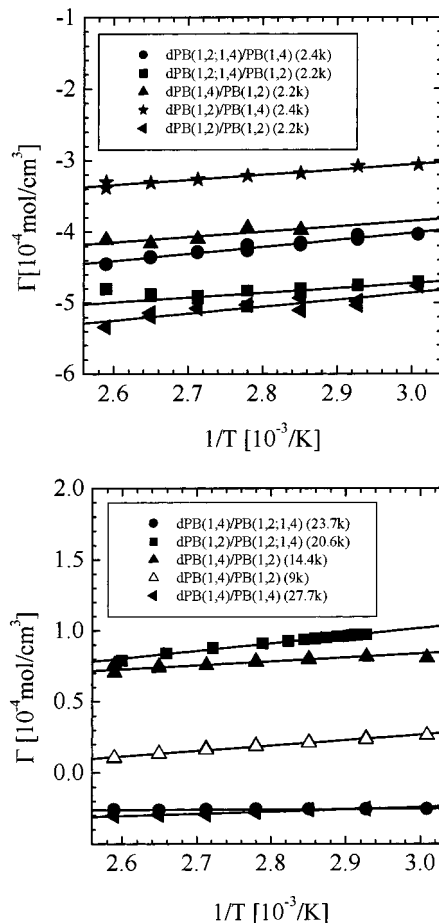
**Table 3. Parameters of Sample dPB(1,2)/PB(1,2;1,4) (20.6K) from Analysis of Crossover Function**

critical temperature $T_C$ (°C)	$69 \pm 0.1$
Ginzburg no. $Gi$	$(1.91 \pm 0.8) \times 10^{-3}$
mean field critical amplitude $C_{MF}$ (cm <sup>3</sup> /mol)	$(2.85 \pm 0.11) \times 10^3$
critical amplitude $C_+$ (cm <sup>3</sup> /mol)	$(1.23 \pm 0.11) \times 10^3$
enthalpic FH parameter $\Gamma_h$ (K mol/cm <sup>3</sup> )	$(6.03 \pm 0.23) \times 10^{-2}$
entropic FH parameter $\Gamma_o$ (mol/cm <sup>3</sup> )	$(0.781 \pm 0.03) \times 10^{-4}$

**Figure 3.** Crossover behavior between mean field and 3D Ising critical behavior of the inverse susceptibility  $S^{-1}(0)$  of the PB(1,2;1,4)/dPB(1,2) sample. Solid line represents the crossover function in eq 11.**Figure 4.** Ginzburg number from a collection of samples including those shown in Figure 3.

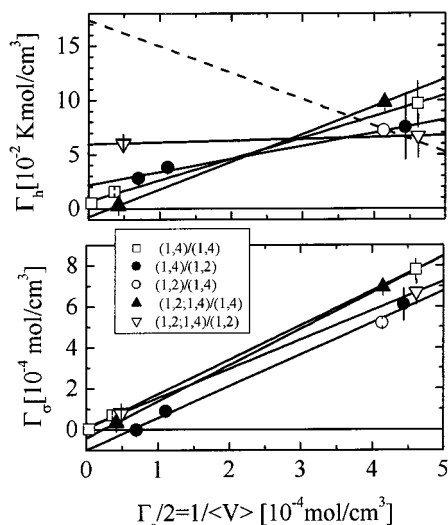
scaling law. The Ginzburg numbers obtained from this fit have been included into a collection of data from other blends as depicted in Figure 4. These Ginzburg parameters were collected by us recently.<sup>3,19</sup> The values for  $Gi$  lie within the range of other Ginzburg numbers as indicated by the two lines representing a  $N^{-1}$  and  $N^{-2}$  power law. A  $N^{-1}$  power law was predicted by deGennes for incompressible polymer blends.<sup>1</sup> The appreciably larger  $Gi$  are caused by the entropic FH parameter  $\Gamma_o$ .<sup>3,19</sup>

**B. Flory–Huggins Parameter and Chain-End Effects.** In Figure 5a,b the Flory–Huggins parameter  $\Gamma$ , determined from  $S^{-1}(0)$  and  $\Gamma_C$  according to eq 10, for all studied samples have been plotted versus inverse temperature, and the values of  $\Gamma_C$  are given in Table 2. Another procedure was necessary for analyzing the data for the dPB(1,2)/PB(1,2;1,4) blend with 20.6K molar volume, as this sample was measured very near  $T_C$ , so the data show the crossover to the 3D Ising critical

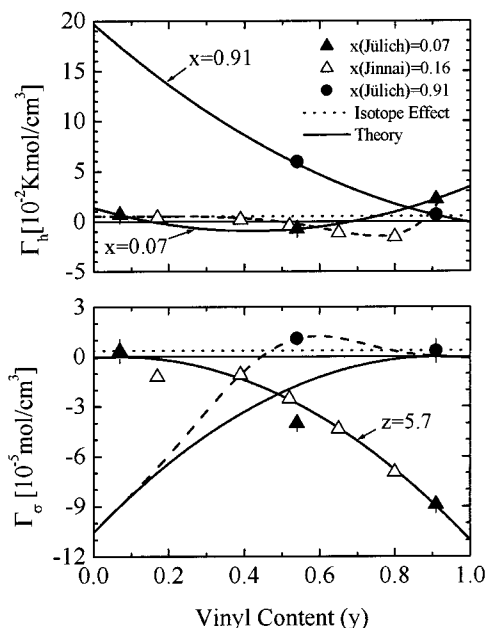
**Figure 5.** FH parameter versus inverse temperature from samples of dPB with (a, top) 2K and (b, bottom) 20K molar volume.

behavior. For this sample the crossover formalism in eqs 11 and 12 had to be applied. Fitting  $\Gamma = \Gamma_h/T - \Gamma_o$  to the experimental values shown by the solid straight lines in Figure 5 delivers the enthalpic ( $\Gamma_h$ ) and entropic parameters ( $\Gamma_o$ ) from the slope and the intercept at  $1/T = 0$ , respectively. In all cases a positive slope is observed indicating a positive  $\Gamma_h$ . The critical temperature is estimated by an extrapolation of  $\Gamma$  to  $\Gamma_C$  or correspondingly by the extrapolated  $S^{-1}(0)$  to 0. It has to be mentioned that below 60 °C an exceptionally long equilibration time is needed in newly prepared samples containing 2K molar volume chains; from unequilibrated measurements for those samples we determined an enthalpic  $\Gamma_h$  near its equilibrium value but we obtained a roughly 5 times too small entropic  $\Gamma_o$ . Then, at about 60 °C a sudden increase of  $\Gamma_o$  to its equilibrium value was observed. According to equation of states theories,  $\Gamma_o$  is related to compressibility effects or to the presence of excess free volume. The formation of the equilibrium free volume fraction seems to be hindered at lower temperature for these samples. After realizing these complications of equilibration, we first heated all samples to 120 °C before starting the SANS experiments.

In Figure 6 the enthalpic and entropic FH parameter terms are plotted versus the averaged inverse molar volume. We also included the FH parameter determined by Bates et al.<sup>15,25</sup> for a  $\langle V \rangle = 1.28 \times 10^5$  cm<sup>3</sup>/mol mixture, depicted as an open square, which is consistent with our results. The FH parameters show a strong



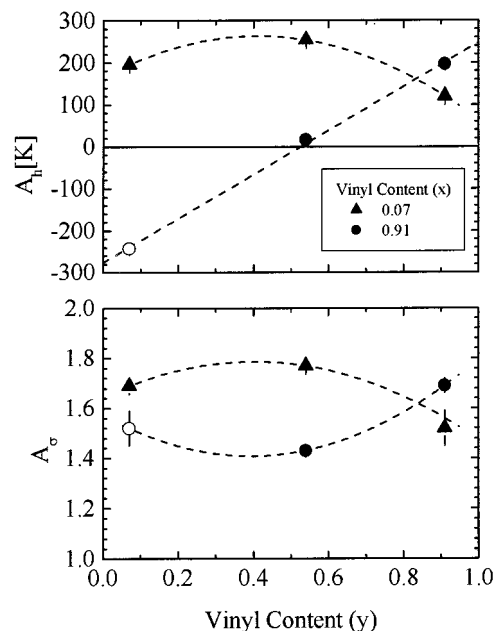
**Figure 6.** Enthalpic and entropic FH parameters versus molar volume.



**Figure 7.** Enthalpic and entropic terms of FH parameters for blends of dPB(1,4) and dPB(1,2) mixed with PB copolymers of different vinyl content. The FH parameters represent the extrapolated numbers for infinite molar volume according to eq 7. The dashed lines are guides for the eye while the solid ones represent a fit of theory.

dependence on molar volume, being to a good approximation proportional to  $1/V$  in accordance with eq 7. The dashed straight line represents the proposed theoretical behavior for the dPB(1,2)/PB(1,4) sample with a negative  $A_h$  as will be discussed later. The extrapolated FH parameters for infinite molar volume and the coefficients  $A$  are plotted in Figures 7 and 8, respectively.

Figure 7 represents all measured  $\Gamma_h$  and  $\Gamma_\sigma$  plotted versus the vinyl content  $y$  of the protonated PB component. The solid and open triangles represent blends with fixed vinyl content of  $x = 0.07$  and  $0.16$  of the deuterated PB as obtained by us and by Jinnai et al.,<sup>13</sup> respectively. Jinnai's values of  $\Gamma_\sigma$  were corrected by us for chain-end effects using the  $A_\sigma$  parameters in Figure 8. Both data sets are in excellent agreement, showing a negative entropic contribution for most of the samples. The blend



**Figure 8.** Coefficients  $A$  in the  $1/V$  dependence for the enthalpic and entropic FH parameters.

with  $x = 0.91$  (dPB(1,2)) and  $y = 0.54$  vinyl content show a relatively large enthalpic  $\Gamma_h$  as already realized from these data for  $S(Q)$ ; on the other hand, we find relatively small  $\Gamma_h$  for the blends with dPB(1,4) which for some vinyl content interval  $y$  of the protonated component even becomes negative. The theoretical approaches of eqs 2 and 6 are depicted by the solid lines. Thus, the theory will explain the physical reason of this quite dramatic behavior. The dashed line is a guide for the eye, while the dotted line shows the isotope effect.

The  $A$  coefficients, describing the dependence of  $\Gamma_h$  and  $\Gamma_\sigma$  on molar volume, changes with vinyl content as shown in Figure 8. A slight maximum is found for the mixture with dPB(1,4) and the copolymer. On the other hand, for the dPB(1,2)/PB(1,2;1,4) blend with  $x = 0.91$  and  $y = 0.5$  there seems no molar volume dependence of  $\Gamma_h$  and a smaller one for  $\Gamma_\sigma$ . This might have to do with the vinyl side groups working similarly as the polymer end groups. Both open dots in the figure show the proposed values for the dPB(1,2)/PB(1,4) sample to be discussed later.

Chain-end effects were already reported in the literature. In the isotopic poly(dimethylsiloxane) PDMS blends, a 2–3 times larger  $1/V$  effect than in the PB isotopic mixture was observed,<sup>16</sup> and in the PS/PEO blend this effect was clearly visible with  $A_h$  values roughly 5 times and  $A_\sigma$  2 times larger than our corresponding PB values.<sup>17</sup> A similar but an order of magnitude larger  $1/V$  effect is predicted if homopolymer mixtures and the corresponding diblock copolymers are compared; such a large effect has indeed been found in PS and PB diblock copolymers and homopolymers.<sup>26</sup>

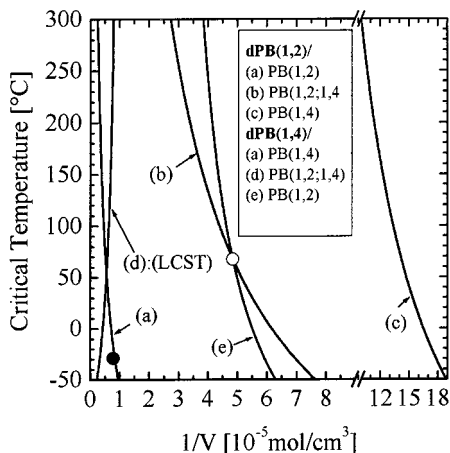
**C. Phase Diagram.** In Figure 9 the critical temperature of some PB mixtures with components of different vinyl content (see inset of Figure 9) have been plotted versus the inverse molar volume. The samples indicated with a, b, c, and e always show an upper critical solution (UCST) behavior. In these samples, a  $T_C$  of about 100 °C is predicted for molar volumes of, respectively, 230K, 21.6K, 7.5K, and 22.6K (in units of  $\text{cm}^3/\text{mol}$ ). These evaluations are consistent with the SANS data; so, for sample b ( $V = 20.6\text{K}$ ) a  $T_C = 67.7$  °C is estimated in



**Table 4. Enthalpic and Entropic FH Parameters in the Limit of  $V \rightarrow \infty$  and the Corresponding Coefficients  $A_o$** 

	$\Gamma_h$ ( $10^{-2}$ K mol/cm <sup>3</sup> )	$A_h$ (K)	$\Gamma_o$ ( $10^{-4}$ mol/cm <sup>3</sup> )	$A_o$
dPB(1,4)/PB(1,4); dPB(1,2)/PB(1,2)	$0.63 \pm 0.26$	$197 \pm 10$	$(3.46 \pm 7) \times 10^{-2}$	$1.69 \pm 0.03$
dPB(1,4)/PB(1,2;1,4)	$-(0.76 \pm 0.08)$	$254 \pm 4$	$-(0.4 \pm 0.02)$	$1.77 \pm 0.008$
dPB(1,2)/PB(1,2;1,4)	$5.97 \pm 0.06$	$16 \pm 2$	$0.11 \pm 0.02$	$1.43 \pm 0.01$
dPB(1,4)/PB(1,2)	$2.2 \pm 0.3$	$120 \pm 8$	$-(0.89 \pm 0.02)$	$1.52 \pm 0.07$

<sup>a</sup> One component is always deuterated the other one protonated.



**Figure 9.** Critical temperature as a function of inverse molar volume. Open and solid circles show critical temperatures determined by us (see Figures 2 and 3) and from Bates et al.,<sup>15</sup> respectively.

**Table 5. Parameters from Fit of Copolymer Theory from Freed and Dudowicz**

$z = 5.7$	$\epsilon_{CD} = 230.56$ K
$\epsilon_{CC} = 211.6$ K <sup>a</sup>	$\gamma = 0.988$
$\epsilon_{DD} = 250.18$ K	

<sup>a</sup> This number was taken from Frielinghaus et al. as a fixed parameter.<sup>27</sup>  $\epsilon_{CC}$ ,  $\epsilon_{DD}$ , and  $\epsilon_{CD}$  describe the interaction between the protonated 1,2–1,2, 1,4–1,4, and 1,2–1,4 pairs of monomers, respectively.

agreement with the experimental  $T_C = 69$  °C shown in Figure 3. While samples with dPB(1,2) always show an UCST phase behavior, a different and more complex situation is found for mixtures with the dPB(1,4) polymer: In sample d the enthalpic term becomes negative for chains of  $V > 33.4$  K molar volume and therefore phase separation at high temperatures (LCST system) is possible. Phase transition, however, can only occur for  $V > 94$  K chains in order to fulfill the necessary conditions of  $\Gamma_o < 0$  and  $|\Gamma_o| > \Gamma_C = 2/V$ ; only for this situation the total entropy is negative and can become active as a driving force for phase decomposition at high temperatures. For  $V < 33.4$  K the enthalpic term becomes positive and the sample switches over to an UCST system, however, with a very low  $T_C$  in the range of  $-200$  °C being much below the glass transition temperature.

**D. Flory–Huggins Parameter Interpreted by Theory of Copolymers.** The solid lines in Figure 7 represent the theoretical description of the enthalpic and entropic FH parameter terms  $\Gamma_h$  and  $\Gamma_o$  (from eqs 2 and 6). A very good agreement is achieved.

The enthalpic  $\Gamma_h$  is fully described by the set of van der Waals energy parameters  $\epsilon_{ij}$  and the polarizability factor  $\gamma$  in Table 5. As these fits are not unique, we have chosen  $\epsilon_{CC}$  as a fixed number and taken the value determined from PVT measurements for a pure dPB(1,2) melt with 91% vinyl content.<sup>27</sup> The obtained  $\gamma =$

0.988 is within expectations of between 0.98 and 0.99.<sup>15</sup>  $\Gamma_h$  very sensitively depends on  $\gamma$ ; so a 1% change of  $\gamma$  for the blend dPB(1,2)/PB(1,4) leads to a 40% change of  $\Gamma_h$  (eq 5). The determined  $\epsilon_{ij}$  values deviate from the combination rule  $\epsilon_{CD} = (\epsilon_{CC}\epsilon_{DD})^{1/2}$  for dispersive interactions by 0.2%.<sup>28</sup> In any case, the very different phase behavior of the samples with the deuterated PB components of  $x = 0.07$  and  $x = 0.91$  vinyl content is well described by the single set of parameters in Table 5.

For a better understanding of the presented results, we have to discuss the effects of deuteration: Neglecting the alteration of the interactions due to deuteration by setting  $\gamma = 1$ , one evaluates from eq 3 and the parameters in Table 5 a  $\Gamma_h = 0.131(x - y)^2$  [ $\Gamma_h$  is always given in units of K mol/cm<sup>3</sup>] which is positive and becomes zero in the case of  $x = y$  when the microstructure in both components is the same. A maximum number  $\Gamma_h = 0.13$  is evaluated in the case of  $|x - y| = 1$ , which represents the PB(1,4)/PB(1,2) blend. If one considers the effect of deuteration as described in eq 5, one gets for  $\Gamma_h$  the very different numbers of 0.044 and 0.228 for dPB(1,4)/PB(1,2) and dPB(1,2)/PB(1,4), respectively (see also Figure 7). So, deuteration leads to, respectively, a decrease or increase of  $\Gamma_h$  by roughly 70% depending on whether the PB(1,4) or PB(1,2) is perdeuterated. The smaller  $\Gamma_h$  of the dPB(1,4)/PB(1,2) is caused by the 18% larger interaction energy between the (1,4) monomer units ( $\epsilon_{DD}$ ) in comparison with those between the (1,2) units ( $\epsilon_{CC}$ ). So, a 1.2% change by deuteration leads to a huge change of the enthalpic FH parameter, and, furthermore, in some cases to a transition from an UCST to LCST phase behavior.

The expression for entropic  $\Gamma_o$  in eq 4 describes the data with the  $x = 0.07$  samples and the results by Jinnai et al.<sup>13</sup> very well assuming  $z = 5.7$  nearest neighbors. Because of obvious limitations inherent in any lattice model, the parameter  $z$  is allowed to vary freely to compensate for deficiencies of the model. The closeness of  $z = 5.7$  to the theoretical  $z = 6$  is, however, quite encouraging. According to theory there seems to occur no isotope effect. Deviations from theory were found for the dPB(1,2)/PB(1,2;1,4) blend showing a positive  $\Gamma_o$ .

## V. Summary and Conclusions

We presented here a SANS study on statistical copolymer mixtures of dPB(1,2; $x$ ;1,4(1- $x$ ))/PB(1,2; $y$ ;1,4(1- $y$ )) with different molar volumes and vinyl contents as a function of  $x$  and  $y$ . These blends represent the simplest model systems for statistical copolymer mixtures to explore inter- and intramolecular interactions and phase behavior with SANS. On the other hand, the simplicity of the blends lead to complications; because of the weak interactions between the (1,2) and (1,4) monomers, effects from chain ends and deuteration became relatively strong and led to a rather complex phase behavior. The principal result of this work is the demonstration of a consistent interpretation of our experimental data in Figure 7 with theoretical approaches obtained from LCT calculations by Dudowicz and Freed.<sup>9–12</sup>



In the following we give a more detailed discussion of our results:

(i) The investigated mixtures with 20K molar volume chains show a very different compatibility: The dPB-(1,2)/PB(1,4) polymers were not miscible at the experimentally accessible temperatures below 200 °C, and we estimate a  $T_C \approx 1200$  °C from the FH parameters in Figure 6. The dPB(1,4)/PB(1,2;1,4) blend shows very good compatibility with an extrapolated critical temperature at  $T_C = -235$  °C, while the dPB(1,2)/PB-(1,2;1,4) blend phase separates below 71 °C. For the latter sample a crossover from mean field to 3D Ising critical behavior was observed.

(ii) Strong chain-end effects on the FH parameter became visible by their dependence on molar volume in agreement with eq 7. Mostly, the change of  $\Gamma_\sigma$  and  $\Gamma_h$  with  $1/V$  is positive: it becomes nearly zero for the dPB-(1,2)/PB(1,2;1,4) blend, and a negative coefficient is predicted for the enthalpic  $\Gamma_h$  of the dPB(1,2)/PB(1,4) blend. The extrapolated entropic  $\Gamma_\sigma$  and enthalpic  $\Gamma_h$  parameters to  $1/V = 0$  have been plotted in Figure 7. A negative  $\Gamma_h$  is found for mixtures of the dPB(1,4) with PB of vinyl content between 10% and 70%, indicating phase separation at high temperatures (LCST).

(iii) The experimental FH parameters in Figure 7 could consistently be described by the theory summarized in eqs 2 and 6 as demonstrated by the solid lines in the figure. A fit of the experimental entropic  $\Gamma_\sigma$  with eq 6 gives  $z = 5.8$  nearest neighbors, which is slightly less than the theoretical  $z = 6$  value. The theory describes the data with the dPB(1,4) component well, while the blend with a dPB(1,2) component shows slight deviations. Some additional entropic contribution seems to be relevant for the dPB(1,2)/PB(1,2;1,4) sample, and this represents a common trend with the LCT, namely, the errors in  $\Gamma_\sigma$  are larger (in percentage) when  $\Gamma_\sigma$  is small. In contrast to the entropic term, the enthalpic  $\Gamma_h$  is much affected by deuteration. Because of the small  $\Gamma_h$  produced by the small van der Waals exchange energy  $\epsilon$ , small changes of the interaction energies  $\epsilon_{ij}$  upon deuteration induce large changes in  $\Gamma_h$  which for the dPB(1,4)/PB(1,2;1,4) blend could even lead to a transition from UCST to LCST behavior.

(iv) A comparison with other work on similar blends shows the following: Krishnamoorti et al.<sup>14</sup> determined the FH parameter of fully protonated PB statistical copolymer blends at room temperature from differential scanning calorimetry. Their results always show UCST behavior in agreement with predictions from eq 2 for  $\gamma = 1$ . They, however, found  $\Gamma/[x - y]^2$  dependent on the average copolymer composition (see their Figure 2) in contradiction with theory and with our findings. From our data we evaluate a  $\Gamma/[x - y]^2 = 5.6 \times 10^{-4}$  mol/cm<sup>3</sup> at room temperature (or in their units a value of 0.03) which is roughly twice as large as their numbers.  $\Gamma$  was calculated from  $\Gamma_h/[x - y]^2 = 0.13$  K mol/cm<sup>3</sup> and  $\Gamma_\sigma/[x - y]^2 = -1.27 \times 10^{-4}$  mol/cm<sup>3</sup>. One reason for the discrepancy might come from the neglect of chain-end effects. A dependence of  $\Gamma/[x - y]^2$  on average copolymer composition may be obtained from the sequence dependent portion of  $\Gamma_h$  in the more refined LCT of ref 11.

SANS experiments by Sakurai et al.<sup>29</sup> were performed on PB copolymers mixtures with components of  $x = 0.63$  (vinyl content of the perdeuterated chain) and  $y = 0.07$  and 0.68 (vinyl content of the protonated chains). The authors found UCST behavior, and for the  $x = 0.63/y =$

0.07 mixture they obtain  $\Gamma_h = 0.0125$  K mol/cm<sup>3</sup> (their eq 9b) which is nearly 8 times smaller than predicted from our data. In their analysis the authors erroneously assumed ( $\chi_2$  in their Table 5) the same  $\Gamma_h$  for PB(1,4)/PB(1,2) irrespective of deuteration.

The SANS data by Jinnai et al.<sup>13</sup> are in good agreement with our data as already mentioned in context with the data in Figure 7. In ref 13 a transition from upper critical (UCST) to lower critical solution temperature (LCST) behavior was predicted the first time, which in the present work could be explained as due to the effects of deuteration on the PB(1,4) component which has the larger van der Waals nearest neighbor energy (Table 5).

(v) The change of the FH parameter with vinyl content (Figure 7) and with molar volume (Figure 6) leads to a rather complex phase behavior as shown in Figure 7. Mixtures with dPB(1,2) chains always show UCST phase behavior while blends with a fixed dPB-(1,4) can reverse from UCST to LCST depending on the other component of the blend. The LCST phase behavior is characterized by negative  $\Gamma_\sigma$  and  $\Gamma_h$ . Phase separation can only occur in the case of  $|\Gamma_\sigma| > \Gamma_s$ , i.e., when the total entropy of mixing is negative and can act as a driving force at high temperatures. In addition, the absolute value of the critical temperature sensitively changes with molar volume and microstructure as shown in Figure 9.

(vi) What do we learn from the results presented here with respect to the failure of copolymer theories to explain the data for the 2K molar volume blends of dPB-(1,2; $x$ ;1,4(1- $x$ ))/PS with  $x = 0.07, 0.54$ , and 0.91 vinyl content which we observed in our earlier work?<sup>8</sup> It appears that the differences between the PS and PB monomers are too strong in order to properly include them into a theoretical description as the LC theory.<sup>12</sup> For a systematic comparison between experiment and theory, a series of studies on systems with increasing complexity seem desirable. This task appears rather difficult as the larger monomer complexity leads to larger interaction energies and therefore to a loss of possible application of a broader range of parameters as for instance the molar volume.

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