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Blends of Polybutadiene with Different Vinyl Contents and Polystyrene Studied with Small-Angle Neutron Scattering in Varying Temperature and Pressure Fields

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ABSTRACT: Blends of polybutadiene with three different vinyl contents and polystyrene were studied by small-angle neutron scattering as a function of temperature and pressure. The data were analyzed with a crossover function combining the universality classes of the 3D-Ising and the mean field behavior and thus yield the spinodal temperature T_S , the Ginzburg number Gi , and the critical amplitude C_{MF} . From these parameters the mean field Flory–Huggins interaction parameter is calculated in terms of entropic and enthalpic contributions. The application of the theory of random copolymers delivers large enthalpic and entropic contributions of the intramolecular interaction between the 1,2- and 1,4-butadiene units. These numbers could not be confirmed from measurements of the corresponding intermolecular interaction contributions in an h-PB(1,2)/d-PB(1,4) blend, which thus leads to speculations about the equivalence of inter- and intramolecular interactions in random copolymers. The Ginzburg number proved to be specific to the vinyl content and thus deviated from the universal behavior $Gi \propto V^{-1}$ predicted by deGennes. By our pressure experiments we find that the Clausius–Clapeyron equation suggests the phase boundary to be influenced by the Flory–Huggins parameter and the Ginzburg number.

I. Introduction

The exploration of the thermodynamic properties of binary polymer melts is of considerable interest in fundamental and applied research.^{1,2} On the fundamental side, the experimental technique of small-angle neutron scattering (SANS) plays a prominent role as it is a very sensitive and direct tool; the scattering contrast between the two polymers can be made very large by the use of fully hydrogenated and deuterated components so that the scattering of neutrons from thermal composition fluctuations become strong and the dominant contribution. By the method of contrast variation cooperative phenomena as well as single-polymer properties can be studied in a blend.^{3,4}

In this paper we present SANS scattering experiments on binary polymer blends to explore thermal composition fluctuation in different pressure and temperature fields. The basic samples are three binary polymer blends of nearly critical composition of polystyrene (PS) and three polybutadienes (PB) of different microstructure. The polybutadienes were fully deuterated (therefore d-PB) for reasons of strong scattering contrast. The d-PB polymers were synthesized by anionic polymerization from perdeuterated butadiene monomers. Three different solvent/cosolvent mixtures were used for the polymerization, leading to polymer chains with different ratios of 1,4 and 1,2 addition: d-PB(1,4) with 7%, d-PB(1,2;1,4) with 54%, and d-PB(1,2) with 91% 1,2 (vinyl) repeat units. The d-PB polymers are effectively considered as “statistical copolymers” of 1,4 and 1,2 repeat units. The molar volumes of the polymers were about 2000 cm³/mol. All samples show a phase boundary at temperatures between 60 and 90 °C and decompose into macroscopic large phases at low temperatures. The phase boundary is elevated by the vinyl

content of the PB chain, and accordingly different values for the Flory–Huggins (FH) interaction parameters are evaluated from the SANS experiments. Because the phase boundary and the FH parameter of the d-PB/PS blend changes with vinyl content, a finite FH parameter must exist between the 1,4 and 1,2 repeat units. The theoretical approach for a blend consisting of statistical copolymers predicts a relatively strong repulsive intramolecular interaction between the 1,4 and 1,2 repeat units. However, an additional SANS experiment on a d-PB(1,4)/h-PB(1,2) blend showed a much smaller FH parameter, in contradiction with the former experiments. The conclusion is that the existing theoretical description of statistical copolymers does not consistently describe our experimental results.

A further aspect of this work is related to the effect of thermal fluctuations on the thermodynamic properties as already discussed in earlier studies.⁵ The FH theory is based on a mean field approach, neglecting the effect of thermal composition fluctuations, and the FH parameter Γ therefore represents a mean field or bare interaction parameter. From SANS experiments one usually gets $\Gamma = \Gamma_h/T - \Gamma_\sigma$ with the corresponding phenomenological enthalpic and entropic terms Γ_h and Γ_σ , respectively. For symmetrical binary blends with polymer components of equal molar volume V the critical composition is $\Phi_C = 0.5$ and the FH parameter at the critical temperature T_C is according to $T_C = 2/V$ inversely proportional to the molar volume of the two components. However, the experiments are usually not performed in the range of mean field approximation. This is true for most binary polymer blends of upper critical solution type (UCST), whose molar volume has to be sufficiently small to show a moderate critical temperature. We therefore cannot directly analyze the experimental data with the FH model but need a more sophisticated model, which includes the effects of thermal fluctuations. We applied a crossover model derived by Belyakov et al.,^{6,7} which sufficiently describes well

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the scattering data, for example, the susceptibility, and derived the mean field parameters as the FH parameter from this model.⁵ This of course means that to get reliable fit parameters we have to study blends of very near critical composition, measure $S(Q)$ over a sufficiently large range of temperature, and in very fine steps near the critical temperature.

A final aspect of this work is related to the effects of high external pressure fields on thermal fluctuations. Relevant insight can be obtained from the pressure dependence of the phase boundaries, the Ginzburg number, and the FH interaction parameter. The d-PB/PS blends show a pressure-induced increase of the phase transition temperature and a decrease of the Ginzburg parameter and the FH parameter terms. The increase of the phase boundary with pressure is the normally expected case as it is usually related to a decrease of the free volume and the corresponding decrease of the entropic FH term Γ_σ .^{8–10} According to the Clausius–Clapeyron equation, the pressure-induced changes of the phase boundary are determined by those of the FH parameter *and* of the Ginzburg number.¹¹ For the d-PB(1,2)/PS sample we find that the pressure-induced change of the critical temperature is dominated by the corresponding change of the Ginzburg number. The Clausius–Clapeyron equation leads to a consistency check of the experimental results and their underlying theoretical basis. Part of this work has already been published in ref 11.

II. Theoretical Background

In this section we will give a short review about the theoretical background of our experiments. The main part is related to the structure factor representing the experimental SANS results and is a measure of the thermal composition fluctuations from which the thermodynamic parameters were evaluated. The second part is related to expressions of the FH parameter for blends containing a statistical copolymer, and finally, the Clausius–Clapeyron equation is introduced.

A. Structure Factor and Susceptibility of Binary Polymer Blends. The scattering experiments were performed in the homogeneously mixed state of the samples at different temperature and pressure fields to measure the degree of thermal composition fluctuations from which equilibrium thermodynamic information is obtained. Thermal composition fluctuations lead to scattering of neutrons, which is expressed by the structure factor $S(Q)$ as a function of momentum transfer Q . The value of Q is expressed by the scattering angle Θ and neutron wavelength λ according to $Q = (4\pi/\lambda) \sin \Theta/2$. At sufficiently small Q values the structure factor can be approximated by the Zimm approximation³ according to

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

The extrapolated $S(0)$ represents a susceptibility and L_2 is related to the correlation length ξ of the thermal fluctuations according to $L_2 = \xi^2/S(0)$. Within the random phase approximation,^{1,2} that is, within the mean field approximation, the radius of gyration R_g and the statistical segment length σ are obtained from L_2 according to the relations $L_2 = R_g^2/3S(0; \Gamma = 0) = 2R_g^2\Gamma_S/3 = R_g^2/[3\Phi(1 - \Phi)V]$ and $R_g^2 = \sigma^2 N/6$ (Γ_S is the FH parameter at spinodal; N is the degree of polymerization), respectively. The thermodynamic information

is derived from the susceptibility $S(0)$, representing a property averaged over a macroscopic volume due to the inverse relationship between the reciprocal momentum Q and real 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; Φ is the volume fraction of one component).^{12,13}

The degree of thermal composition fluctuations and thereby $S(Q)$ sensitively depends on temperature and pressure. At sufficiently high temperature above the critical temperature, the 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. That is, most of the critical exponents are the same.¹³ On the other hand, thermal fluctuations become very strong and interacting near the phase boundary and especially near the critical temperature, leading to nonlinear effects. These nonlinear effects become visible in scattering experiments by a crossover behavior of the susceptibility to the universality class of the three-dimensional (3D) Ising critical behavior, describing the fluctuations asymptotically close to the critical temperature.^{1,2} So asymptotically far and close to the critical temperature thermal composition fluctuations in polymer blends are described respectively within the universality classes of mean field and 3D-Ising model. Within these two models the susceptibility $S(0)$ is described by simple scaling laws according to $S(0) = C\tau^{-\gamma}$ with the reduced temperature $\tau = |T_C - T|/T$ (critical temperature T_C) and with the critical exponent γ being equal to 1 and 1.239 in the mean field and 3D-Ising case, respectively.¹³ To describe the susceptibility $S(0)$ over the whole temperature range above the critical temperature, one needs a crossover function. We applied the asymptotic crossover model by Belyakov and Kiselev^{6,7} according to

$$\hat{\tau} = (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{(\gamma-1)/\Delta} \times [\hat{S}^{-1}(0) + (1 + 2.333\hat{S}(0)^{\Delta/\gamma})^{-\gamma/\Delta}] \quad (2)$$

with the exponents $\gamma = 1.234$ and $\Delta = 0.5$ of the 3D-Ising model; the rescaled reduced temperature $\hat{\tau} = \tau/Gi$ ($\tau = |T_C - T|/T$) is formulated as a function of the rescaled susceptibility $\hat{S}(0) = S(0)Gi/C_{MF}$. The parameters Gi , C_{MF} , and T_C are the experimental results characterizing the system; Gi and C_{MF} are the Ginzburg number and the mean field critical amplitude of $S(0)$, respectively. In the asymptotic limits $\tau \gg 1$ and $\tau \ll 1$ the susceptibility in eq 1 follows the well-known scaling laws $S(0) = C_{MF}\tau^{-1}$ of the mean field approximation and $S(0) = C_+\tau^{-\gamma}$ of the 3D-Ising model, respectively. This crossover function was already applied by us to other blend samples in earlier SANS work.^{5,11}

The crossover between the two universality classes of mean field and 3D-Ising behavior is estimated by the Ginzburg criterion, delivering the Ginzburg number Gi , which is a reduced crossover temperature and is related to the ratio of the critical amplitudes of the 3D-Ising and mean-field case according to^{5,7}

$$Gi = 0.069(C_+/C_{MF})^{1/(\gamma-1)} \quad (3)$$

with the 3D-Ising exponent γ . Within the FH model the susceptibility is given as $S(0)/V = [2(\Gamma_C V - \Gamma V)]^{-1}$ with

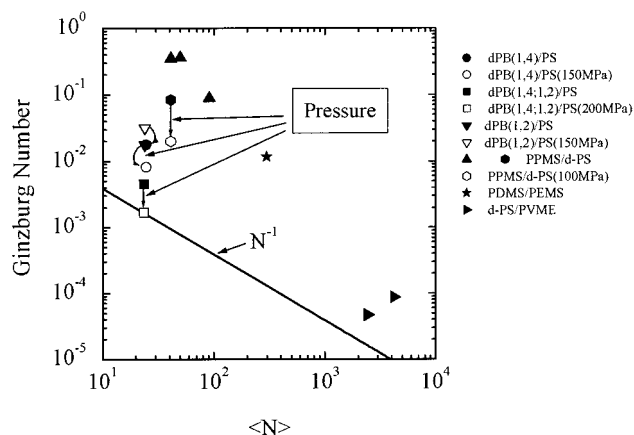


Figure 1. Ginzburg number Gi versus mean degree of polymerization for a collection of polymer blends. The values of Gi of the present blends at ambient- and high-pressure fields are shown (see legend at the figure).

the FH parameters Γ and Γ_C , representing Γ at the critical temperature T_C . So the mean field critical amplitude is related to the FH parameters according to

$$C_{MF} = 1/2[\Gamma_S + \Gamma_\sigma] = T_C^{MF}/2\Gamma_h \quad (4)$$

with the corresponding enthalpic and entropic terms of Γ . The expressions of the critical amplitudes of the mean field case in eq 4 and of the 3D-Ising case according to $C_+ \propto V^{(2-\gamma)}$ as derived by Binder¹⁴ leads to

$$Gi \propto [V^{(2-\gamma)}(2/V + \Gamma_\sigma)]^{1/(\gamma-1)} \quad (5)$$

and which in the case of $\Gamma_\sigma = 0$ becomes a universal scaling law according to $Gi \propto 1/V$. The last relationship was originally derived by deGennes for incompressible polymer blends.¹ So according to its dependence on molar volume, a very small Gi is expected in polymer blends if compared with a typical Gi in low molecular liquids, which is of the order of 10^{-2} .⁷ On the other hand, it becomes apparent from the large exponent $1/(\gamma - 1) \cong 4.17$ in eq 5 that the entropic term Γ_σ strongly enhances Gi . Such a behavior of Gi was indeed experimentally found demonstrated in Figure 1, showing a collection of Gi numbers from different polymer blends as determined by us over the recent years. All Gi values are appreciably larger (in some cases by 2 orders of magnitude and even larger than those for low molecular liquids) compared with the solid $1/N$ line for incompressible melts. These findings clearly indicate that the entropic term Γ_σ (according to equation of states theories Γ_σ is related to the compressibility²) leads to a strong increase of thermal composition fluctuations near the critical temperature. These large Gi numbers imply a need for a more sophisticated analysis of the scattering data, considering the effect of thermal fluctuations as has been done in the crossover function of eq 2. The FH parameter will therefore be evaluated from the mean field critical amplitude C_{MF} of $S(0)$ in eq 4 and from the "mean field" critical temperature T_C^{MF} , which is related to the "real" critical temperature T_C according to $T_C^{MF} = T_C/(1 - Gi)$.⁷ T_C is smaller than T_C^{MF} by some degree Kelvin because of the stabilization effect of thermal fluctuations. In comparison with the mean field analysis the crossover function typically gives about 100% and 50% larger entropic and enthalpic portions of the Flory–

Huggins parameter, respectively, for a $S(0)$ with a Ginzburg number of the order of 10^{-2} .

B. Clausius–Clapeyron Equation within the Flory–Huggins Model for Polymer Blends. The Clausius–Clapeyron equation describes the line of coexistence between two phases in the T – P plane of the phase diagram according to

$$\Delta T_C/\Delta P = T_C V_m/H_m \quad (6)$$

For example, the change of the phase transition (critical) temperature T_C with pressure is related to the differences of volume V_m and enthalpy H_m between the two phases.¹² For further analysis the Gibbs free energy of mixing is needed

$$G_m(T, P, \Phi) = G_{12} - \Phi G_1 + (1 - \Phi) G_2 = H_m - TS_m \quad (7)$$

with the symbols Φ representing the volume fraction of the component "1", G_1 and G_2 the Gibbs potentials of the two components, and $G_{1,2}$ that of the mixture. Within mean field theory the Flory–Huggins (FH) model describes polymer blends; the enthalpy and entropy of mixing are given as

$$H_m/RT = \Phi(1 - \Phi)\chi_h/T \quad (8)$$

and

$$S_m/R = -\{(\Phi/V_1) \ln \Phi + [(1 - \Phi)/V_2] \ln(1 - \Phi)\} + \Phi(1 - \Phi)\chi_\sigma \quad (9)$$

with the molar volumes V_1 and V_2 of the two molecular species.^{1,2} The first term of ΔS_m is the configurational part while the second one contains all the other entropic contributions as from polymer end effects and compressibility.² The entropic term χ_σ is a phenomenological parameter that had to be included to describe the (mainly scattering) experiments. Usually, the enthalpic and entropic terms χ_h and χ_σ are comprised within the FH interaction parameter according to $\chi = \chi_h/T - \chi_\sigma$.

The Gibbs free energy of mixing $G_m(T, P, \Phi)$ contains all thermodynamic information. It was already mentioned that the susceptibility $S(0)$ measured in SANS experiments is related to the second derivative of $G_m(T, P, \Phi)$ with respect to composition. This also means that in scattering experiments one measures an effective FH parameter Γ defined as $\partial^2[\phi(1 - \phi)\chi]/\partial \phi^2$. The effective FH parameter Γ is given in units (mol/cm³). The product of (ΓV) has the same meaning as (χN) , sometimes given in corresponding SANS and theoretical papers. From now on we will denote Γ as the FH parameter. In the case of a symmetrical blend with $V = V_1 = V_2$ the critical composition is equal to $\Phi_C = 0.5$ with $\Gamma_C = 2/V$, which is the FH parameter at T_C .

The Clausius–Clapeyron equation for polymer blends can now be written as¹¹

$$\partial T_C/\partial P = T_C(1)[\partial \Gamma_h/\partial P - T_C(1)\partial \Gamma_\sigma/\partial P]/\Gamma_h(1) - [T_C(1)/(1 - Gi(1))]\partial Gi/\partial P \quad (10)$$

The first term has been derived from eqs 7–9 and $V_m = \partial G_m/\partial P$. The second term describes the stabilization effect of thermal fluctuations described by the Ginzburg number Gi and the relationship between the critical temperature T_C and its mean field value T_C^{MF} according

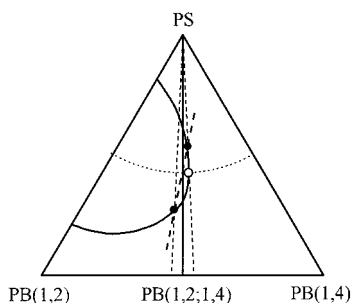


Figure 3. Schematic plot of a three-component blend to make plausible the observed characteristic features of binodal and spinodal of the d-PB(1,2;1,4)/PS blend in Figure 2. In this blend the critical point is not found at the largest temperature of the phase boundary in contrast to the other two and which can be explained from polydispersity of the FH parameter.

composition of the phase-separated domains may be given by the full dots in Figure 3; this means that the d-PB component in the two domains will have different vinyl distributions. In case of such a fractionation the d-PB/PS blend can only be considered as a “quasi” binary system.

III. Experimental Section

The scattering experiments were performed with the SANS diffractometer KWS1 at the FRJ2 reactor of the “Forschungszentrum Jülich”.²⁰ For these studies a steel-bodied temperature–pressure cell was used, which allows an in situ change of pressure and temperature in the range of $0.1 \leq P(\text{MPa}) \leq 200$ and $-20 \leq T(^{\circ}\text{C}) \leq 200$, respectively, 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. After each change of the temperature we waited for half an hour before proceeding with the neutron measurements to safely achieve a stationary temperature field in the relatively large volume of the pressure cell. The temperature of the sample could be rather accurately determined from the thermocouple and the always-existing temperature gradient between the sample and the 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 $1/\text{cm}$ 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 $\Sigma c_i b_i / \Omega_i$ (numerical values are given in Table 1) and the Avogadro number N_A . The scattering experiments were performed in the momentum transfer range of $0.01 \leq Q(\text{\AA}^{-1}) \leq 0.1$ using the settings of 7- \AA neutron wavelength and the detector-to-sample distances of 4 and 8 m with the corresponding collimations distances.

The polymers were synthesized by anionic polymerization using high vacuum and break seal technique. *sec*-Butyllithium was used as the initiator for all polymerizations. The purification of solvents and monomers was performed according to the standards required for anionic polymerization.²¹ Protonated polystyrene (PS) and deuterated polybutadiene (d-PB) with a 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) was the cosolvent for polymers with high vinyl content (h-, d-PB-(1,2)) while diethyl ether was used for the polybutadiene with almost equal distribution of 1,4 and 1,2 units in the chain (d-PB(1,2;1,4)).

The polydispersity, M_w/M_n , of the polymers was determined by size exclusion chromatography using a Waters 150C instrument. This instrument was equipped with four μ -Styragel

Table 2. Critical Point of Polymer Blends with PS#2 Component According to the Results in Figure 2

sample	d-PB(1,4)/PS	d-PB(1,2;1,4)/PS	d-PB(1,2)/PS	d-PB(1,4)/PB(1,2)
$\Phi_c(\text{PB})$	0.43	0.477	0.484	0.5
$T_c(^{\circ}\text{C})$	64	72.2	88	≈ -120

columns with a porosity range of 10^5 –500 \AA 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 (Tosoh Corporation) were used for calibration. In all cases M_w/M_n values were smaller than 1.1. The number-averaged molecular weight of the polymers, M_n , was measured with a Knauer vapor pressure osmometer at 45 $^{\circ}\text{C}$ 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 ΔV is the change of the thermistors in voltage and c is the concentration.²² The calibration constants K and α 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}C NMR spectroscopy with a Bruker 300-MHz spectrometer. For the h-PB(1,2) polymer the composition was additionally determined by ^1H NMR. The characteristic parameters of the polymers are summarized in Table 1.

The polymer blends were prepared by dissolving in and freeze-drying from benzene. The thermal stability of the samples was improved by the addition of 0.1% 2,6 di-*tert*-butyl-4-methylphenol and by filling them in an argon box into a leak-proofed sample holder. In this way the blends were protected from degradation and cross-linking at the experimental temperatures.

To measure precisely the effect of thermal fluctuations and their pressure dependence, we had to prepare samples very near the critical composition. In a first step we therefore determined the binodal and spinodal phase boundaries of the samples at different compositions by SANS measurements. The so-obtained phase diagram of the three samples is plotted in Figure 2 and the corresponding critical composition and temperature are given in Table 2. For these samples a PS component (PS#2) of $V_w = 1700 \text{ cm}^3/\text{mol}$ molar volume was used, which is slightly smaller than the PS component (PS#1) $V_w = 1800 \text{ cm}^3/\text{mol}$ mainly used later in the pressure experiments (Table 1) and is the reason of slightly smaller phase boundary temperatures. The critical temperatures given in Figure 2 are different by 22 K and are increasing with the vinyl content of the d-PB polymer. The chosen composition of the three samples for the pressure experiments are given in Table 3. The composition for the samples used in pressure experiments were chosen to be the critical ones within the accuracy of determination. For the d-PB(1,2;1,4)/PS blend the first phase boundary experiments gave misleadingly a critical composition of 0.505, which had to be corrected afterward.

IV. Experimental Results

In this section we first present the SANS data and then will give an interpretation in terms of the crossover function, the theory for statistical copolymers, and the Clausius–Clapeyron equation.

A. SANS Data. Structure factors $S(Q)$ have been plotted in Zimm representation in Figure 4, namely, the inverse $S(Q)$ versus the momentum transfer Q^2 . The experimental data follow in all cases a straight line in accordance with the Zimm approximation (eq 1). From the fit of the straight line the susceptibility $S(0)$ and from the slope the coefficient L_2 is evaluated. In Figure 4a the temperature was changed in a constant pressure field while in Figure 4b the pressure was changed at constant temperature. Decreasing the temperature leads to a strong enhancement of $S(Q)$ as one approaches the critical temperature and thereby to stronger thermal fluctuations. A similar increase of $S(Q)$ is observed at constant temperature by increasing the

Table 3. Experimental Results of the Blends from Pressure Experiments^a

sample	d-PB(1,4)/PS#2		d-PB(1,2;1,4)/PS#1	
	$X(P=0.1 \text{ MPa})$	$\partial X/\partial P$ (*MPa)	$X(P=0.1 \text{ MPa})$	$\partial X/\partial P$ (*MPa)
$\Phi(\text{d-PB})$	0.42		0.505	
\bar{N}_W	24.8		23.4	
Γ_S (10^{-3} mol/cm^3)	1.05		1.06	
T_B (°C)	65.2 ± 0.1	$(7.6 \pm 0.1) \times 10^{-2}$	85.5 ± 0.2	$(6.64 \pm 0.1) \times 10^{-2}$
$T_{S,C}$ (°C)	63.4 ± 0.1	$(7.7 \pm 0.1) \times 10^{-2}$	82.6 ± 0.1	$(6.6 \pm 0.1) \times 10^{-2}$
Ginzburg number	$(1.8 \pm 0.2) \times 10^{-2}$	$-(6.4 \pm 1) \times 10^{-5}$	$(0.45 \pm 0.15) \times 10^{-2}$	$-(2.3 \pm 1.1) \times 10^{-5}$
C_{MF} (cm^3/mol)	152 ± 1.1	$(1.65 \pm 0.04) \times 10^{-1}$	181 ± 3	$(4.2 \pm 0.2) \times 10^{-1}$
C_+ (cm^3/mol)	111 ± 1.3	$-(2.7 \pm 0.1) \times 10^{-2}$	92 ± 3	$(4.5 \pm 0.3) \times 10^{-2}$
Γ_h (mol K/cm^3)	1.12 ± 0.02	$-(8.9 \pm 0.2) \times 10^{-4}$	0.99 ± 0.02	$-(1.6 \pm 0.08) \times 10^{-3}$
Γ_σ (10^{-3} mol/cm^3)	2.24 ± 0.05	$-(3.1 \pm 0.2) \times 10^{-3}$	1.7 ± 0.05	$-(4.8 \pm 0.3) \times 10^{-3}$

sample	d-PB(1,2)/PS#1	
	$X(P=0.1 \text{ MPa})$	$\partial X/\partial P$ (*MPa)
$\Phi(\text{d-PB})$	0.5	
\bar{N}_W	23.9	
Γ_S (10^{-3} mol/cm^3)	1.03	
T_B (°C)	101 ± 0.6	$(2.5 \pm 0.1) \times 10^{-2}$
$T_{S,C}$ (°C)	101 ± 0.5	$(2.6 \pm 0.1) \times 10^{-2}$
Ginzburg number	$(3.2 \pm 0.3) \times 10^{-2}$	$-(0.94 \pm 0.1) \times 10^{-4}$
C_{MF} (cm^3/mol)	134 ± 2	$(1.6 \pm 0.04) \times 10^{-1}$
C_+ (cm^3/mol)	112 ± 4	$(1.7 \pm 0.09) \times 10^{-2}$
Γ_h (mol K/cm^3)	1.44 ± 0.03	$-(1.5 \pm 0.05) \times 10^{-3}$
Γ_σ (10^{-3} mol/cm^3)	2.7 ± 0.05	$-(3.7 \pm 0.1) \times 10^{-3}$

^a The given error bars in all Tables were obtained from the statistical methods of the fitting routines including the statistical errors of neutron data.

pressure field from 0.1 to 150 MPa; the phase boundaries were enhanced by pressure. In Figure 4c $S(Q)$ of a PB mixture is shown with components of the d-PB(1,4) and h-PB(1,2) microstructure (see Table 1). The scattering of this mixture is appreciably weaker with a slightly enhanced scattering at 10 °C with respect to 153 °C. The phase boundary of the latter sample is expected at around -210 °C, as estimated from extrapolation of the corresponding susceptibilities in Figure 13.

In Figure 5a–c the inverse susceptibility of all investigated d-PB/PS samples and all pressure fields are plotted versus inverse temperature. These measured $S(0)$ values were fitted by the crossover function (eq 2) depicted as solid lines. The agreement of the fitted lines with the corresponding experimental $S(0)$ is very good. From these fits the spinodal or critical temperature at $S^{-1}(0) = 0$, the critical mean field amplitude C_{MF} and the Ginzburg number Gi were obtained and are summarized in Table 3. In Figure 6 the inverse susceptibility of the two blends d-PB(1,4;1,2)/PS and d-PB(1,4)/PS have been plotted; their measurements were repeated at 0.1 MPa in our standard heater instead of the pressure cell for reasons that will become clear below. The corresponding fit parameters are given in Table 4.

B. Analysis of the SANS Data. In Figure 7 the spinodal (critical) and binodal temperatures of the three samples have been depicted versus pressure. The spinodal temperature is obtained from the extrapolated $S^{-1}(0) = 0$ and the binodal is determined from a sudden decrease of $S(0)$, which occurs after passing the binodal line; below the binodal one measures thermal fluctuations within the precipitated domains, which strongly decrease with decreasing temperature. The corresponding $S^{-1}(0)$ have not been plotted in Figure 5 but similar observations have been discussed in ref 23. In all samples an increase of the phase boundaries with pressure is observed. The shape of the phase boundary is linear for the blends with the d-PB(1,4) and d-PB(1,4;1,2) copolymer and it is more parabolic for the blend with the d-PB(1,2). The critical composition was very

well found for the d-PB(1,2) sample while the other two samples are slightly off the critical composition as seen from the distances of the spinodal and binodal temperatures. The worst compatibility is observed for the d-PB(1,2)/PS sample, the best one for the d-PB(1,4)/PS, and for the copolymer sample in between.

The Ginzburg numbers are depicted in Figure 8 versus pressure. The fitted lines are a guide for the eye. Appreciable differences are observed; the largest Gi is found for the d-PB(1,2) blend while the lowest one for the copolymer blend and an intermediate Gi for the d-PB(1,4) blend. In all cases Gi decreases with increasing pressure; for the d-PB(1,4) blend one observes a linear decrease, for the d-PB(1,2) a constant Gi up to 100 MPa and then a rather strong decrease, and for the copolymer blend a decrease at low pressure and a constant Gi at larger pressure, suggesting a saturated value of $Gi = (1.7 \pm 0.5) \times 10^{-3}$. This value seems to be very near the Gi estimated originally for incompressible polymer blends (see Figure 1).

In Figure 9 the critical amplitudes of the susceptibility have been plotted versus pressure. The mean field critical amplitude C_{MF} is a fit parameter of the crossover function. The critical amplitude C_+ of the 3D-Ising model has been evaluated from Gi and C_{MF} (eq 3). Within an accuracy of 3% and 30% the C_+ critical amplitude is independent of pressure and of microstructural effects, respectively. The C_{MF} critical amplitudes increase with pressure and the largest value is observed for the copolymer blend.

From the mean field critical amplitude C_{MF} the FH parameter was evaluated. According to eq 4, the entropic term Γ_σ is directly obtained from C_{MF} and Γ_C while the calculation of the enthalpic term Γ_h needs the mean field critical temperature according to $T_C^{MF} = T_C/(1 - Gi)$. The enthalpic and entropic terms of the FH parameter are plotted in Figure 10 versus pressure. In all cases slightly declining values are observed with pressure. The terms of the FH parameter are largest for the d-PB(1,2) and smallest for the copolymer. While

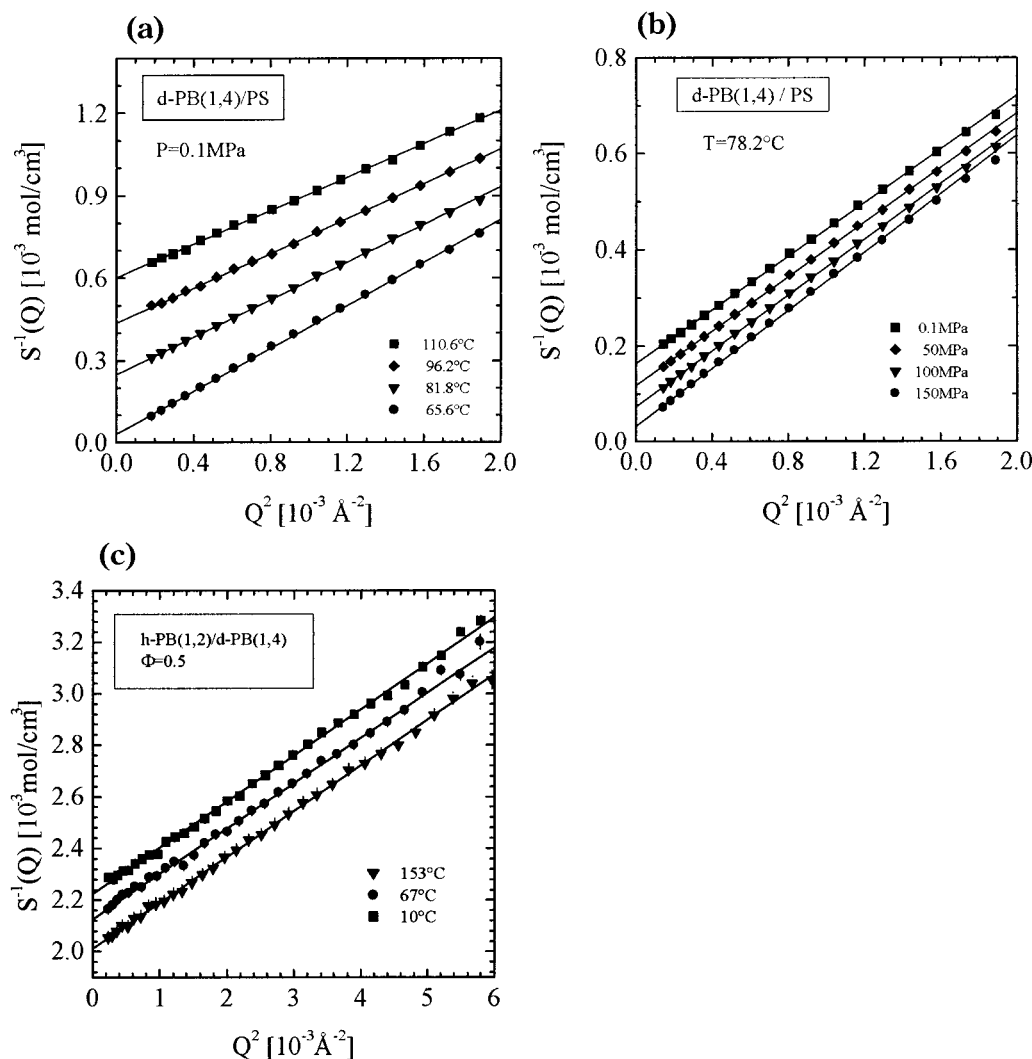


Figure 4. Structure factor in Zimm representation for the d-PB(1,4)/PS blend at constant pressure (a) and temperature (b) and for varying temperature and pressure fields, respectively. The third plot (c) shows the structure factor of the h-PB(1,2)/d-PB(1,4) blend; its temperature dependence comes mainly from a finite FH parameter between the PB(1,2) and PB(1,4) units.

the pressure dependence is linear for the d-PB(1,4) blends, it is different for the other two samples; at ambient pressure the d-PB(1,2) blend shows nearly no change of the FH parameter while in this pressure range it is rather strong for the copolymer blend becoming constant above 100 MPa.

C. Interpretation in Terms of the Theory of Copolymers. The enthalpic and entropic terms of the FH parameter in Figure 10 have been plotted in Figure 11 versus the vinyl content and fitted with the theoretical ansatz of statistical copolymers (eq 11). These fits are shown by the solid lines. In Figure 12 both corresponding terms of the FH parameter of the 1,4 and 1,2 butadiene repeat units with PS and with each other are depicted versus pressure. Equation 11 was originally derived for the enthalpic term; we applied the same ansatz also for the entropic term. The relatively small terms of the FH parameter obtained for the copolymer sample (see Figure 11) are interpreted by relatively strong terms of the intramolecular FH parameter between the 1,4 and 1,2 units. As shown in Figure 12, these values are even larger than the corresponding intermolecular interaction terms between the d-PB and PS units. This result is a rather surprising finding. It is known from literature that a finite intramolecular interaction leads to an improved compatibility of the

blends. Such an improved compatibility between PS and the d-PB(1,2;1,4) polymers, however, was not observed, as seen from the phase diagrams in Figures 2 and 7; the phase boundaries of the copolymer blend is between the two other ones. The phase boundaries are of course consistent with the evaluated FH parameter; according to eq 4 the mean field spinodal temperature is needed for the evaluation of the enthalpic term of the FH parameter.

In a subsequent SANS experiment the FH parameter between the 1,2 and 1,4 repeat units was determined directly from the h-PB(1,2)/d-PB(1,4) mixture whose parameters are given in Tables 1 and 2. The corresponding inverse susceptibility has been plotted versus the inverse temperature in Figure 13. The L_2 values not shown here are constant within the error bars and deliver a mean statistical segment length of $\sigma = 6.9 \text{ \AA}$ from the random phase approximation according to $L_2 = 2R_g^2\Gamma_C/3$, $R_g^2 = \sigma^2 V/(6\Omega)$, and $\Gamma_C = 2/V$. The corresponding FH parameter has been evaluated from the susceptibility according to the mean field approximation $S(0)/V = [2(\Gamma_C V - \Gamma V)]^{-1}$ and plotted in Figure 13. The observed enthalpic and entropic terms of the FH parameter are of the order of magnitude smaller than the values in Figure 12 predicted by the copolymer theory. The accuracy of the entropic term is mainly determined

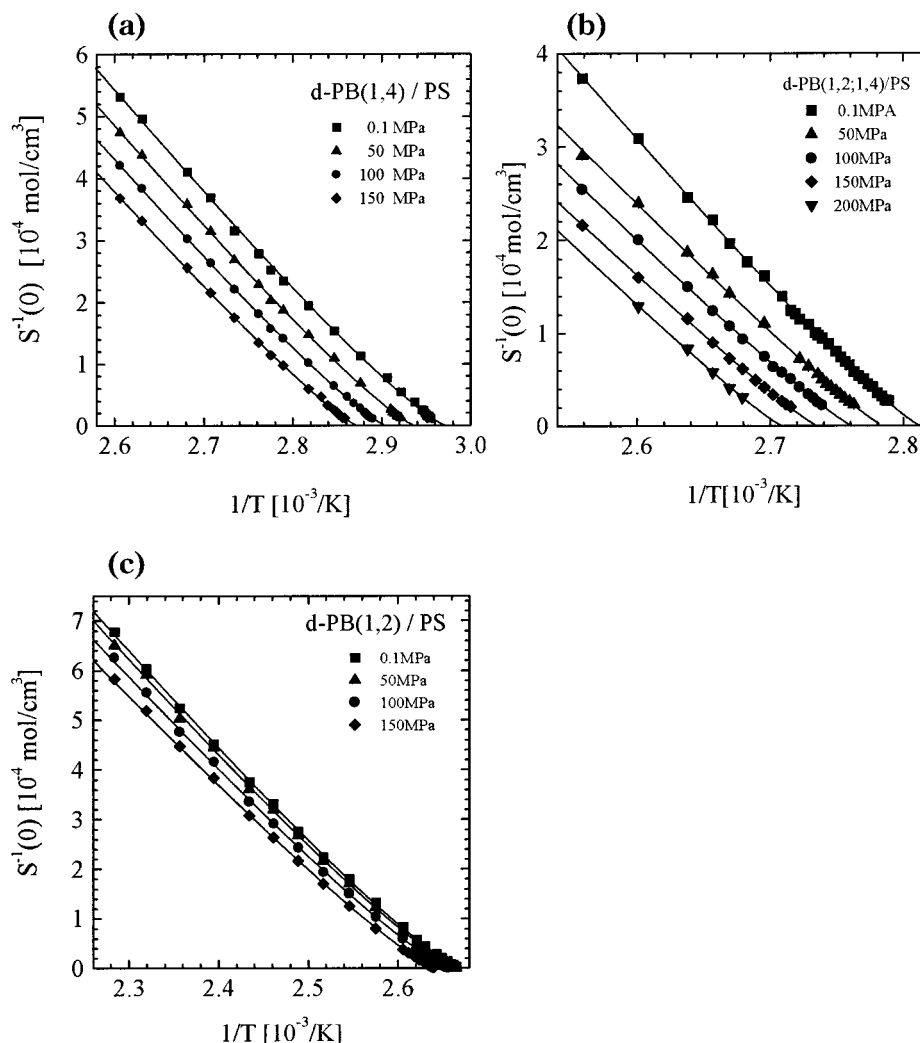


Figure 5. Inverse susceptibility versus inverse temperature for the three investigated d-PB/PS blends for the pressure fields studied. The solid lines represent the fit with the crossover function formulated in eq 2. Parameters are given in Table 3.

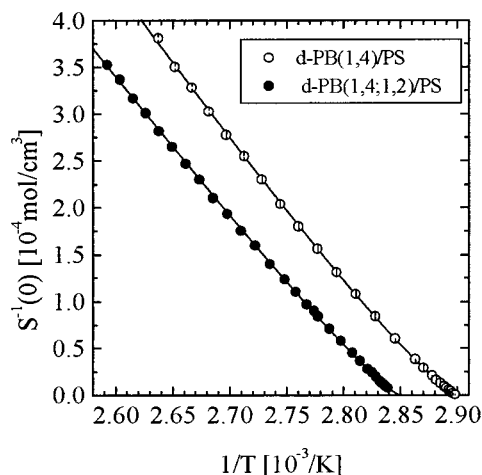


Figure 6. Inverse susceptibility versus inverse temperature of two blends with (1,4) and the statistical copolymer (1,4;1,2) d-PB component measured at ambient pressure with our standard heater. Parameters are given in Table 4.

by Γ_C , which can be determined roughly within $\pm 5\%$ according to the accuracy of the molar volume. As Γ_σ in Table 5 is about half as large as Γ_C , its value is reliable within $\pm 10\%$.

In Figure 14 the FH parameter of the blends of d-PB (1,4), d-PB(1,2;1,4), and d-PB(1,2) components mixed

Table 4. Results of Two d-PB/PS Blends with PS#1 as the Component Measured with the Heater

sample	d-PB(1,4)/PS	d-PB(1,4;1,2)/PS
$\Phi(\text{d-PB})$	0.42	0.505
N_W	25.6	23.4
$\Gamma_C (10^{-3} \text{ mol/cm}^3)$	1.02	1.06
$T_C (^\circ\text{C})$	71.8 ± 0.1	78.1 ± 0.1
Ginzburg number (10^{-2})	1.56 ± 0.25	0.46 ± 0.06
$C_{MF} (\text{cm}^3/\text{mol})$	156 ± 3.7	193 ± 3
$C_+ (\text{cm}^3/\text{mol})$	110 ± 2	101 ± 2
$\Gamma_h (\text{mol K/cm}^3)$	1.12 ± 0.03	0.91 ± 0.02
$\Gamma_\sigma (10^{-3} \text{ mol/cm}^3)$	2.19 ± 0.08	1.53 ± 0.04

with PS have been plotted versus $1/T$. Their phase transition temperatures were determined by the intercepts with Γ_C as plotted. In addition, Γ of the h-PB(1,2)/d-PB(1,4) from Figure 13 has been plotted. We find a strong discrepancy of the enthalpic and entropic terms of the FH parameter between the 1,4 and 1,2 units of the PB components, depending on whether they were determined directly from intermolecular interactions of the d-PB(1,4)/PB(1,2) blend or from intramolecular interactions of the d-PB(1,2;1,4) statistical copolymer mixed with the PS polymer, applying the theoretical approach in eq 11.

The experiments with our pressure were partly reconsidered with our standard heating system on the d-PB(1,4)/PS and the copolymer d-PB(1,4;1,2)/PS blends

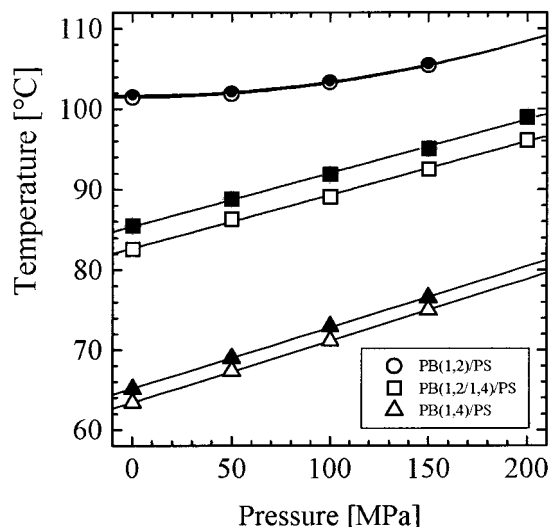


Figure 7. Spinodal and binodal versus pressure of the three blends.

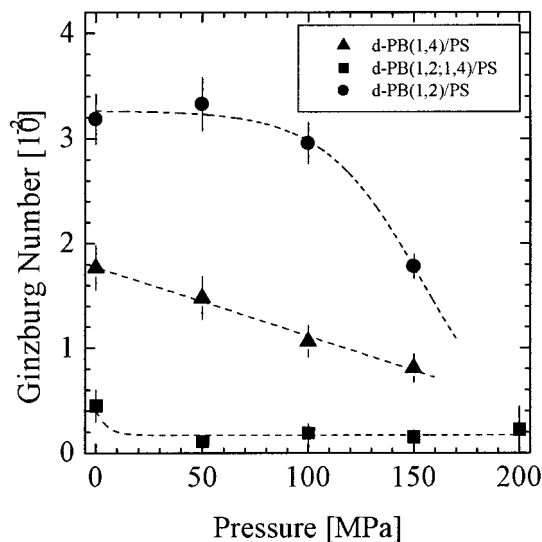


Figure 8. Ginzburg number G_i versus pressure of the three blends.

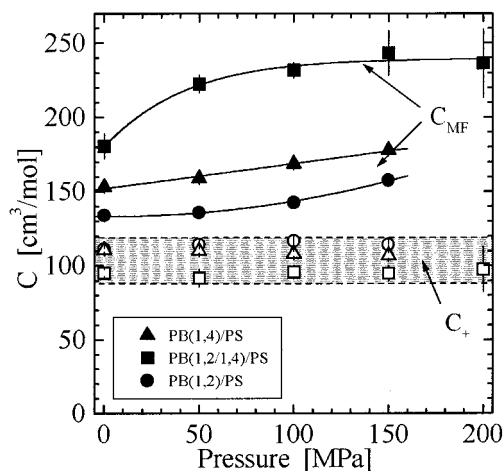


Figure 9. Critical amplitudes of mean field (C_{MF}) and 3D-Ising (C_+) susceptibility versus pressure. C_+ is constant within 3% versus pressure and 30% versus the vinyl content.

to cross-check the experimental procedure. In Figure 6 the susceptibility and the fitted crossover functions (eq 2) have been plotted versus temperature. The evaluated

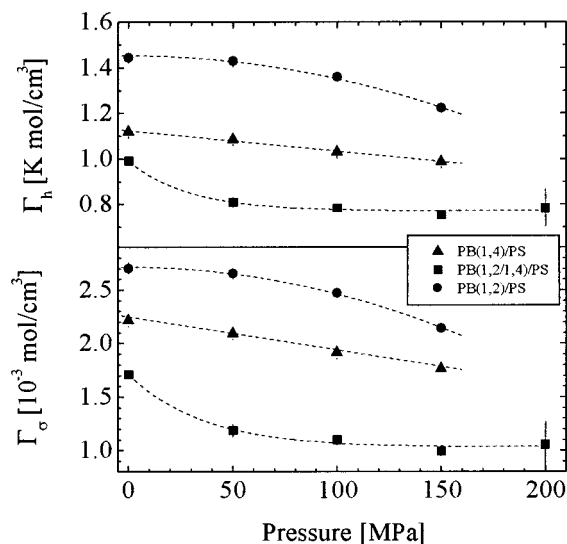


Figure 10. Enthalpic and entropic terms of the FH parameter versus pressure for the three d-PB/PS blends. The parameter is largest for the d-PB(1,4) and smallest for the statistical copolymer blend.

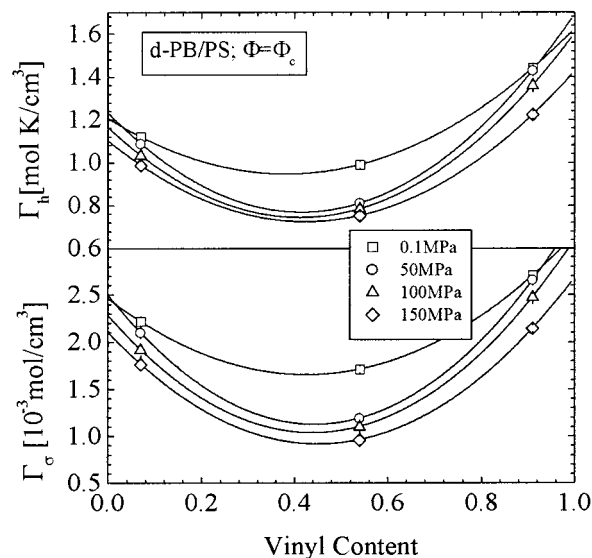


Figure 11. Enthalpic and entropic terms of the FH parameter versus vinyl content and for the pressure fields. The solid lines represent fits with the ansatz for statistical copolymers as given in eq 11.

results are summarized in Table 4; they are consistent with the corresponding parameters in Table 2. So from the experimental side we can safely conclude that the statistical copolymer theory in eq 11 leads to inconsistent interpretations.

While the enthalpic and entropic FH parameter portions of the PB(1,4)/PB1,2) blend obtained from the d-PB/PS blend are large in comparison with the corresponding intermolecular values (Figure 12), the FH parameter itself is rather small near the critical temperatures of the d-PB/PS blends (Figure 14). The reason is the large entropic contribution according to the observed negligible compatibilization effect of the copolymer mixture. This also means that an entropic term of the FH parameter has to be considered in contrast to the presently available theoretical description of copolymers.^{17,18}

D. Application of Clausius–Clapeyron Equation. In Figure 15 the pressure-induced changes of the phase

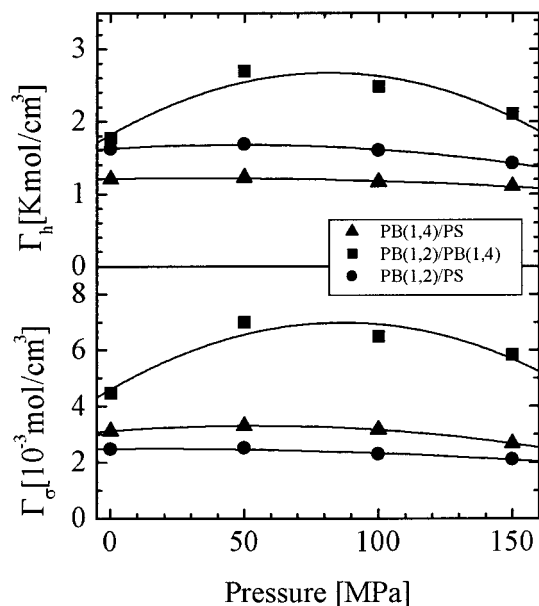


Figure 12. Parameters from the fit in Figure 11 versus pressure. The enthalpic and entropic terms are largest for the PB(1,2) and PB(1,4) representing an intramolecular interaction.

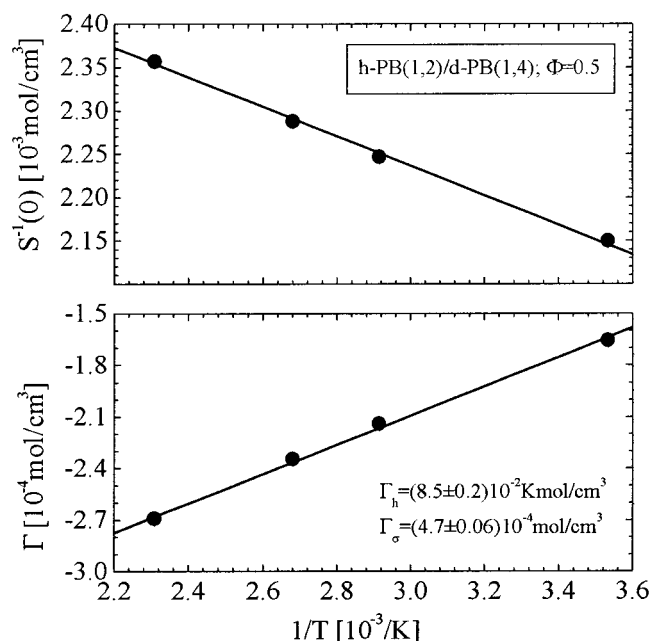


Figure 13. Inverse susceptibility and FH parameter versus inverse temperature of (1,2) and (1,4) PB blends. The FH parameter represents an intermolecular interaction. These values are 30–50 times smaller than the corresponding intramolecular values given in Figure 13.

Table 5. Results of the h-PB(1,2)/d-PB(1,4) Blend

sample	h-PB(1,2)/d-PB(1,4)
Φ	0.5
segment length σ (Å)	6.92 ± 0.05
Γ _C (10 ⁻⁴ mol/cm ³) (N _W)	9.09 (36.4)
T _C (°C)	≈ -210
Γ _h (10 ⁻² mol K/cm ³)	8.5 ± 0.2
Γ _σ (10 ⁻⁴ mol/cm ³)	4.7 ± 0.06

boundary temperatures have been depicted versus the vinyl content. The derivative of temperature with respect to pressure was always averaged over the pressure range between 0.1 and 150 MPa. The full dots show $\Delta T_C/\Delta P$ directly derived from the temperature of

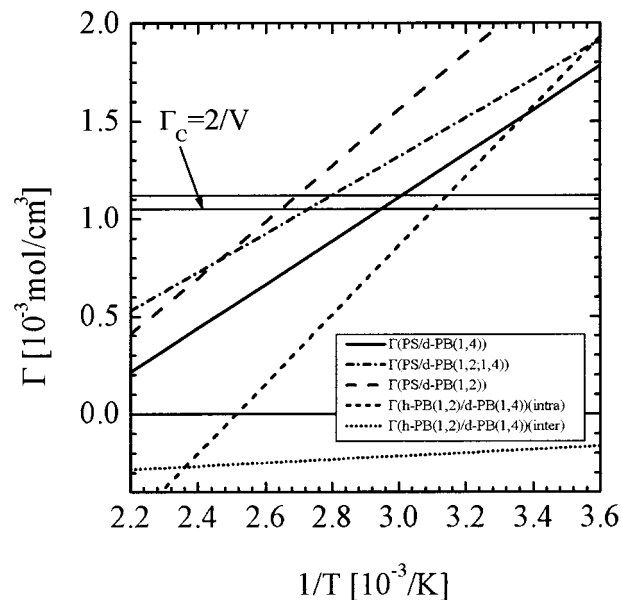


Figure 14. FH parameter at ambient pressure versus inverse temperature for the three d-PB/PS blends together with inter- and intramolecular FH parameter of the h-PB(1,2)/d-PB(1,4) blend. In the ranges of the critical temperatures of the PB/PS blends the FH parameters of the PB(1,2)/PB(1,4) are small and therefore no improved compatibility can be expected. If only the enthalpic term would be important as suggested from the theory of copolymers, then such an effect should occur in contrast to observation.

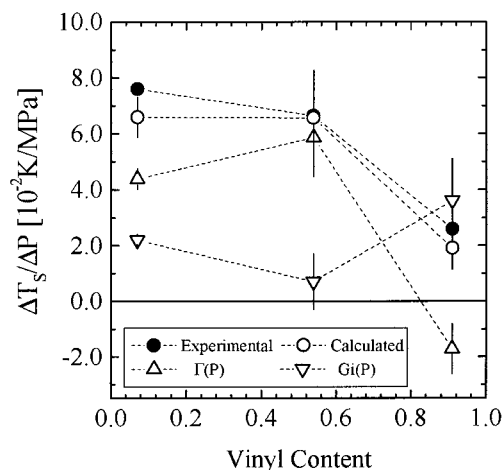


Figure 15. Change of spinodal (critical) temperature with pressure averaged over a pressure range of 150 MPa obtained from experiment (full dots) and from Clausius–Clapeyron equation (open dots). In all cases a positive change is observed, which is largest for (1,4) and smallest for the (1,2) blend. There are two contributions, namely, from pressure-induced changes of the Ginzburg number and the FH parameter, as indicated by the triangles. In the (1,2) blend the FH parameter causes a negative change of the spinodal temperature according to the data in Table 6.

the phase boundary while the open symbols represent the $\Delta T_C/\Delta P$ evaluated from the Clausius–Clapeyron equation in eq 10. The two triangular symbols show changes of temperature caused by the pressure-induced changes of the FH parameter and by the corresponding changes of the Ginzburg number; the open dots represent the sum of both contributions. For the two samples with the smaller vinyl content the effect from the FH parameter is about twice as large as those from the Ginzburg number Gi , while for the d-PB(1,2)/PS sample a negative $\Delta T_s/\Delta P$ is obtained from $\Gamma(P)$, which is more

than compensated by $Gi(P)$, giving a resulting positive $\Delta T_C/\Delta P$. The values of $\Delta T_C/\Delta P$ evaluated from the Clausius–Clapeyron equation are in good agreement with the experimental values.

V. Summary and Discussion

In this paper we present SANS experiments on three d-PB/PS polymer blends of nearly critical composition and molar volumes of about 2000 cm³/mol. The three samples differ by the vinyl content of the d-PB component being 7%, 54%, and 91% and thereby approximately representing d-PB(1,4), d-PB(1,2;1,4), and d-PB(1,2) polymer chains. The experiments were performed at external fields of pressure between 0.1 and 200 MPa and of temperature within the disordered regime from high to low temperatures until the direct neighborhood of the critical point. In SANS experiments the susceptibility $S(0)$ is determined from extrapolation of the structure factor $S(Q)$ at $Q = 0$; $S(0)$ is the basic experimental parameter and is a measure of the thermal composition fluctuations from which according to the fluctuation–dissipation theorem all the other thermodynamic information is derived.

The basic part of this paper is related to the observation that thermal composition fluctuations are too strong over the investigated temperature range to be described within the mean field approximation. This means that the Flory–Huggins (FH) theory in general cannot be applied to the data analysis. Instead, we used a crossover function for $S(0)$ that describes the observed crossover behavior between mean field and 3D-Ising behaviors well. From the fit of the crossover function one gets three parameters, namely, the Ginzburg number Gi , the critical mean field amplitude of the susceptibility C_{MF} , and the critical temperature T_C . From these parameters one evaluates the FH interaction parameter and the critical amplitude C_+ of the susceptibility within the 3D-Ising region. The values for C_+ are found constant within 30% for all three d-PB/PS samples and for all pressure fields. The phase boundaries of the three samples are different; the critical temperature continuously increases with increasing vinyl content of the d-PB component from about 65 to 100 °C.

An external pressure field leads to an increase of the critical temperature with a rate between 8×10^{-2} and 3×10^{-2} K/MPa; the lowest rate is observed for the sample with the highest vinyl content. The Ginzburg number and the FH parameter of the three samples react differently on pressure: Gi is largest for the d-PB(1,2) and strongly decreases above 100 MPa, while it is smallest for the d-PB(1,2;1,4) copolymer, which above 20 MPa already approaches a constant value. This low Gi seems to correspond to the incompressible blend. The Gi for the d-PB(1,4) blend is intermediate between the two other samples and linearly decreases with pressure. A pressure-induced decrease of Gi is expected from a decrease of the entropic term Γ_σ (eq 5) and its relationship to compressibility predicted by equation of states theories.² The critical amplitude C_{MF} is another fit parameter of the crossover function (Figure 8); from Gi and C_{MF} , the critical amplitude C_+ is derived as shown in Figure 9. From C_{MF} and the critical temperature one evaluates the FH parameter as depicted in Figure 10; the d-PB(1,4) sample shows the largest values while the d-PB(1,2;1,4) copolymer sample the lowest ones, and in all samples the enthalpic and entropic terms decrease with pressure.

Table 6. Changes of Enthalpic and Entropic FH Parameter with Pressure Leading to $\Delta T_B/\Delta P$ as Plotted in Figure 15

	Γ_B/Γ_B	$\partial\Gamma_B/\partial P$	$T_B\partial\Gamma_B/\partial P$	$\Delta T_B/\Delta P$
d-PB(1,4)/PS	>0	$-(9 \pm 0.2) \times 10^{-4}$	$-(10.5 \pm 0.06) \times 10^{-4}$	>0
d-PB(1,2;1,4)/PS	>0	$-(16 \pm 0.8) \times 10^{-4}$	$-(17 \pm 1) \times 10^{-4}$	>0
d-PB(1,2)/PS	>0	$-(15 \pm 0.5) \times 10^{-4}$	$-(13.8 \pm 0.4) \times 10^{-4}$	<0

According to the Clausius–Clapeyron equation in eq 10, the pressure-induced changes of the critical temperature are interrelated by those of the Ginzburg number and the FH parameter. The always observed pressure-induced decrease of $Gi(P)$ leads to an increase of the critical temperature because of the stabilization effect of thermal fluctuations; the corresponding change of temperature has been depicted in Figure 15. The effects from pressure-induced changes of $\Gamma(P)$ are slightly more complicated as seen from eq 10. As the enthalpic term is always positive and both FH parameter terms decrease with pressure (see values in Table 6), one expects at low temperatures always a negative change of critical temperature with pressure. From the values in Table 6 one derives temperatures of 14, 60, and 132 °C for the d-PB(1,4), d-PB(1,2;1,4), and d-PB(1,2) samples, respectively, below which a negative $\Delta T_B/\Delta P$ is expected. So for the first two mentioned samples one evaluates a positive change of temperature in agreement with the experimental findings, as the corresponding critical temperatures are larger than 14 and 60 °C. For the d-PB(1,2) sample, however, the critical temperature of 101 °C is smaller than the calculated 132 °C and therefore a negative change of critical temperature with pressure is evaluated from the corresponding change of $\Gamma(P)$ (see Figure 15). The sum from the contributions of $\Gamma(P)$ and $Gi(P)$ yield values depicted as open dots in Figure 15 and are compared with the actually measured ones plotted as full dots. The agreement between both numbers is very good; they are within the experimental accuracy the same. This shows that the underlying theory of the crossover function (eq 2) used for the analysis of the susceptibility and the subsequent evaluation of the FH parameter and Ginzburg number leads to consistent results. It, furthermore, shows that pressure-induced changes of the phase boundaries are generally influenced by two effects, namely, by changes of the interaction parameter and by changes of the degree of thermal composition fluctuations.

The Ginzburg number of the three d-PB/PS samples and their changes with pressure have been plotted in Figure 1 versus the mean degree of polymerization and are compared with other Gi numbers. At ambient pressure one generally finds Ginzburg numbers that are larger and sometimes even of the order of magnitude larger than estimated by deGennes' universal N^{-1} scaling. So Gi of the d-PB(1,4)/PS and the d-PB(1,2)/PS blends are consistently found to be 10–15 times larger than estimated. On the other hand, the PB(1,2;1,4)/PS copolymer blend shows only a 2.5 times larger Ginzburg number. So it can be concluded from the different Gi s of the three d-PB/PS blends with approximately the same molar volume that the Ginzburg criterion of polymer blends is not described by a universal function of the degree of polymerization or molar volume. As motivated by eq 5 and also shown by former pressure experiments¹⁰ (see also PPMS/d-PS in Figure 1), the Ginzburg number sensitively depends on the entropic term of the FH parameter Γ_σ . This finding is clearly

confirmed by our work. The pressure dependence of the Ginzburg number (Figure 8) is consistently much stronger than the corresponding pressure dependence of Γ_σ (Figure 10) for all vinyl contents because of the large exponent in eq 5. The values of Gi and Γ_σ depend on the vinyl content in the same manner (Figures 8 and 10) because of the constant critical amplitude C_+ (Figure 9), which is within 3% and 30% independent of pressure and of vinyl content, respectively. The Ginzburg number and Γ_σ of the d-PB(1,2;1,4)/PS blend approach constant values at pressures of larger than 50 MPa; at these pressure fields Γ_σ and Gi seem to be near their incompressible values. Thus, our detailed experiments confirm that the Ginzburg number sensitively depends on the entropic contribution Γ_σ , which is the reason that (i) it is a nonuniversal quantity and (ii) it sensitively depends on external pressure fields and on polymeric microstructure. Only at sufficiently high pressure fields Gi seems to approach a value estimated originally by deGennes.¹

Another aspect of this work is related to the observed FH parameter of the three samples and its interpretation within the theory of copolymers given in eq 11. Its analysis leads to surprisingly large intramolecular enthalpic and entropic FH parameter terms between the PB(1,4) and PB(1,2) units as depicted in Figure 12 and which are even larger than the corresponding intermolecular interaction terms between the PS and d-PB(1,4) and d-PB(1,2) units. These experimental findings were confirmed from additional SANS measurements of the d-PB(1,4)/PS and the d-PB(1,2;1,4)/PS blends with our standard heater system. The corresponding results in Figure 6 and in Table 4 are consistent with those obtained from the pressure cell (see Table 3). The large intramolecular FH parameters evaluated for the PB(1,4)/PB(1,2) units from the theoretical approach for statistical copolymers in eq 11 were later tested on a h-PB(1,2)/d-PB(1,4) mixture by additional SANS experiments. The corresponding intermolecular terms of the FH parameter given in Figure 14 are of the order of magnitude smaller and therefore in disagreement with the findings from the d-PB/PS blends. This means that the theory of copolymers as given in eq 11 does not lead to consistent results, at least for the presently investigated system. On the other hand, the FH parameter itself is very small in the temperature range of the critical temperatures because of the large entropic contribution (Figure 14).

There are only a few SANS experiments that study the effect of intramolecular interaction in polymer blends with statistical copolymer components and no experiments are known to us where intra- and intermolecular interactions have been studied simultaneously. Up to now the theoretical approach for statistical copolymers in eq 11 was mainly tested from determination of the phase boundary; the observation of an improved compatibility of statistical copolymers was then interpreted by a positive intramolecular enthalpic interaction.^{15–17} Those experiments cannot distinguish whether the FH parameter is a purely enthalpic or a free energy parameter. In the SANS investigations of the d-PB/PS blends presented here we find a large positive intramolecular enthalpic FH parameter between the 1,4 and 1,2 d-PB units, even though we did not find any improved compatibility between the two components (see Figures 2 and 7). The reason is the large entropic contribution of the FH

parameter that makes the “total” intramolecular FH parameter relatively small in the temperature range of phase separation as depicted in Figure 14.

Studies on the FH parameter between polybutadiene units of different vinyl content were performed by Sakurai et al.²⁴ They assumed that there are three different interaction parameters to explain their experiment. One FH parameter describes the interaction between the monomer units of different microstructures, but with the same labeling (protonation or deuteration). The second FH parameter describes the interaction between monomer units of different microstructures and labelings. The third FH parameter describes the isotope effect between identical microstructures, which is an order of magnitude smaller. Despite this simplification the predicted FH parameter agrees well within a cross-check. The enthalpic and entropic FH parameters of the h-PB(1,2)/d-PB(1,4) blend measured in this work are larger by a factor of, respectively, 2.6 and 8.8 in comparison with the values of Sakurai. These discrepancies can be understood from a molecular weight dependence of the FH parameter coming from the chain ends and showing an additional $1/V$ term²⁵ and whose relative effect seems to be quite strong.^{26–28} Thus, the large difference of the PB(1,2)/PB(1,4) FH parameter as measured directly and as predicted by the intramolecular FH parameter of the PB/PS blend remains to be significant.

The FH parameters of polybutadiene blends with different vinyl contents n were also discussed by Krishnamoorti et al. in ref 29. The theory predicts for the enthalpic portion of the FH parameter a dependence on the vinyl content difference $\Delta\varphi$, according to $\Gamma_h(\text{blend}) = (\Delta\varphi)^2 \Gamma(1,2;1,4)$. Experimentally, however, a more complicated dependence on the vinyl contents was found and, finally, the authors had to conclude that the model for statistical copolymers could at least not be applied to polybutadiene copolymer blends.

Lattice-cluster theory calculations on random copolymers yield a similar dependence of the entropic portion of the FH parameter due to the “monomer site occupancy index” and as formulated in eq 12.¹⁸ In the case of two polybutadiene components the proportionality $\Gamma_\sigma \propto (\Delta\varphi)^2$ is predicted, which is the same as that in the theory of random copolymers. When d-PB/PS blends are regarded, a monotonic proportionality $\Gamma_\sigma \propto -(\varphi - 1.5)^2$ is predicted. Neither prediction matches our experimental results. One reason might be a molar volume dependence of the FH parameter, which seems to be rather large for the $V_W = 2200 \text{ cm}^3/\text{mol}$ PB(1,2)/d-PB(1,4) blend.^{26–28} One might further speculate that compressibility, chain semiflexibility, and specific interactions between the 1,2- and 1,4-butadiene monomers have to be included because they are neglected at the present stage of the lattice-cluster theory for pedestri-ans.¹⁸

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