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Ginzburg Number and Phase Behavior of Binary Polymer Blends in Pressure Fields

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SUMMARY: In some polymer blends the temperature and pressure dependence of thermal composition fluctuations have been measured with small angle neutron scattering. The Ginzburg number Gi, the Flory-Huggins parameter Γ, and the phase boundaries were determined for pressure fields up to 150 MPa. In polymer blends the compressibility leads to a strongly increased Gi which could be appreciably larger than in low molecular liquids and which decreases with increasing pressure fields. Usually, the phase boundaries of UCST as well as of LCST blends shift with pressure to higher temperatures. One blend having PDMS as one component, however, shows an abnormal decrease of the phase boundaries with increasing pressure. The Clausius-Clapeyron equation correctly predict from the experimentally determined Γ and Gi the observed pressure dependence of the phase boundaries.

Introduction

Besides its technical relevance polymer blends represent model systems used in statistical physics for basic investigations of equilibrium and non-equilibrium properties. These are for instance the morphology of the possible phases, the degree of thermal composition fluctuations, and the kinetics of phase separation[1,2]. In Fig.1 a schematic phase diagram of a binary polymer blend is depicted. The binodal separates the one-phase and the two-phase regime at high and low temperatures. The spinodal separates the metastable from the unstable regimes and meets the binodal at the critical temperature. Phase separation occurs by nucleation and growth and by spinodal decomposition after a rapid change of an external field as temperature or pressure shifting the sample from a state within the one-phase regime into the metastable and unstable regimes, respectively. The spinodal appears as a sharp interface only within mean field approximation when thermal composition fluctuations are weak. If thermal composition fluctuations become strong near the critical temperature the spinodal line

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is smeared out and a distinction between the metastable and unstable processes of phase separation cannot be made any more[2-4]. The area of the phase diagram where thermal fluctuations are relevant is determined by the Ginzburg number Gi. The value of Gi is evaluated from the Ginzburg criterion which for polymer blends was first derived by deGennes[1]; it follows a universal scaling behavior according to $\mathrm{Gi} := |T^* - T_C| / T^* \propto N^{-1}$ with the degree of polymerization N and the crossover temperature T^*. The crossover regime is indicated in Fig. 1; its lower limit is determined by T^* defined from a 10% deviation of the measured susceptibility from the corresponding 3d-Ising behavior[5-7]. As in low molecular liquids Gi is of the order of 10^{-2} a roughly N times smaller value for Gi is expected in polymer blends[6]. This means that polymer blends should in principle be sufficiently well described within the mean field approximation except within the very near neighborhood of the critical point. The mean field theoretical approach for the thermodynamic description of polymer blends is the well known Flory-Huggins theory[1,2]. Usually, polymer blends showing a two-phase regime at low temperature (UCST) must have a relatively low molecular weight in order to have the critical point and miscibility region at a moderate temperature where the polymers

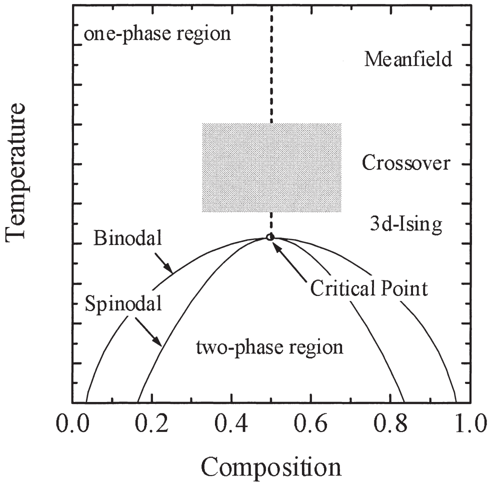

Fig. 1: Schematic phase diagram of a binary polymer blend. Thermal composition fluctuations are usually measured at critical composition along the dashed line. Mean field approximation and 3d Ising behavior is found far above and near the critical temperature, respectively.
The position of the crossover regime is estimated by the Ginzburg criterion.

will not be destroyed. In this respect only a few binary polymer blends of large molecular weight of the order of 10^5 to 10^6 g/mol are miscible; those blends must have either an extremely small or a negative interaction parameter (Flory-Huggins parameter) as observed in isotopic blends of d-PS/PS and in LCST blends showing phase decomposition at high temperatures, respectively8). So, for most UCST blends the influence of thermal composition fluctuation should be relevant over an extended temperature range with the corresponding limited validity of the Flory-Huggins theory.

In this manuscript we will give a short overview on measurements of thermal composition fluctuations within the one-phase regime in different binary polymer blends using the small angle neutron scattering (SANS) technique. All samples were chosen of near critical composition as shown by the dashed line in Fig.1 in order to approach the critical point as near as possible. We determined the binodal and spinodal phase boundaries, the Flory-Huggins interaction parameter, and the Ginzburg number. We will give first a theoretical background, then a collection of Ginzburg numbers from several polymer blends and finally show the effects of external pressure fields on the phase boundaries and the Ginzburg numbers. It will be demonstrated that polymer blends are much more influenced by thermal composition fluctuations originated by the compressibility or polymer packing.

Structure Factor S(Q)

The structure factor S(Q) measuring thermal composition fluctuations in the disordered state of polymer blends can be described by the Ornstein-Zernike approximation according to

$$S^{-1}(Q) = S^{-1}(0) + AQ^2 \qquad (1)$$

if the experiments are performed at scattering vectors Q sufficiently small in comparison with the inverse correlation length ξ of the thermal composition fluctuations1-3). An experimental example from a d-PB/PS blend at constant temperature and different pressure fields is shown in Fig.2. The data which are depicted in a Zimm representation, e.g. $S^{-1}(0)$ versus Q^2, appear as straight lines in accordance with Eq.(1). The degree of thermal fluctuations increases with increasing pressure according to a shift of the phase boundaries to higher temperatures. From the fit of S(Q) two parameters are obtained, the slope A and the extrapolated S(0). The slope

A is related to the chain flexibility according the random phase approximation and S(0) represents a susceptibility according to

$$S^{-1}(0) = \delta^2(\Delta G / RT) / \delta\Phi^2 \qquad (2)$$

as it is related to the Gibbs free energy of mixing ΔG (R gas constant, Φ composition) [1,2].

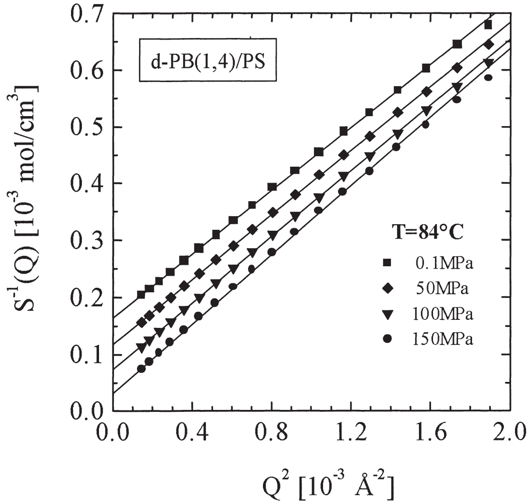

Fig. 2: Structure function in Zimm representation at fixed temperature and different strong pressure fields

Eq.(2) represents the Gibbs condition for the stability of the disordered phase; it is positive in the one phase regime, becomes zero at the spinodal and the critical point, and becomes negative in the unstable part of the phase diagram below the spinodal (see Fig.1). The susceptibility will be discussed in the following and from it thermodynamic parameters as the Flory-Huggins parameter will be derived.

Susceptibility S(0) in a Pressure Field

The susceptibility extrapolated from S(Q) as shown in Fig.2 is plotted in Fig.3 versus the inverse temperature for pressure fields between 0.1 and 150 MPa. The spinodal (critical) temperature is found from $S^{-1}(0)=0$ and the binodal from a deviation of the experimental data from the plotted solid lines. Entering the two-phase region, one measures within the Q range of Fig.2 only the fluctuations within the precipitated domains as the scattering from the shape of the order of μm large domains is outside the accessible Q range of the SANS method[10)]. Below the critical temperature the composition fluctuations within the precipitated domains become smaller with decreasing temperature. The solid lines describing the experimental susceptibility in Fig.3 are the result of a fit of a crossover function derived by Belyakov and Kiselev[5)]

$$\hat{t} = \left(1 + 2.333\hat{S}(0)^{\Delta/\gamma}\right)^{(\gamma-1)/\Delta} \times \left[\hat{S}^{-1}(0) + \left(1 + 2.333\hat{S}(0)^{\Delta/\gamma}\right)^{-\gamma/\Delta}\right] \tag{3}$$

according to Eq.(3) with $\hat{t} = t/Gi$ and $\hat{S}(0) = S(0)Gi/C_{MF}$, the renormalized reduced temperature $t := (T - T_C)/T$ and the susceptibility, respectively. The Ginzburg number Gi and the critical amplitude of the susceptibility of the mean field approximation C_{MF} according to $S^{-1}(0) = C_{MF}^{-1}t$ are the two fit parameters, γ and Δ are critical exponents of the 3d-Ising model[11)]. As seen from the correspondence of the experimental data and the fit of Eq.(3) the crossover function gives a good description of thermal composition fluctuations within the total disordered regime. Well above and very near the critical temperature, S(0) is described by

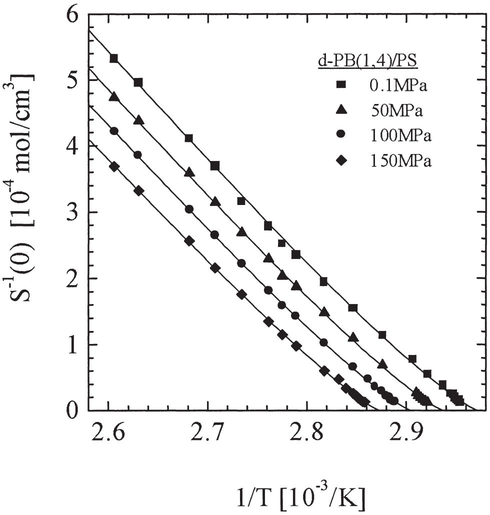

Fig. 3: Inverse susceptibility versus inverse temperature in different external pressure fields.

the universality classes of the mean field approximation and the 3d-Ising model, respectively. In both cases the susceptibility is described by a scaling law according to $S(0) = C t^{-\gamma}$ with $C=C_+$ and $\gamma=1.24$ in the 3d-Ising and $C=C_{MF}$ and $\gamma=1$ in the mean field case[11)]. The mean field critical amplitude is evaluated from the Flory-Huggins model according to[7)]

$$C_{MF} = \frac{1}{2\left|(2/V_w) + \Gamma_\sigma\right|} = T_C^{MF} / 2\Gamma_h \tag{4}$$

with the entropic term of the Flory-Huggins parameter according to $\Gamma = \Gamma_h / T - \Gamma_\sigma$ and $2/V_w$ representing Γ at the critical temperature in case of equal weight averaged molar volumes V_w for both polymer components. So, the Flory-Huggins parameter Γ can be evaluated from Eq.(4) and the two fit parameters obtained from the experimental S(0) and Eq.(3).

The Ginzburg Numbers of Polymer Blends

The Ginzburg numbers measured so far by us have been plotted in Fig. 4 versus the mean

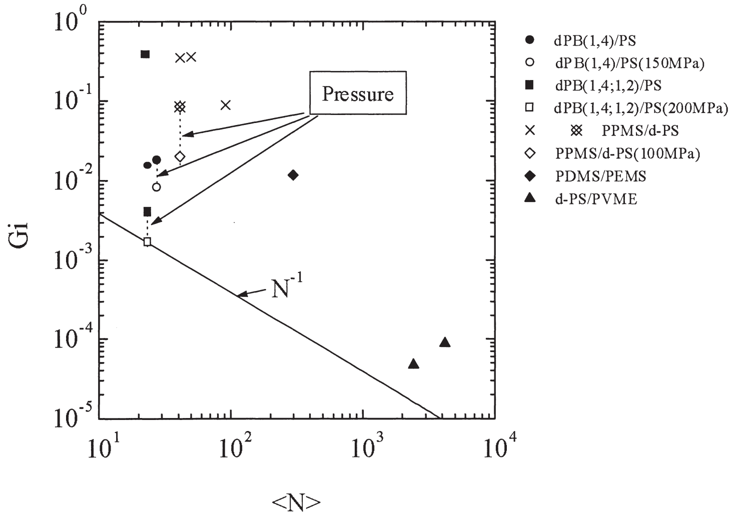

Fig. 4: Ginzburg number for various polymer blends and in a pressure field

degree of polymerization. A strong decrease of Gi with <N> is observed. In addition three examples of a pressure dependent Gi have been given. The Ginzburg criterion obtained from the crossover function is determined by the critical amplitudes of the S(0) according to[5-7]

$$\mathrm{Gi}=0.069(C_+/C_{\mathrm{MF}})^{1/(\gamma-1)} \tag{5}$$

which in case of $\Gamma_\sigma = 0$ becomes $\mathrm{Gi} \propto V^{-1} \propto N^{-1}$ being the expression derived by deGennes[1] and plotted in Fig.4 as a solid line. The entropic Γ_σ has a strong effect onto the value of Gi which can be understood by the large exponent $1/(\gamma-1) = 4.17$. The data for Gi in Fig.4 clearly show that thermal composition fluctuations in binary polymer blends are not negligible al least for conventional partially miscible blends of UCST type having a maximum degree of polymerization of the order of N=100. Those blends could have a Gi orders of magnitude larger than the typical value $\mathrm{Gi} \cong 10^{-2}$ for low molecular liquids. An interpretation of this large Gi is related to an understanding of the phenomenological entropic term Γ_σ. According to equation of states theories Γ_σ is related to the compressibility or packing of the chains[12]. This aspect of Γ_σ can experimentally be studied in an external pressure field and thereby with more strongly packed polymer chains[12,13]. According to the expected $\partial|\Gamma_\sigma|/\partial P \leq 0$ a decrease according to $\partial \mathrm{Gi}/\partial P \leq 0$ is expected and indeed observed as shown in Fig. 4 for three different blends systems. This means that at large pressure field polymer blends better fulfill the condition of the Flory-Huggins theory.

Pressure dependent Phase Diagram and Flory-Huggins Parameter

The change of the phase boundaries with pressure is expressed by the Clausius-Clapeyron equation which has been formulated for polymer blends according to[14]

$$\Delta T_B/\Delta P = [\partial\Gamma_h/\partial P - T_B\partial\Gamma_\sigma/\partial P]/(\Gamma_h/T_B) - K\,\partial\mathrm{Gi}/\partial P. \tag{6}$$

The first term describes the shift of the phase boundaries by the Flory-Huggins parameter and the second by the change of Gi according to the stabilization effect of the thermal fluctuations. In a scattering experiment the phase boundaries, the Ginzburg parameter, and the Flory-

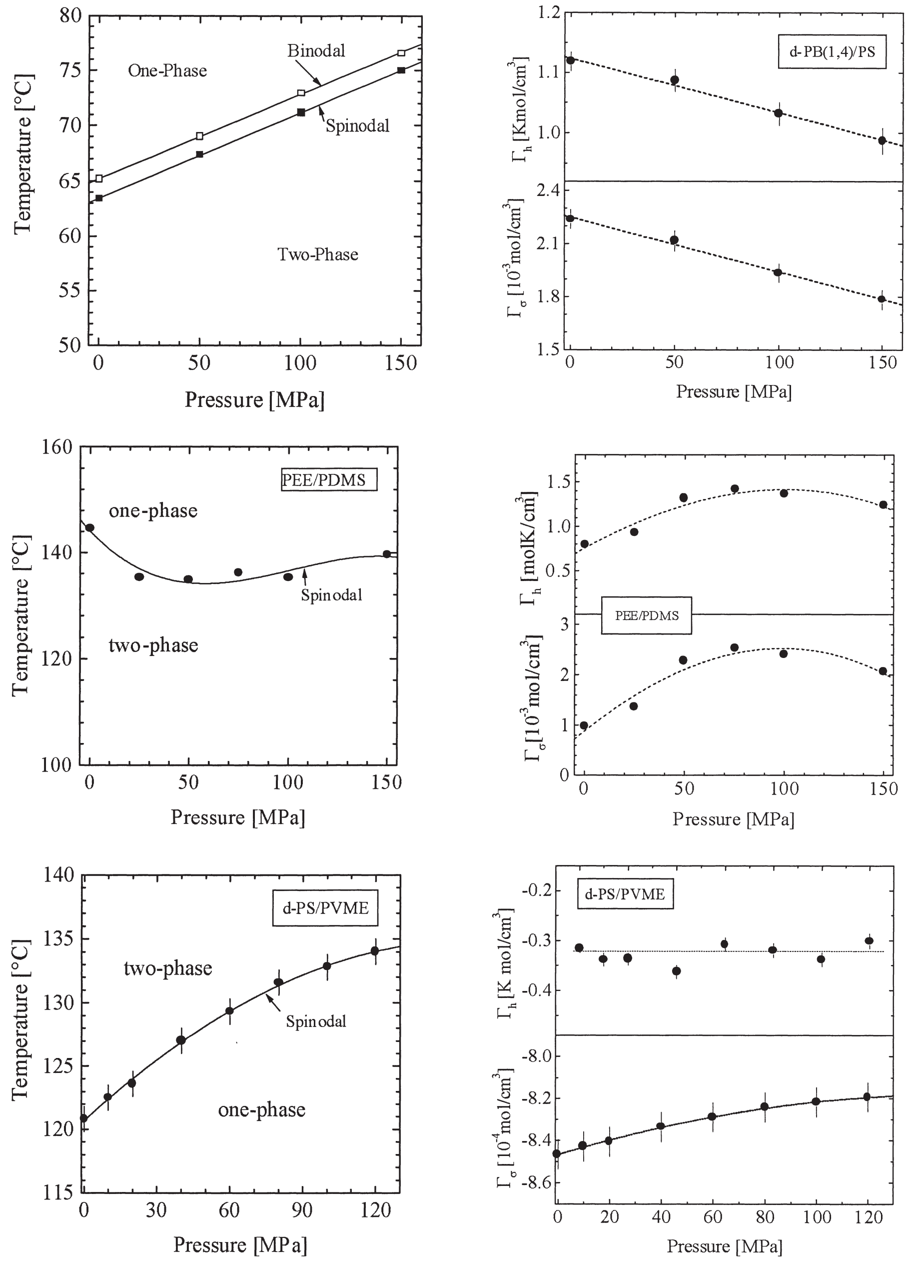

Fig. 5: Spinodal phase boundary of near critical polymer blends and the corresponding Flory-Huggins parameter versus pressure.

Huggins parameter are determined independently. So, the Clausius-Clapeyron equation leads to an independent consistency check. In Fig.5 the pressure dependent phase boundaries of the three characteristic different polymer blends of critical composition and their corresponding Flory-Huggins parameters have been plotted. There are two UCST blends, namely PB/PS and PEE/PDMS with different pressure dependencies and the LCST system d-PS/PVME. The PB/PS shows a linear increase of binodal and spinodal and a corresponding decrease of the enthalpic and entropic Flory-Huggins parameter terms. The PEE/PDMS on the other hand shows at low pressure fields an unusual decrease and at higher pressure a slight increase of the phase boundaries accompanied by a increase and decrease of the term of Γ similar to observations in ref. [15)]. The LCST blend PS/PVME show the expected increase of the spinodal with pressure originated from the corresponding decrease of the absolute Γ_σ which is negative as it is the driving force for phase separation of a LCST system[8)]. In Table 1 the numerical numbers for the relevant interaction parameters in the Clausius-Clapeyron equation have been given for the three blends presented in Fig.5. The pressure dependent Ginzburg numbers show always a $\partial Gi / \partial P < 0$ and thereby in all cases a $\Delta T_B / \Delta P|_\Gamma > 0$. From the partial derivatives of Γ_h and Γ_σ with respect to pressure one gets the correct direction of T_B with pressure as experimentally observed in Fig.5.

Table 1. Flory-Huggins Parameter:

	Γ_h / T_B	$\partial \Gamma_h / \partial P$	$T_B \partial \Gamma_\sigma / \partial P$	$\Delta T_B / \Delta P$
d-PB/PS	>0	$-(9 \pm 0.6)10^{-4}$	$-(10.5 \pm 0.06)10^{-4}$	>0
d-PS/PVME	<0	$\cong 0$	$(1.5 \pm 0.08)10^{-4}$	>0
PEE/PDMS[*)]	>0	$(9 \pm 1.5)10^{-3}$	$(9.3 \pm 1.7)10^{-3}$	<0

[*)] For P<70 MPa

Conclusion

In this paper we present a SANS study of several polymer blends in an external pressure field and give an interpretation of the susceptibility S(0) in terms of a crossover function from which the Ginzburg number and the Flory-Huggins parameter Γ were evaluated. Our results can be summarized as follows: (1)Gi strongly depends on molecular weight. The observed values are much larger than expected from deGennes' estimation. SANS experiments in external pressure fields demonstrated, that Gi sensitively increases with the segmental entropy Γ_σ in accordance with the Ginzburg criterion of Eq.(5). (2)With increasing pressure the phase boundaries in UCST and in LCST blends usually shift to higher temperature. For the UCST blend PEE/PDMS a decrease of T_B with pressure is observed. (3)The evaluated Flory-Huggins parameters and Ginzburg numbers Gi as a function of pressure give consistently with the Clausius-Clapeyron equation the direction of change of the phase boundary observed by experiment.

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