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Small angle neutron scattering studies of a polybutadiene/polystyrene blend with small additions of ortho-dichloro-benzene for varying temperatures and pressures. I. Mean field to 3D-Ising crossover behavior

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Thermal composition fluctuations were studied in the blend of polybutadiene (PB) and polystyrene (PS) in temperature and pressure fields using the technique of small angle neutron scattering. The blends had a critical composition and were mixed with different amounts of the nonselective solvent ortho-dichloro-benzene. In this part we discuss the critical behavior as measured along the critical isochore and interpret the results in terms of a crossover function describing the transition between mean field and 3D-Ising behavior. In particular, we will discuss the Ginzburg number and the critical amplitudes of the susceptibility and correlation length. For the Ginzburg number Gi we found a much stronger increase with solvent content as predicted while the pressure fields always lead to a decrease of Gi as expected. In "pure" PB/PS blends we found a further crossover to a so-called renormalized Ising behavior; such a crossover proposes density fluctuations of the total polymer concentration near the critical point. This crossover was not observed in the blend–solvent mixtures. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1429959]

I. INTRODUCTION

Thermal composition fluctuations are always present in multicomponent systems. If the interaction energy prefers clustering of identical particles phase separation will be observed at low temperatures. In those systems thermal composition fluctuations will be strong at low temperatures near the critical point and will be weak at high temperatures when the entropy of mixing is dominating. The critical point represents a particular position on the phase boundary where a continuous phase separation is observed. According to the fluctuation–dissipation theorem the mean-square deviation of thermal composition fluctuations is related to the first derivative of the order parameter with respect to the chemical potential. If the order parameter is defined as the composition Φ of component "A" then the conjugate field is represented by the difference of the chemical potentials $\Delta\mu$ ($=\mu_A - \mu_B$); so, the degree of thermal fluctuations is related to $\partial\Phi/\partial\Delta\mu$ which is equivalent to $1/(\partial^2 G_m/\partial\Phi^2)$, G_m representing the Gibbs free energy of mixing with the natural parameters temperature T, pressure P, and composition Φ. This means that thermodynamic parameters can be determined from measurements of thermal fluctuations. Scattering technique is a sensitive tool to measure spatial inhomogeneities; in particular, the method of small angle neutron scattering (SANS) has several important advantages as the scattering contrast of the two molecular species can be made very large by selective deuteration and as all other scattering contributions are usually weak.

Here, we present SANS experiments on several three-component mixtures consisting of a symmetrical polymer blend of similar molecular weight and different amounts of a nonselective solvent. The composition of the polymer blends was always chosen very near the critical one and the maximum solvent content was 20%. The samples were explored in their homogeneous state over a wide range of temperature along the critical isochore and in pressure fields between 0.1 and 200 MPa.

The Ginzburg number as derived from the Ginzburg criterion estimates the borderline between strong and weak thermal fluctuations. Fluctuations are weak if they do not interact with each other; in this limit they can be described within the Gaussian approximation and mean-field theory is a sufficiently good approximation which in case of polymer blends is represented by the Flory–Huggins theory. Near the critical point, however, thermal fluctuations become strong and lead to nonlinear effects dominating the thermodynamic behavior. In this range more sophisticated theories are needed. In polymer blends fluctuation effects are usually neglected and considered of minor importance. This might be explained with the original estimate of the Ginzburg criterion by deGennes proposing an extremely small Ginzburg number following a $1/N$ (N degree of polymerization) scaling behavior and therefore showing a number being roughly N times smaller than $\cong 10^{-2}$, the typical number for low molecular liquids.[1,2] On the other hand, experiments have to be performed very carefully in small temperature steps near the critical point.

Thermal fluctuations have been systematically studied in binary polymer blends over the recent years mainly with small SANS.[3–7] The outcome of these studies is that in most cases the range of relevant thermal fluctuations and thereby the Ginzburg number is at least an order of magnitude larger than originally estimated. The susceptibility could be analyzed in terms of a crossover function from which the relevant thermodynamic parameters were determined with good

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precision.[6] It was found that the Ginzburg number is a non-universal function; in addition to the degree of polymerization it depends sensitively on the noncombinatorial entropy of mixing which is part of the Flory–Huggins parameter.[6] Only in the limit of negligible noncombinatorial entropy of mixing, one gets a universal Ginzburg criterion following a $1/N$ (or $1/V$; V molar volume) scaling behavior. This generally means that thermal fluctuations cannot be neglected in polymer blends and that a proper crossover function has to be used to correctly interpret the susceptibility and the correlation length. For practical purposes one might apply the Flory–Huggins mean-field approach also very near the critical point in order to obtain some estimation of the phase boundaries; such a procedure is nothing else as a linearization of the temperature-dependent susceptibility which might be sufficient for engineering purposes, but not for a correct determination of the thermodynamic parameters.

We split our presentation in two parts because of the large amount of experimental results and theoretical ideas behind our experiments. In the present paper, which we will refer to as Part I, we will focus on the "critical behavior" of thermal composition fluctuations and discuss their crossover behavior. In Part II (Ref. 8) we will concentrate on the discussion of the mean-field parameters as evaluated from the crossover function and give an interpretation of the phase boundary and Flory–Huggins parameter in terms of the lattice cluster theory.

II. THEORETICAL BACKGROUND

In this chapter we give a short overview of the theoretical background needed. First, we will describe the scattering law for polymer blend–solution systems and then discuss the susceptibility of thermal polymer composition fluctuations as derived from the scattering law. In particular, we will describe the crossover from the situation near the critical temperature to that far from the critical temperature. A detailed derivation of the scattering law can be found in the textbook of Ref. 9 and the effect of thermal fluctuations is discussed in Refs. 10 to 17.

A. Scattering cross section of polymer blend–solvent system

The macroscopic cross section is generally described as

$$d\Sigma/d\Omega(\underline{Q}) = (1/V_S)\left|\sum \bar{b}_i \exp(i\underline{Q}\underline{r}_i)\right|^2, \tag{1}$$

with the sample volume V_S, the total coherent scattering length $\bar{b}_i$ of the solvent molecules and the polymer chain monomers, and r_i their spatial position. $d\Sigma/d\Omega$ is a function of the momentum transfer Q determined by the scattering angle Θ and the neutron wavelength λ according to $|\underline{Q}| = (4\pi/\lambda)\sin\Theta/2$. Assuming incompressibility, thereby neglecting the total polymer fluctuations, one gets with

$$d\Sigma/d\Omega(Q) = (1/V_S)[\Delta\rho_A^2 S_{AA} + \Delta\rho_B^2 S_{BB}$$
$$+ 2\Delta\rho_A\Delta\rho_B S_{AB}] \tag{2}$$

the scattering cross section in terms of the partial structure factors S_{AA}, S_{BB}, and S_{AB} of the two polymers A and B. The scattering length density differences $\Delta\rho_{A(B)} = (\rho_{A(B)} - \rho_S)$ are determined by the scattering length densities $\rho_{A(B)}$ and ρ_S of the polymers and solvent, respectively. We consider here polymer chain components of same degree of polymerization which is approximately fulfilled in our case. The corresponding cross section is given as

$$d\Sigma/d\Omega(Q) = K_{AB}\Phi_P S(Q) + K_{PS}S_{PP}(Q). \tag{3}$$

The first term is determined by the structure factor $S(Q) = \Phi(1-\Phi)VP(Q)$ being proportional to the polymer form factor $P(Q)$, the polymer composition Φ, and the polymer molar volume V, and the total polymer concentration Φ_P. $S(Q)$ is proportional to the polymer form factor only when the Flory–Huggins interaction parameter is zero. The second term is represented by the polymer–polymer partial structure factor $S_{PP}(Q)$ describing the overall polymer density fluctuations and which would become zero in case of a polymer melt with $\Phi_P = 1$. The scattering contrasts $K_{AB} = (\rho_A - \rho_B)^2/N_A$ and $K_{PS} = (\bar{\rho} - \rho_S)^2/N_A$ are determined by the coherent scattering length densities of the polymers and solvent molecules, the average $\bar{\rho} = (\Phi_A\rho_A + \Phi_B\rho_B)/\Phi_P$, and the Avogadro number N_A. The scattering contrasts of the samples studied here are chosen that the relevant contrast K_{AB} is an order of magnitude larger than K_{PS} (see numbers in Table II), which means that $S(Q)$ is the dominating scattering contribution.

B. Structure factor

Thermal composition fluctuations lead to diffuse scattering of neutrons expressed by the structure factor $S(Q)$, which at sufficiently small Q can be approximated by the Zimm approximation according to

$$S^{-1}(Q) = S^{-1}(0) + L_2 Q^2. \tag{4}$$

The extrapolated $S(0)$ represents a susceptibility which is related to the Gibbs free energy of mixing G_m according to $S^{-1}(0) = \partial^2(G_m/RT)/\partial\Phi^2$ (R gas constant).[1,2,10] The coefficient L_2 is determined by the ratio of the correlation length ξ of the thermal fluctuations and the susceptibility according to $L_2 = \xi^2/S(0)$. Within the random phase approximation one finds $L_2 = R_g^2/3S(0;\Gamma=0) = 2R_g^2\Gamma_C/3 = (4/3)R_g^2/V$ ($\Gamma_C = 2/V$ is the FH parameter at the critical temperature of a polymer blend with equal molar volumes $V = V_A = V_B$) from which the radius of gyration R_g can be evaluated.[1,2] The thermodynamic information derived from the susceptibility $S(0)$ represents a property averaged over a macroscopic volume due to the inverse relationship between the reciprocal momentum Q and real space.

C. Mean field to 3D Ising crossover behavior of susceptibility and correlation length in polymer blends

The degree of thermal composition fluctuations and thereby $S(Q)$ sensitively depends on temperature and pressure. At sufficiently high temperatures above the critical temperature, the thermal fluctuations can be described within the

Gaussian approximation; in this state the system is well described by the mean-field approximation, e.g., most of the critical exponents are the same.[10] On the other hand, thermal fluctuations become strong near the critical temperature leading to nonlinear effects. These nonlinear effects become visible in scattering experiments by a crossover behavior of the susceptibility and correlation length following the universality class of the 3D-Ising critical behavior asymptotically close to the critical temperature.[1,2] Within the mean-field and 3D-Ising model the susceptibility $S(0)$ and the correlation length ξ are described by simple scaling laws according to $C\tau^{-\gamma}(\xi_0\tau^{-\nu})$ with the reduced temperature $\tau=|T-T_C|/T$ (T_C critical temperature), the critical amplitudes $C(\xi_0)$ and the critical exponents $\gamma(\nu)$ being equal to 1 and 1.239 ± 0.003 (0.5 and 0.634 ± 0.001) in the mean-field and 3D-Ising case, respectively.[11] In order to describe the susceptibility and correlation length over the whole temperature range one needs a crossover function, which we will discuss now.

In recent theoretical and experimental work it has been shown that the crossover from mean-field to 3D-Ising behavior could be nonuniversal and rather complex. In the asymptotic critical regime of the 3D-Ising regime the correlation length ξ is the only relevant length while in the crossover regime an additional microscopic length could become relevant and enforce a nonuniversal and nonhomogeneous crossover behavior.[12,13] Such a nonuniversal crossover behavior has been observed in diluted polymer solvent systems in which the size of the polymer was quite naturally interpreted as the microscopic length scale.[14] In polymer blends, so far, $S(0)$ could always be described by a crossover formalism derived by Belyakov et al. which represents a universal and continuous crossover function and is solely determined by the Ginzburg number; this function will be described in the next section.[15] This means that in polymer blends a relevant microscopic length scale did not appear yet and can therefore be neglected. A corresponding crossover formalism for the susceptibility and correlation length has been derived from the more general formalism as

$$S^{-1}(0)=(1/C_+^{\mathrm{MF}})\tau Y^{(\gamma-1)/\Delta}\left[1+\frac{u^*\nu}{\Delta}\left(\frac{1}{2\Delta}+\frac{Y}{1-Y}\right)^{-1}\right],$$
(5)

$$\xi=\xi_0^{\mathrm{MF}}\tau^{-1/2}Y^{-(2\nu-1)/2\Delta},$$
(6)

taking the wave number $\Lambda\rightarrow\infty$ and which corresponds to a zero microscopic length.[13,16] Susceptibility and correlation length are a function of the reduced temperature and a crossover function Y. The critical exponents are those of the 3D-Ising model and $\Delta=0.54\pm0.03$ is a universal correction-to-scaling exponent. The crossover function Y is either given as an implicit function of the inverse correlation length $\kappa=\xi_0^{\mathrm{MF}}/\xi$ or of the reduced temperature τ according to $1-Y=(\bar{u}\Lambda/\kappa)Y^{\nu/\Delta}$ or $(1-Y)^2Y^{-1/\Delta}=\bar{u}^2\Lambda^2/\tau$, respectively. The limit $\Lambda\rightarrow\infty$ also means that the reduced coupling constant $\bar{u}\rightarrow0$ because of its definition $\bar{u}=u/u^*\Lambda$. The parameters u and $u^*\cong0.472$ represent the coupling constant in the Ginzburg–Landau Hamiltonian and the RG fixed-point coupling constant, respectively. For the mean-field approach one gets, with $\bar{u}^2\Lambda^2/\tau\ll1$ and $Y=1$ the scaling laws, $S(0)$

$=C_+^{\mathrm{MF}}\tau^{-1}$ and $\xi=\xi_0^{\mathrm{MF}}\tau^{-1/2}$ with the corresponding mean-field critical amplitudes C_+^{MF} and ξ_0^{MF}. Within the asymptotic regime of the 3D-Ising behavior one has $\tau\rightarrow0$ and $Y\rightarrow0$; therefore, $Y=(\bar{u}^2\Lambda^2/\tau)^{-\Delta}$. From Eqs. (5) and (6) one then gets, with $S(0)=C_+\tau^{-\gamma}$ and $\xi=\xi_0\tau^{-\nu}$, the asymptotic scaling laws of the 3D-Ising model. The ratios of the 3D-Ising and mean-field critical amplitudes are given as

$$(C_+/C_+^{\mathrm{MF}})^{1/(\gamma-1)}=\bar{u}^2\Lambda^2,\quad(\xi_0/\xi_0^{\mathrm{MF}})^{2/(2\nu-1)}=\bar{u}^2\Lambda^2.$$
(7)

Within the limit of $\Lambda\rightarrow\infty$ the crossover between the two universality classes of mean-field and 3D-Ising behavior is determined by a single parameter $(\bar{u}\Lambda)^2$ being proportional to the Ginzburg number Gi, which we define in accordance with our earlier work as $\mathrm{Gi}=0.069\bar{u}^2\Lambda^2$, so that we finally obtain, with

$$\mathrm{Gi}=0.069(C_+/C_+^{\mathrm{MF}})^{1/(\gamma-1)}=0.069(\xi_0/\xi_0^{\mathrm{MF}})^{2/(2\nu-1)},$$
(8)

relations between the ratios of the critical amplitudes of the 3D-Ising and mean-field case.[6,7] The value of Gi can be identified with the reduced temperature at which the difference between the 3D-Ising approximation and the crossover function of Belyakov et al. reaches 10%.[15]

Within the FH model the susceptibility and correlation length are, respectively, given as $S(0)=1/[2(\Gamma_C-\Phi_P\Gamma)]$ and $\xi^2=S(0)L_2=R_g^2\Gamma_C/[2(\Gamma_C-\Phi_P\Gamma)]$. In the dilution approximation of blend–solvent systems Γ is replaced by $\Phi_P\Gamma$, with Φ_P being the total polymer content.[18] So, for blend–solvent systems the mean-field critical amplitudes are related to the FH parameters according to

$$C_+^{\mathrm{MF}}=1/(2|\Gamma_C+\Phi_P\Gamma_\sigma|)=T_C^{\mathrm{MF}}/2(\Phi_P\Gamma_h),$$

$$\xi_0^{\mathrm{MF}}=\sqrt{2R_g^2\Gamma_C C_{\mathrm{MF}}/3}=R_g/\sqrt{3(1+\Phi_P\Gamma_\sigma/\Gamma_C)},$$
(9)

with the correspondingly enthalpic Γ_h and entropic Γ_σ terms of $\Gamma=\Gamma_h/T-\Gamma_\sigma$.[6] The expressions of the critical amplitudes of the mean-field case in Eq. (9) and of the 3D-Ising case according to $C_+\propto V^{(2-\gamma)}$ and $\xi_0\propto V^{(1-\nu)}$ as derived by Binder[2,17] leads to

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

and

$$\mathrm{Gi}\propto[V^{(2-2\nu)}(2/V+\Phi_P\Gamma_\sigma)]^{1/(2\nu-1)},$$
(10)

and in the case of zero Γ_σ to the universal scaling law Gi $\propto1/V$. So, according to its dependence on molar volume a very small Gi is expected in polymer blends if compared with a Gi of the order of 10^{-2}, which is typical for low molecular liquids.[10,16] On the other hand, it becomes apparent from the large exponents $1/(\gamma-1)\cong4.23$ and $2/(2\nu-1)\cong7.46$ in Eq. (10) that the entropic term Γ_σ strongly enhances Gi. Such a behavior was indeed found in earlier experimental work; all Gi values are appreciably larger (in some cases by two orders of magnitude and even larger than for low molecular liquids) compared with the universal $1/V$ estimation for incompressible melts. This clearly indicates that the entropic term Γ_σ (according to equation of states theories Γ_σ is related to the compressibility[19]) leads to a strong increase of thermal composition fluctuations near the critical temperature.[6,7] These large Gi numbers also imply

the need for a more sophisticated analysis of the scattering data using Eqs. (5) and (6). This also means that the FH parameter has to be evaluated from the mean-field critical amplitudes in Eq. (9) and from the "mean-field" critical temperature T_C^{MF}, which is related to the "real" critical temperature T_C according to $T_C^{MF} = T_C/(1 - Gi)$.[16] T_C is smaller than T_C^{MF} by some degrees Kelvin because of the stabilization effect of thermal fluctuations.

E. Susceptibility derived from Belyakov and Kiselev

The analysis of the susceptibility crossover behavior was performed with an asymptotic crossover function according to

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

derived by Belyakov and Kiselev[15,16] on the basis of a renormalization group approach and an ϵ-expansion. The crossover functions in Eq. (11) and Eq. (5) should describe a similar situation as in both cases a microscopic length scale was extrapolated to zero. So, we have chosen the more easily applicable Eq. (11) for the analysis which was also successfully used in all our former studies on polymer blends.[6,7] The parameters Gi, C_{MF}, and T_C in Eq. (11) are the experimental numbers characterizing the system; the rescaled reduced temperature $\hat{\tau} = \tau/Gi$ is an explicit function of the rescaled susceptibility $\hat{S}(0) = S(0)Gi/C_{MF}$; the critical exponents γ and Δ are of the 3D-Ising model.

F. Hidden variables—Fisher renormalization

Three-component samples as polymer blend–solvent systems can be considered as quasibinary blends as long as the total polymer concentration $\Phi_P = \Phi_A + \Phi_B$ is constant and thermal fluctuations are only observed for the order parameter represented by the composition of one component $\Phi = (\Phi_A \text{ or } \Phi_B)$. Under such condition the systems obeys 3D-Ising critical behavior asymptotically close to the critical temperature T_C. If the Gibbs free energy of mixing G_m is considered as the relevant thermodynamic potential, the equilibrium states in blends are determined by the order parameter Φ, the temperature and pressure fields. In polymer–solvent systems one has in addition the solvent volume fraction Φ_S and its conjugate chemical potential according to $\mu_S = \partial G_m/\partial \Phi_S|_{P,T,\phi}$ (polymer and solvent concentrations give $\Phi_P + \Phi_S = 1$). Both parameters are considered as "hidden" variables. In the so-called isomorphism approach discussed by Anisimov et al., the "fluctuation" part of G_m is described by the well-known scaling form[10] being a function of two relevant parameter fields, namely the temperature and the order parameter, both being a function of pressure and the solvent chemical potential.[20,21]

Generally, one observes 3D-Ising critical exponents when pressure and the solvent chemical potential fields are constant during the isochoric approach to T_C. Experimentally, however, an approach to T_C under the condition of $\mu_S = \text{const}$ is not possible; such an approach can only be realized in samples with homogeneous solvent concentration.

In the experimental case a crossover from 3D-Ising to a critical behavior with the renormalized critical exponents is expected near T_C and is determined as

$$\gamma^* = \gamma/(1 - \alpha), \quad \nu^* = \nu/(1 - \alpha), \quad (12)$$

with the critical exponent $\alpha = 0.11$ of the heat capacity.

For polymer blend–solvent systems the transition temperature T^{**} or the temperature range $\Delta T^{**} = (T^{**} - T_C)$ to a renormalized Ising behavior has been estimated by Broseta et al.;[22] on the basis of mean-field parameters they found a scaling law according to $\Delta T^{**} \cong N^{-13.6} \phi^{-17}$. This expression leads to an extemely small temperature interval around T_C which is not visible in our samples and proposes the behavior of a "quasibinary" blend characterized by 3D-Ising universality near T_C. Extensive studies on polymer blend–solvent systems were performed by the group of Nose as reviewed in Ref. 23.

III. EXPERIMENT

The description of SANS scattering instruments, polymer synthesis, and sample preparation has already been given in a former publication where we have studied the same dPB/PS blend but without solvent.[24]

A. SANS experiment

The scattering experiments were performed at the SANS diffractometer KWS1 at the FRJ2-reactor of the "Forschungszentrum Jülich." [25] 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 $-20 \leq T(°\text{C}) \leq 200$, 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 temperature we waited for half an hour before proceeding with the neutron measurements in order to safely achieve a stationary temperature field in the relative 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, radially averaged, and calibrated in absolute units by a Lupolen secondary standard.

For blend–solvent systems the relationship of the absolute macroscopic cross section $d\Sigma/d\Omega(Q)$ is given in Eq. (3). The scattering experiments were performed in the momentum transfer range of $0.01 \leq Q (\text{Å}^{-1}) \leq 0.1$ using the settings of 7 Å neutron wavelength, the detector to sample distances of 4 and 8 m with the corresponding collimations distances.

B. Polymer synthesis and characterization

The polymers were synthesized by anionic polymerization using high vacuum and break seal technique. Sec.-

TABLE I. Polymer chain and solvent characteristics.

$$\overbrace{—(CD_2—CD\!=\!CD—CD_2)_x}^{1,4}\overbrace{—(CD_2—CD)_{(1-x)}—}^{1,2(vinyl)}$$
$$\underset{\displaystyle CD\!=\!CD_2}{\big|}$$

Polymer	Polybutadiene dPB (C_4D_6)		PS (C_8H_8)	Solvent $C_6H_4Cl_2$
Vinyl content [%][a]	7	54	⋯	⋯
	dPB (1,4)	dPB (1,2; 1,4)		
Ω [cm³/mol][b]		60.4	99.1	112.6
ρ [10^{10} cm⁻²][c]		6.76	1.46	2.36
σ [Å]	6.84	6.27	6.74	⋯
M_n[d]	2100	1900	1700	⋯
V_w [cm³/mol]	2200	2000	1750	⋯
M_w/M_n[e]	1.05	1.07	1.069	⋯
$\bar{N}_w$	36.4	33.1	17.2	⋯

[a]By ^{13}C-NMR in CDCl, ^{1}H-NMR for h-PB (1,2).
[b]Monomer volume; densities: d-PB=1 g/cm³; h-PB=0.9 g/cm³; h-PS = 1.04 g/cm³.
[c]Coherent scattering length density of the polymers determining the neutron scattering contrast.
[d]VPO (vapor pressure osmometry) at $T=45$ °C in benzene. Their accuracy is within ±5% by SEC in THF.

Butyllithium was used as initiator for all polymerizations. The purification of solvents and monomers was performed according to the standards required for anionic polymerization.[26] Protonated polystyrene (PS) and deuterated polybutadiene (d-PB) 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) 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 columns with a porosity range of 10^5–100 Å 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 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 $(\Delta V/c)_{c\to0}=KM_n^{\alpha}$, where c is the polymer concentration and ΔV the change in voltage being proportional to the temperature difference between the two thermistors.[27] The calibration constants K and α were determined with benzil and PS standards of $440\leqslant M_n\leqslant9600$ with an accuracy of about ±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 ^{1}H-NMR. The characteristic parameters of the polymers are summarized in Table I.

TABLE II. Parameters of the polymer blends (see also results in Fig. 2 of Ref. 24).

Sample	dPB (1,4)/PS	dPB (1,2; 1,4)/
Φ_c (PB)	0.43±0.02	0.477±0.02
T_C [°C] at 0.1 MPa	64	72.2
Γ_C [10^{-3} mol/cm³]	1.07	1.12
$(\rho_{PB}-\rho_{PS})^2$ [10^{21} cm⁻⁴]		2.81
$\bar{\rho}$ [10^{10} cm⁻²]	3.74	3.99
$(\bar{\rho}-\rho_S)^2$ [10^{21} cm⁻⁴]	0.19	0.27

C. Sample preparation

The polymer blends were prepared by dissolving in and freeze drying from benzene. 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. The solvent ortho-dichloro-benzene was added after the freeze-drying process. The sample was stirred under inert nitrogen atmosphere at approximately 100 °C and quenched to 20 °C after half an hour.

In order 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 three samples without solvent at different compositions by SANS measurements. The so-obtained phase diagrams are shown in Fig. 2 of Ref. 24 and the corresponding critical composition and temperature are given in Table II.

IV. EXPERIMENT RESULTS

In this section we first present the structure factor, susceptibility, and correlation length as obtained from the SANS experiments and will then give an interpretation in terms of the Ginzburg number and critical amplitudes as drived from the crossover functions in Eqs. (6) and (11).

A. SANS data—structure factor, susceptibility, and correlation length

In Figs. 1(a) and 1(b) the structure factor $S(Q)$ of the two dPB/PS polymer blends have been plotted in Zimm representation. Both blends are distinguished by their deuterated PB component having different vinyl content [for details of the polymers PS, dPB(1, 4) and dPB(1, 2; 1, 4) see Table I]. In these plots the scattering curves follow a straight line in accordance with Eq. (4). Figure 1(a) shows $S(Q)$ of four dPB(1,4)/PS samples mixed with different amounts of solvent between 0% and 10% and which were measured at ambient pressure and at 76.2 °C. With increasing solvent content the scattering power becomes appreciably weaker because of an improved polymer miscibility shifting the phase boundary to lower temperatures. Figure 1(b) shows $S(Q)$ of the dPB(1,2;1,4)/PS sample with a fixed 20% volume fraction of the solvent and at constant temperature slightly above room temperature but in varying pressure fields between 0.1 and 200 MPa. The scattering enhances
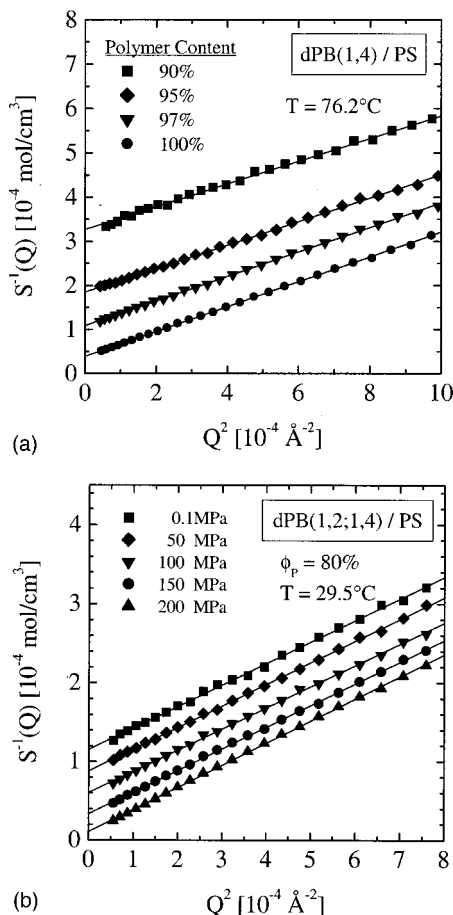
FIG. 1. Structure factor of the two binary blends of critical composition in Zimm representation (a) at different polymer concentrations and (b) at different pressure fields with the other parameters constant.
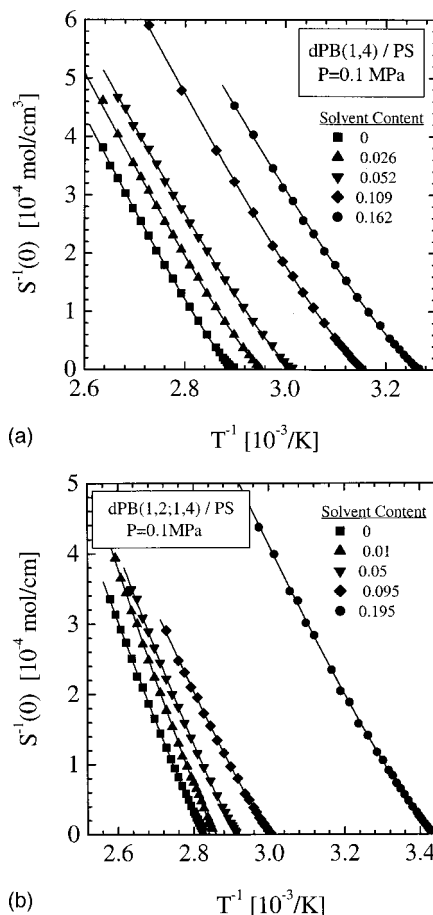

FIG. 2. Inverse susceptibility $S^{-1}(0)$ vs inverse temperature at ambient pressure for the different solvent concentrations in (a) the dPB(1,4)/PS and (b) dPB(1,2; 1,4)/PS blends. $S(0)$ was normalized with total polymer concentration Φ_P. All blends are very near the critical concentration as $S^{-1}=0$ could be well approached and the solvent leads to a better polymer compatibility.

with increasing pressure field indicating lower compatibility at larger pressure fields. The susceptibility $S(0)$ and the correlation length ξ are obtained from fitting $S(Q)$ with Eq. (4) as demonstrated by the solid lines; the susceptibility represents the extrapolated $S(Q{\rightarrow}0)$ and the slope together with $S(0)$ delivers the correlation length ξ.

The susceptibility measured under different conditions as microstructure, solvent content, and external pressure field is depicted in Figs. 2 and 3 versus inverse temperature. In Fig. 2(a) and 2(b) $S^{-1}(0)$ from the two blend systems are shown as determined at ambient pressure field mixed with five given solvent contents. In both samples a higher solvent content causes a strong decrease of the critical temperature, thereby improving the miscibility. Figures 3(a) and 3(b) demonstrate the effect of pressure; increasing pressure always enhances the critical temperature, as is generally expected from the Clausius–Clapeyron equation.[28,29] All susceptibilities presented in Figs. 2 and 3 were analyzed with the asymptotic crossover function of Eq. (11) as shown by the solid lines; the agreement between experiments and theory is excellent. From the fit we obtain the critical temperature, the Ginzburg number, and the mean-field and 3D-Ising critical amplitudes. The critical temperature is defined to occur at $S^{-1}(0)=0$, which corresponds to an infinite correlation length. In nearly all samples we could approach the critical condition of $S^{-1}(0)=0$ very well, indicating that the

experiments were performed very near the critical composition.

The inverse square of the correlation length ξ have been plotted in Figs. 4 and 5 versus inverse temperature; the experimental conditions of the correlation length corresponds to those of the susceptibility in Figs. 2 and 3. The solid lines in Figs. 4–6 represent fits with the crossover function in Eq. (6) using the same Ginzburg number and critical temperature as for the corresponding $S(0)$. The correlation length shows qualitatively the same behavior as $S(0)$ and leads to a new parameter, the critical amplitude ξ_0.

B. Ginzburg number

The Ginzburg number of various polymer blends has been depicted in Fig. 6 versus the average degree of polymerization. These data were determined over recent years mainly by SANS from fitting the crossover function of Eq. (11).[3,6,7,24,30–33] All data are lying between the two dashed lines representing a power law with the exponents of -1 and -2. The N^{-1} power behavior is consistent with the Ginzburg criterion in Eq. (10) in case of a zero noncombinatorial entropy of mixing ($\Gamma_\sigma=0$).[1] A finite Γ_σ and the large exponent in Eq. (10) are the reason for the relatively large values of Gi which could become even an order of magnitude larger
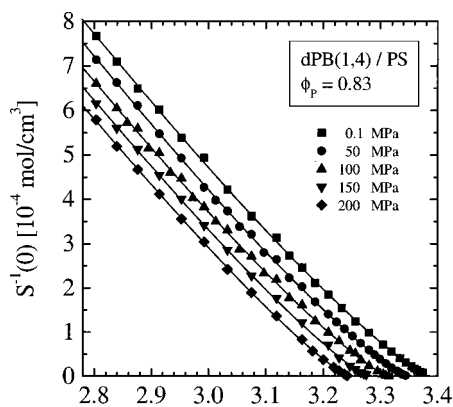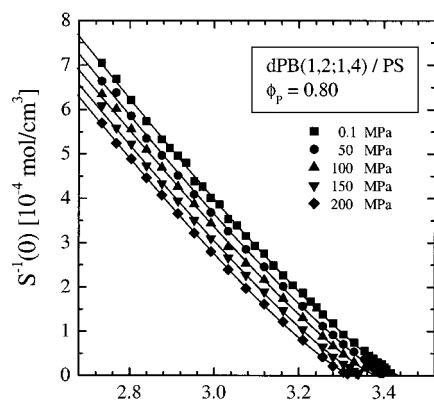
FIG. 3. $S^{-1}(0)$ vs inverse temperature for different pressure fields of dPB(1,4)/PS with a polymer concentration of (a) 0.83. In all cases the pressure field leads to a worse polymer compatibility. In (b) similar experiments are shown for the dPB(1,2; 1,4)/PS blend.

FIG. 4. Inverse square of correlation length vs $1/T$ in correspondence to $S^{-1}(0)$ in Fig. 2.

in comparison with a typical $Gi \cong 10^{-2}$ of low molecular liquids; the Ginzburg number of polymer blends with N larger than 100 becomes equal and less than 10^{-2}; on the microscopic scale it is related at least in some part to the compressibility or free volume because of the relationship between compressibility and Γ_σ in the corresponding equation of states theories.[19] A first experimental proof of these relationships was the reported decrease of the Ginzburg number in a pressure field in Ref. 31.

The effect of solvent on Gi is shown in Fig. 7 for the two dPB/PS blends. Gi has been plotted versus the total polymer concentration in double logarithmic scale. A strong increase of Gi with solvent content is observed; at 80% polymer concentration a 5 to 10 times larger Gi is observed than in the pure blend. The Ginzburg numbers approximately follow a scaling behavior with a large exponent between -8.6 and -10.8. This observation is in strong contrast to theory predicting a -2 power-law behavior; the estimation of the -2 exponent was performed within mean-field approach on the basis of bare parameters from the Ginzburg–Landau Hamiltonian.[22] Similar experiments by Nose *et al.* with light scattering also show deviations from the -2 power law; in Ref. 23 (their Fig. 7) they show Gi from two samples with much larger solvent concentrations of about 50% and 80%,
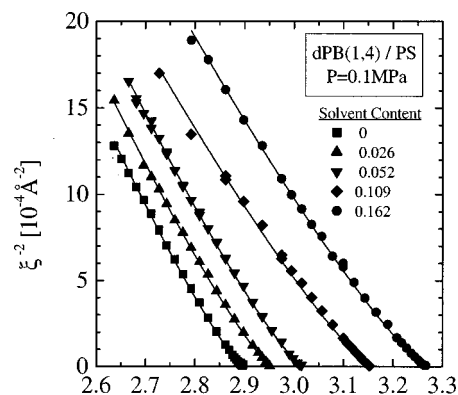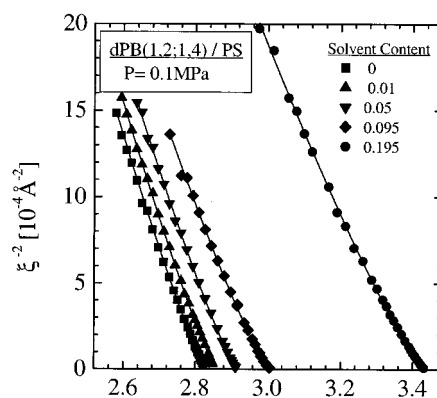
and find a power law with an exponent of about -4.

In Figs. 8(a) and 8(b) the behavior of the Ginzburg number in a pressure field has been depicted for the two blend systems with 0%, 5%, and 20% (16%) solvent concentration. In all cases we find a strong decrease of Gi in large pressure fields and a stronger effect of the more dilute blend–solvent samples.

C. Critical amplitudes of susceptibility

The critical amplitudes of the susceptibility in mean-field and 3D-Ising approximation have been plotted in Fig. 9 as a function of solvent content. While C_+ shows a slight increase, which is about 20% at 0.2 solvent content and linear within the plotted band, the mean-field amplitudes show a decrease, which is linear for the dPB(1, 4)/PS and shows some oscillatory behavior for the dPB(1, 2; 1, 4)/PS blend. For the PB(1, 4)/PS sample in double logarithmic representation of the same data versus Φ_P, one would obtain the exponents of (1.1 ± 0.1) and $-(1 \pm 0.25)$ for mean-field and Ising regimes, respectively, while for the PB(1,2;1,4)/PS blends the corresponding exponents of (0.35 ± 0.5) and $-(2.4 \pm 0.5)$. Putting these exponents into the expressions for Gi one gets the corresponding exponents in Fig. 7 which is quite trivial as C_+ is a derived number [see Eq. (8)].

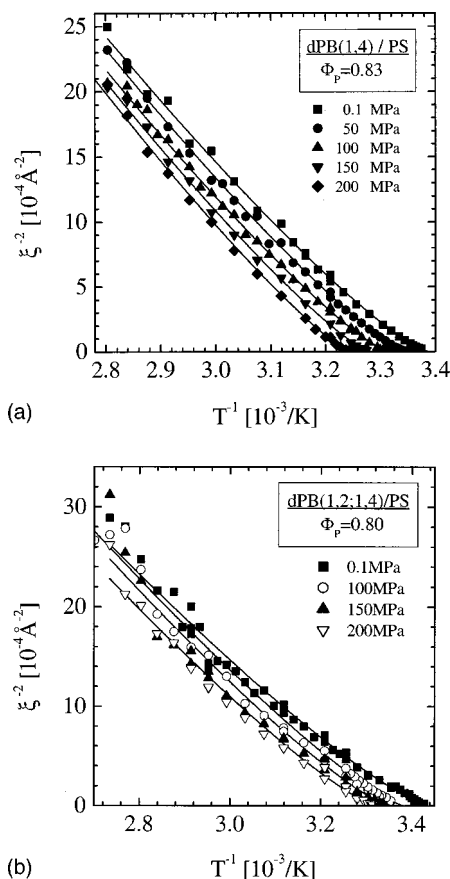In Figs. 10(a) and 10(b) the pressure dependence of the critical amplitudes of both polymer blends with different

(a)

(b)

FIG. 5. Inverse square of correlation length vs $1/T$ in correspondence to $S^{-1}(0)$ in Fig. 3(a) and (b).
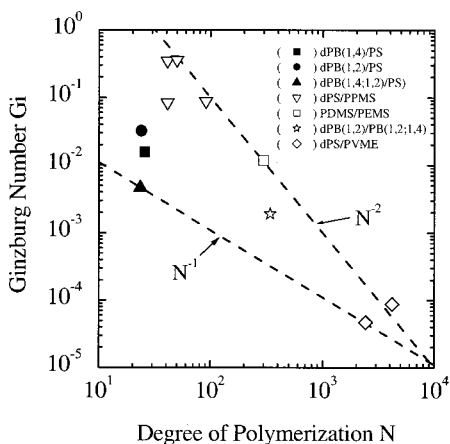

FIG. 6. Ginzburg number vs degree of polymerization from different polymer blends determined over recent years. The N^{-1} was predicted as a universal law for incompressible polymer blends. In reality compressibility expressed by a noncombinatorial entropy of mixing has a strong influence on Gi.
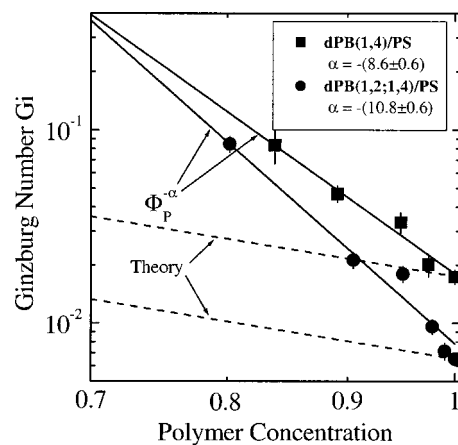

FIG. 7. Ginzburg number vs total polymer concentration. Gi in both blends shows scaling behavior with exponent between -9 and -11, which is in strong contrast to theoretical estimation of -2, which relies on purely mean-field or bare parameters.

D. Critical amplitude of correlation length

The critical amplitude of the correlation length ξ_0 of both blends has been plotted in Fig. 11 versus the solvent concentration. The mean-field amplitude of both blends is the same within the experimental uncertainty and decreases

amounts of solvent are shown. The Ising critical amplitude C_+ is constant with pressure, while a systematic increase of the corresponding mean-field number C_+^{MF} with pressure is observed. The last observation is quite plausible as according to Eq. (9) C_+^{MF} is inversely proportional to Γ_σ.
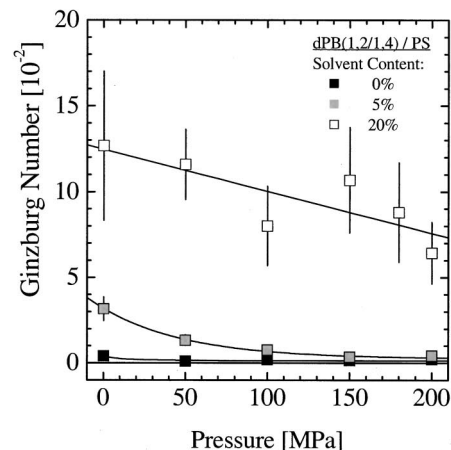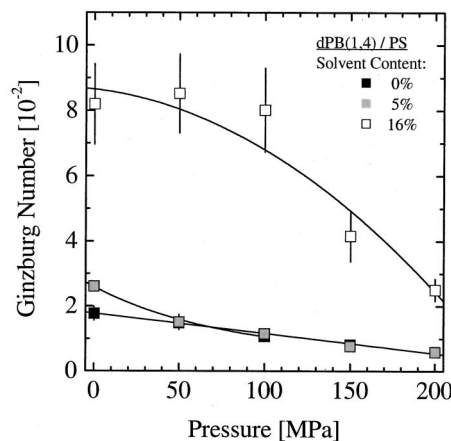

FIG. 8. Ginzburg number vs pressure field and for three solvent concentrations in the (a) dPB(1,4)/PS and (b) dPB(1,2;1,4)/PS blends. In all cases pressure reduces the Ginzburg number and thereby the range of strong influence of thermal fluctuations around T_C.
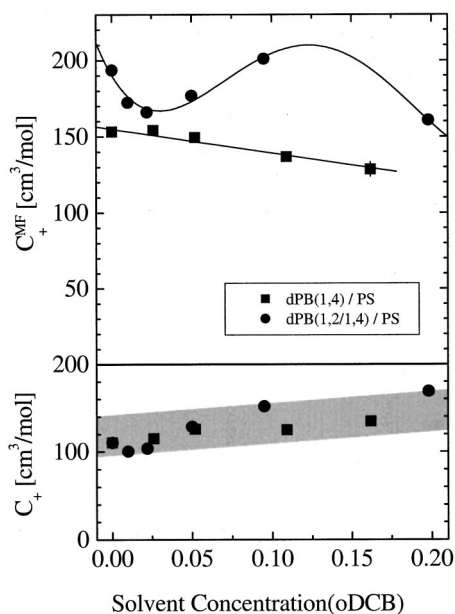
FIG. 9. Critical amplitudes C of $S(0)$ vs solvent concentration. The "Ising" C slightly increases by about 10%; the mean-field amplitude show a relatively stronger decrease of 20%. The dPB(1,2;1,4)/PS shows a characteristic oscillation at lower concentrations.

by about 10% for a 20% solvent content. The "Ising" amplitudes are smaller than their mean-field numbers and, instead, they increase with solvent content by about 20%. In addition, they differ in both blends; the PB(1, 4)/PS blend shows slightly more than 10% larger values. The mean-field amplitude ξ_0 is proportional to the polymer radius of gyration and the square root of $(1+\Gamma_\sigma/\Gamma_C)$ [Eq. (9)]; the polymer parameters are very similar (Tables I and II) and so the result of equal amplitudes is not surprising. The Ising critical amplitudes seem to depend more sensitively on the microstructure of the PB polymer component and may be affected by the smaller segment length of PB polymer chains with higher vinyl content; a 62% vinyl content PB shows a 9.3% smaller segment length than a 7% one (see also Table I).[34]

In Figs. 12(a) and 12(b) the pressue dependence of the critical amplitudes of both polymers with different amounts of solvent are shown. The Ising critical amplitudes ξ_0 decreases with pressure, whereas the mean-field critical amplitude ξ_0^{MF} increases with pressure. While the first observation can hardly be interpreted, the latter behavior will be explained in terms of R_g [see Eq. (9)], which will be discussed in Part II.

E. Renormalization of 3D-Ising exponents

The susceptibility and correlation length depicted in Figs. 2–5 show a transition from mean-field to 3D-Ising critical behavior which could mostly be well described by the crossover functions in Eqs. (6) and (11). This means that we can consider all samples as quasibinary blend systems. The only exception we found is the solvent-free dPB(1,4)/PS blend sample as plotted in Figs. 13(a) and 13(b) at about 2 K (Table III) above T_C a crossover to a critical behavior was observed showing the renormalized critical exponents ac-
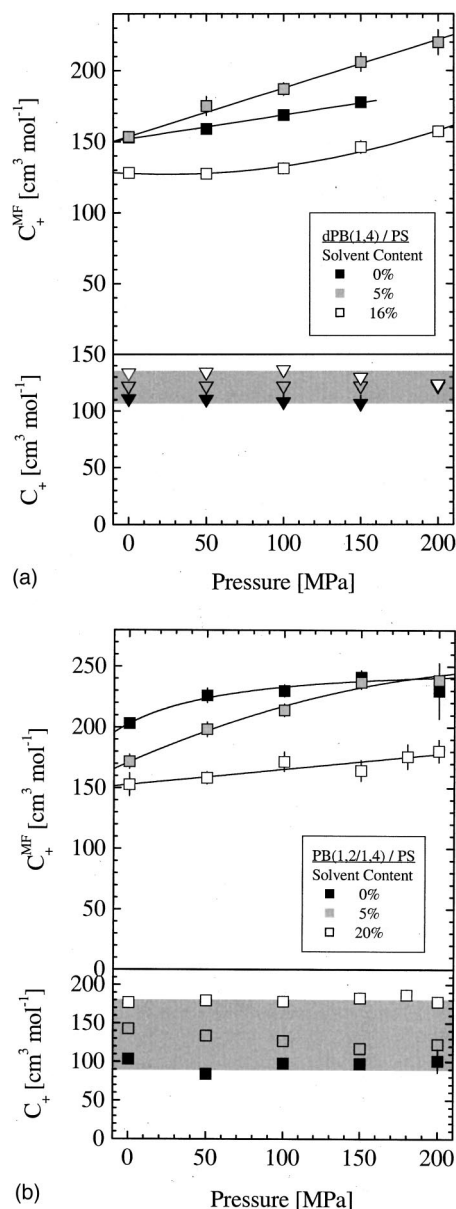

FIG. 10. Critical amplitudes of $S(0)$ of three solvent concentrations vs pressure for the two blends in (a) and (b). The Ising C_+ is constant with pressure, while for the mean field C an increase is observed.

cording to $\gamma/(1-\alpha)$ and $\nu/(1-\alpha)$ of susceptibility and correlation length, respectively, and the critical exponent of the specific heat $\alpha=0.11$, and, as indicated by the dotted lines, a slight enhancement of the critical temperature. It furthermore appears that the correlation length is more sensitive to this crossover transition.

In some way these results are consistent with former experiments on dPB(1,2)/PB plotted in Figs. 14.[33] In this sample we also found a transition to the renormalized Ising behavior, however, over a much larger temperature range of about 18 K (Table III) and an appreciable decrease of T_C. Figure 14(b) shows a double logarithmic presentation of L_2 determined in Eq. (4) versus the correlation length and which should follow a scaling law according to $\xi^{\eta=(2-\gamma/\nu)}$ and which should be insensitive to the renormalized 3D-Ising crossover behavior.[32] The position of the crossover at T^{**} is
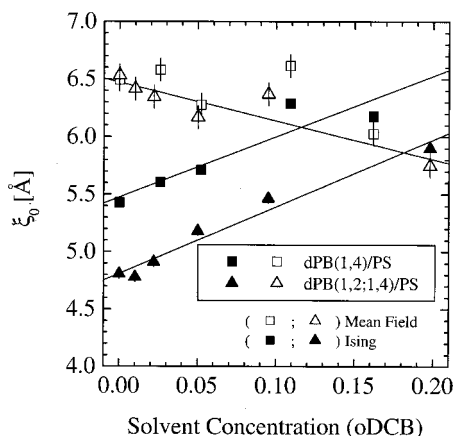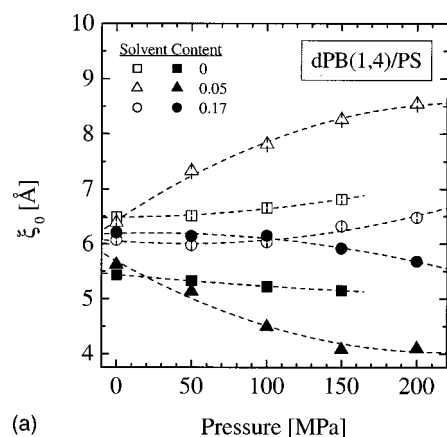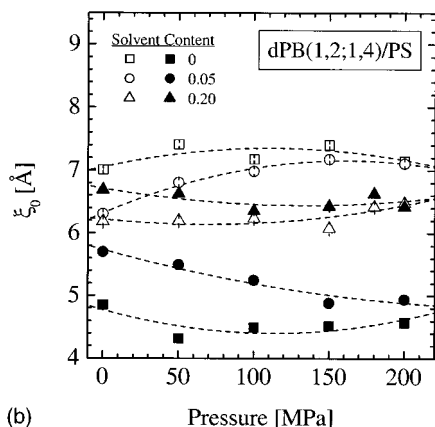
FIG. 11. Critical amplitude of the correlation length vs solvent concentration similar to the C in Fig. 9. The mean-field values of both blends are roughly the same and are decreasing. The Ising numbers of both blends are different and are increasing by about 20%.

indicated by the dashed line; no transition is visible. From these findings there appears in "pure" polymer blends another "third" component active which can only be identified with free volume.
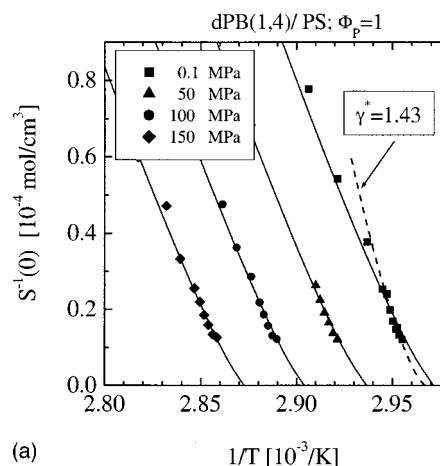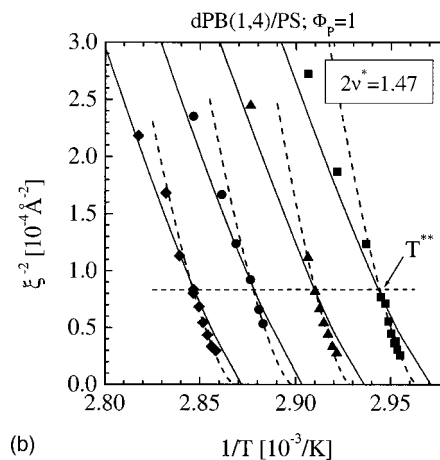

FIG. 12. Critical amplitudes of correlation length vs pressure for the two blends in (a) and (b) and with three solvent contents. Globally, all mean-field and Ising numbers increase and decrease with pressure, respectively.

FIG. 13. Near the critical point of the susceptibility (a) and correlation length (b) of PB(1,4)/PS blend [see Fig. 5(a)]. Very near the critical temperature a crossover to the Fisher renormalized behavior is observed. Such a behavior was more expected but not observed in the blend–solution system. So, it seems that free volume in the form of void density starts to fluctuate near T_C.

V. SUMMARY AND DISCUSSIONS

We presented extensive research on two dPB/PS blends mixed with different amounts of the nonselective ortho-dichloro-benzene up to 20%. Two polybutadiene components different in vinyl content, namely dPB(1,4) and dPB(1, 2; 1, 4) with, respectively, 7% and 54% vinyl content were chosen; both PB components were deuterated for good scattering contrast conditions. These samples were measured with small angle neutron scattering in varying temperature and pressure fields. The thermal composition fluctuations are characterized by the susceptibility $S(0)$ and the correlation length ξ; both parameters are well described in terms of a universal crossover function describing the transition from mean-field to 3D-Ising behavior asymptotically close to the critical temperature. This crossover function is a universal function of the Ginzburg number because the correlation length is the only relevant length scale.[12–14] The same critical temperature and Ginzburg number were found for the susceptibility and correlation length.

Here in Part I we concentrate on the discussion of the critical crossover behavior expressed by the critical

TABLE III. Parameters of Fisher "renormalized" critical behavior.

Sample	T^{**} [°C]	T_C [°C]	$\gamma^* = 2\gamma/(1-\alpha)$	$2\nu^* = 2\nu/(1-\alpha)$	$\eta = (2-\gamma/\nu)$
PB (1,4)/PS	66.2	64.2	1.43	1.47	0.054
PB(1,2)/PS	125	107.1	1.39	1.43	0.056

amplitudes of susceptibility and correlation length and the Ginzburg number, while the Flory–Huggins interaction parameter and critical temperature is discussed in Part II. All parameters have to be considered by two aspects, namely, their dependencies on solvent content and on pressure.

(1) The critical amplitudes of susceptibility and correlation length are depicted in Figs. 9 to 12. The mean-field amplitudes are expressed in terms of the FH parameter and radius of gyration in Eq. (9) and will be discussed separately in Part II. For the "Ising" amplitudes there is no theory available. Quite generally, they reflect the microscopic nature of a system; various ratios of critical amplitudes leads to universal numbers[35] and in polymer blends C_+ and ξ_0 follow the respective scaling relations according to $V^{(2-\gamma)}$ and $V^{(1-\nu)}$.[17] For the susceptibility critical amplitude we find a slight increase with solvent content but no pressure dependence. A stronger change was observed for the correlation length critical ampli-

tude: An 11% larger Ising number has been observed for the dPB(1,4)/PS blend and about a 20% linear increase with solvent content. Pressure always induces a decrease which sometimes looks rather irregular, e.g., the 5% sample [Fig. 12(a)] shows a stronger decrease than the pure blend and the 17% sample.

(2) A remarkably strong increase with solvent content was found for the Ginzburg number as depicted in Fig. 7; there, a power law between −9 and −11 is observed. This result is in strong contrast to theoretical mean-field predictions proposing an exponent of −2.[22,23] Considering the Ginzburg criterion in Eqs. (8) and (10), it seems that the noncombinatorial Flory–Huggins entropy of mixing Γ_σ must have an important influence on Gi. Generally, pressure and solvent addition lead to opposite effects on the Ginzburg number, which might be caused by, respectively, polymer compression and dilution.

(3) In the two PB(1, 4)/PS and PB(1, 2)/PS blends without any solvent, we found near T_C a further crossover to the so-called renormalized Ising behavior showing the renormalized critical Ising exponents in accordance with Eq. (12) (see Figs. 13 and 14). The results from the PB(1, 2)/PS blend were obtained from former SANS experiments.[33] This observation appears surprising as we originally expected such a behavior in the blend–solvent systems. The crossover to a renormalized 3D-Ising behavior was extensively studied in polymer blend–solution mixtures by Nose and co-workers.[23] They found a similar crossover behavior in strong asymmetric polymer blends mixed with a solvent but not such a transition in symmetric blends as ours. In this respect our results are consistent with those of Nose *et al.* However, if we look to their data obtained from asymmetric blend–solvent samples a large effect was found if a highly selective solvent was chosen, and only a small effect was observed in case of a nonselective solvent. This observation seems rather clear as polymer composition fluctuations and solvent concentration are strongly correlated in case of highly selective solvents. Their results look qualitatively very similar to our findings; the dPB(1, 4)/PS blend shows a crossover very near T_C similarly to their nonselective solvent case, while the crossover in dPB(1, 2)/PS qualitatively agrees with their system mixed with a highly selective solvent. Voids or free volume are present in compressible polymer blends; so, the free volume might represent a third component leading to the observed renormalized critical behavior. From these experimental findings one may speculate about a possible selectivity of voids in polymer blend systems (see the corresponding discussions in Part II).
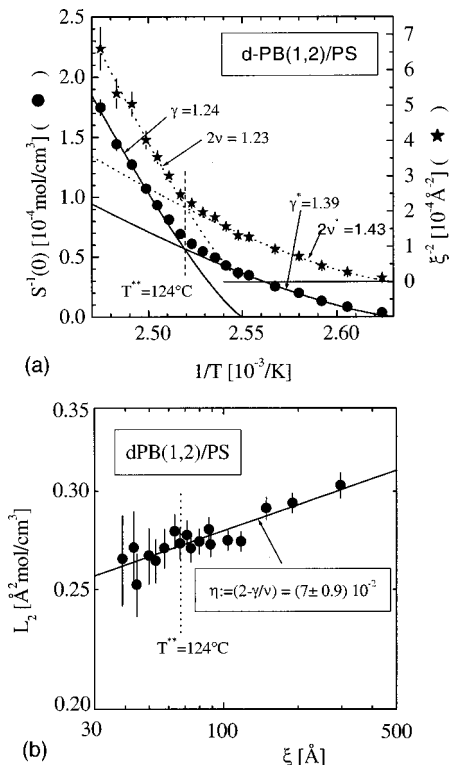

FIG. 14. (a) Transition of $S(0)$ and ξ^2 to a Fisher renormalization of the dPB(1,2)/PS blend from a former study. In this system the effect is very much larger. Comparing these data with studies of asymmetric polymer blend–solvent system, one could speculate that voids are more selective to the PB(1,2) than PB(1,4) monomers. (b) L_2 [Eq. (4)] vs ξ in double logarithmic scale. The slope of the fitted straight line gives the Fisher exponent η regardless of the crossover at T^{**}.

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