

## Ginzburg criterion for the mean-field to three-dimensional Ising crossover in polymer blends

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(Received 26 September 1994)

Composition fluctuations within the mean-field and three-dimensional Ising range were measured in a homogeneous binary polymer blend by small angle neutron scattering as a function of temperature and pressure. The experimental data were analyzed in terms of the crossover function of Belyakov and Kiselev [Physica A **190**, 75 (1992)]. It is shown that the reduced-crossover-temperature, the Ginzburg number  $Gi$ , decreases with pressure sensitively, in accordance with the prediction of Belyakov and Kiselev. On the other hand, de Gennes' crossover criterion for polymer blends predicts an increase of  $Gi$  with pressure which contradicts our results.

PACS number(s): 05.70.Jk, 36.20.-r, 64.60.Fr

Composition fluctuations in homogeneous polymer blends are generally described by the universality classes of mean-field approximation and three-dimensional (3D) Ising behavior very far and very near the critical point of phase decomposition, respectively. The characteristic crossover temperature separating mean-field and 3D Ising behavior is proportional to the Ginzburg number,  $Gi$ , determined by the Ginzburg criterion [1]. For polymer blends, the Ginzburg number was derived by de Gennes [2], who showed that  $Gi$  depends on the molecular volume of the two components in a way that in high-molecular-weight systems the Ginzburg number is significantly reduced, thereby making the critical exponents mean-field-like even close to the critical point. It was therefore generally accepted that polymer blends are described by the Flory-Huggins mean-field theory [2]. Recent experiments on a variety of different polymer systems have, however, shown that the Ginzburg number in polymer blends is appreciably higher than that calculated from the de Gennes expression. It was observed, e.g., that (i) the high-molecular-weight blend of poly(vinylmethylether) and deuterated poly(styrene), PVME/d-PS, has a non-mean-field transition range of more than 2 K which should be compared with the predicted 0.1 K [3]; (ii) blends of polymers with a degree of polymerization  $N \cong 50$  can have a Ginzburg number more than one order of magnitude *larger* than the value typical for low molecular liquids [4]; and (iii) the microstructure of polymers can sensitively influence the crossover range [5]. The reason for the anomalously high values of  $Gi$  is suspected to be related to the packing of the polymers, i.e., the free volume in the blend [4–6]. Presently, two theoretical predictions are proposed for the Ginzburg criterion with different implications of  $Gi$  with respect to the free volume. The one expression is an extended theory based on the de Gennes derivation [2] given by Bates *et al.* [7,8]. The other expression is based on the crossover expression of Belyakov and Kiselev [9,4]. The two theories have different implications on  $Gi$  with respect to the free volume. In the present paper we provide alternative experimental studies in which the pressure dependence of the critical composition fluctuations near the critical composition, including the crossover regime, has been explored. Since pressure directly affects the free volume, these experiments will give direct insight into the

physics of the crossover behavior, and thus a better basic understanding of the Ginzburg criterion on high-molecular-weight materials.

Bates *et al.* [7] extended the de Gennes' derivation of  $Gi$  by including asymmetry (both polymer components can have a different molecular volume) in the polymer blend. In a formally modified form [8], their result for the Ginzburg number  $Gi$  reads as

$$Gi \propto \left[ \frac{1}{V_1 \phi_1^3} + \frac{1}{V_2 \phi_2^3} \right]^2 / [(1 + \Gamma_\sigma / \Gamma_c) \Gamma_c A^3 N_A^2], \quad (1)$$

where  $V_i$  and  $\phi_i$  is the molecular volume and concentration of component  $i$ . The quantity  $\Gamma_\sigma$  is the segmental entropic term of the Flory-Huggins parameter  $\Gamma = (\Gamma_h / T) - \Gamma_\sigma$ ,  $\Gamma_h$  being the corresponding enthalpic term.  $\Gamma_c$  is the Flory-Huggins parameter at the critical temperature  $T_c$  given by

$$\Gamma_c = 0.5 \left( \frac{1}{V_1 \phi_c} + \frac{1}{V_2 (1 - \phi_c)} \right).$$

$N_A$  is Avogadro's number and  $A$  is the slope of the inverse structure factor  $S^{-1}(Q) = S^{-1}(0) + A Q^2$  in the Zimm representation where  $A$  is proportional to the square of the correlation length of the composition fluctuations.  $Q$  is the scattering vector. For a blend with off critical composition,  $\Gamma_c$  in Eq. (1) must be replaced by the corresponding Flory-Huggins parameter at the spinodal,  $\Gamma_S$ , which is calculated from the same relationship as  $\Gamma_c$ .

A second expression for the crossover temperature was given by Belyakov and Kiselev [9] in context with a derivation of a crossover function for the susceptibility  $S(0)$ . This expression, reformulated in a more appropriate form in [4], reads as

$$Gi = 0.069 (C / C_{MF})^{1/(\gamma-1)}, \quad (2)$$

where  $C$  and  $C_{MF}$  are the critical amplitudes of  $S(0)$  in the asymptotic 3D Ising and mean-field regimes, respectively. The amplitude  $C_{MF}$  is evaluated from the Flory-Huggins

TABLE I. Sample parameters:  $\phi=0.5$ ,  $\Gamma_c=4.84\times 10^{-4}$  mol/cm<sup>3</sup>,  $\langle N \rangle=37.8$ , and  $\langle N \rangle=(\phi_2/N_1+\phi_1/N_2)^{-1}$ .

System	$M_w$ (g/mol)	$M_w/M_n$	$V_w$ (cm <sup>3</sup> /mol)	$N$
PPMS	4530	1.22	3960	33.3
d-PS	4880	1.04	4320	43.6

theory as  $C_{MF}=0.5/|\Gamma_\sigma+\Gamma_c|$ , while  $C\propto N^{(1-\gamma)}$  [10] follows a scaling law with the critical 3D Ising exponent of  $S(0)$ , namely  $\gamma\cong 1.24$ .

If one compares the two expressions for the Ginzburg criteria [Eqs. (1) and (2)] for  $\Gamma_\sigma\ll\Gamma_c$ , one gets the same scaling law, namely  $Gi\propto V^{-1}$  as predicted by de Gennes [2]. This form of the criterion is universal in the sense that it is inversely proportional to the molecular volume. For  $|\Gamma_\sigma|\geq\Gamma_c$ , on the other hand, the cases Eqs. (1) and (2) are different and no scaling law is observed. The striking difference is their dependence on the segmental entropy term  $\Gamma_\sigma$ . While Eq. (1) leads to a negative derivative  $\partial Gi/\partial|\Gamma_\sigma|$ , Eq. (2) gives a positive value. As discussed in [11]  $\Gamma_\sigma$  is related to the packing or the free volume of the blend. Therefore, the absolute value of  $\Gamma_\sigma$  is expected to decrease with pressure, namely  $\partial|\Gamma_\sigma|/\partial P<0$ , and the two expressions for  $Gi$  lead to an opposite pressure dependence. From experimental studies of the pressure dependence of  $Gi$  it is therefore possible to exclude one of the proposed expressions.

In this paper we report small angle neutron scattering (SANS) experiments in the near critical mixture of poly(phenylsiloxane) and deuterated poly(styrene), PPMS/d-PS. We have measured the composition fluctuations in the homogeneous phase at three pressures, ranging from 1 to 1000 bar, as a function of temperature in a range of about 50 K above the critical temperature  $T_c$ . The relevant experimental quantity is the extrapolated structure factor  $S(Q\rightarrow 0)$ . According to the fluctuation-dissipation theorem [2]  $S(0)$  is the generalized susceptibility, described by the crossover function in the homogeneous part of the phase diagram

$$\hat{\tau}=[1+2.333\hat{S}(0)^{\Delta/\gamma}]^{(\gamma-1)/\Delta}\{\hat{S}^{-1}(0)+[1+2.333\hat{S}(0)^{\Delta/\gamma}]^{-\gamma/\Delta}\} \quad (3)$$

as derived by Belyakov and Kiselev [9] with  $\hat{\tau}=\tau/Gi$ ,  $\tau=(T_c^{-1}-T^{-1})/T_c^{-1}$  being the reduced temperature, and  $\hat{S}(0)=S(0)Gi/C_{MF}$ . Equation (3) is a universal function of  $\hat{S}(0)$  and  $\hat{\tau}$  with  $Gi$  and  $C_{MF}$  as the characteristic parameters of the system.  $Gi$  is the reduced crossover temperature where the crossover function Eq. (3) deviates 10% from the asymptotic 3D Ising scaling law:  $S^{-1}(0)=C^{-1}\tau^\gamma$  [12]. This form of the crossover function was successfully applied to SANS and light scattering data [4,5,12]. The route of data treatment is thus the following: From a fit of the experimental data with the Zimm approximation one extrapolates the temperature and pressure dependent susceptibility  $S(0)$ , and with Eq. (3) one thereby gets  $Gi$  and  $C_{MF}$ . The critical amplitude  $C$  is obtained from Eq. (2), and  $\Gamma_\sigma$  from  $C_{MF}$ .  $\Gamma_c$  (or, generally,  $\Gamma_s$  for off-critical composition) is calculated from the molecular volume (Table I) and from the composition of the

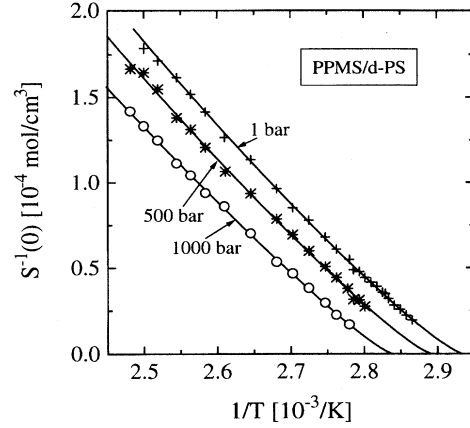


FIG. 1. Inverse and extrapolated  $S(Q\rightarrow 0)$  vs  $1/T$  in the one phase region above  $T_c$  for  $P=1$  bar ( $-\times-$ ), 500 bar ( $-*-$ ), and 1000 bar ( $-o-$ ). The solid lines are fits of the crossover function Eq. (3). At low temperatures the experimental points are restricted by the binodal temperatures whose values are given in Table II.

blend.

The SANS experiments have been performed at the DR3 reactor at the Risø National Laboratory. A steel bodied pressure cell was used which allows an *in situ* change of pressure and temperature in the range of  $1\text{ bar}\leq P\leq 1500\text{ bar}$  and  $-20\text{ }^\circ\text{C}\leq T\leq 200\text{ }^\circ\text{C}$ , respectively. This pressure cell is an improved version of the cell described in Ref. [11] insofar as the steel body can be directly cooled or heated. In this way a much better temperature control of  $\pm 0.2\text{ K}$  could be achieved (this improved temperature stability was necessary for this experiment). The scattering data were corrected for background, detection probability of the single detector cells, and calibrated in absolute units by a Lupolen standard. The resulting absolute macroscopic cross section  $d\Sigma/d\Omega$  is related to  $S(Q)$  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 components. The experiments were performed in the resolution range of  $0.003\leq Q[1/\text{\AA}]\leq 0.03$  using the settings of  $\lambda=9.6\text{ \AA}$  neutron wavelength and 6 m detector to sample distance. In this  $Q$  range the scattering of the sample can be described by the Zimm representation [13]. The polymers were obtained from PSS-Mainz (Germany) and their parameters are given in Table I. The sample was prepared as a  $\phi=0.5$  mixture without solvent by mechanical stirring. After each temperature setting we waited about 30 min before starting the measurements in order to have equilibrated conditions in the pressure cell.

In Fig. 1 the SANS results  $S^{-1}(Q\rightarrow 0)$  are plotted versus  $1/T$  for pressures of 1, 500, and 1000 bar. The data are described by the crossover function [Eq. (3)] as shown by the solid lines. Apparently, the data do not follow the mean-field approximation, namely  $S^{-1}(0)=C_{MF}^{-1}\tau$ . During the experiments we realized that the  $\phi=0.5$  mixture is slightly off critical composition in contrast to our estimation, using the relation  $\phi_c=V_1^{0.5}/(V_1^{0.5}+V_2^{0.5})$  [2]. The temperature gap between binodal and spinodal temperature is of the order of 8 K (Table II and Fig. 2). Below the binodal temperature  $T_B$  the system decomposes by nucleation and growth. Therefore the experiments are limited to temperatures above  $T_B$ . The

TABLE II. Results from the crossover function Eq (3).

$P$ (bar)	1	500	1000
$T_S$ ( $^{\circ}\text{C}$ )	67.9	72.9	79.4
$\partial T_S / \partial P$ ( $10^{-2}$ K/bar)		$1/15 \pm 0.09$	
$T_B$ ( $^{\circ}\text{C}$ )	$75.5 \pm 0.5$	$83.5 \pm 0.5$	$86 \pm 1$
$\partial T_B / \partial P$ ( $10^{-2}$ K/bar)		$1.1 \pm 0.3$	
$G_i$ (units of $10^{-2}$ )	$8.4 \pm 2.6$	$4.8 \pm 2.5$	$2 \pm 0.7$
$C_{MF}$ ( $\text{cm}^3/\text{mol}$ )	$432 \pm 25$	$486 \pm 43$	$583 \pm 30$
$C$ ( $\text{cm}^3/\text{mol}$ )	$452 \pm 43$	$445 \pm 68$	$432 \pm 43$
$\Gamma_{\sigma}$ ( $10^{-4}$ mol/ $\text{cm}^3$ )	$6.8 \pm 0.8$	$5.5 \pm 0.7$	$3.8 \pm 0.4$
$(T_B - T_S)$ (K)	7.6	10.6	6.6

susceptibility  $S^{-1}(0)$  below  $T_B$  (not shown in the figure) increases within our  $Q$  range following the composition fluctuations within the domains. Composition fluctuations above and below  $T_c$  were systematically studied in the system PPMS/d-PS [13]. The spinodal temperature  $T_S$  is obtained from the condition  $S^{-1}(0) = 0$ , which for the critical composition approaches  $T_c$ . All relevant parameters of the fit in Fig. 1 are summarized in Table II.

In Fig. 2 the phase transition temperatures  $T_S$  and  $T_B$  are plotted versus pressure. A linear increase of both temperatures with pressure is observed. The slopes of  $T_S$  and  $T_B$  with  $P$  are the same within the error bars, namely 0.011 K/bar (Table II) indicating that the critical composition does not change significantly with pressure. Our pressure coefficients of the phase transition temperatures are about three times larger than those found for the same system in [11]. In Fig. 3 the Ginzburg number  $G_i$  is plotted as a function of  $P$ .  $G_i$  decreases by a factor of about 4 upon a pressure increase of 1000 bar. The decrease of  $G_i$  with  $P$  is in agreement with the Ginzburg criterion in Eq. (2) but it contradicts Eq. (1). In Fig. 4 the segmental entropy of the Flory-Huggins parameter  $\Gamma_{\sigma}$  is plotted versus  $P$  and compared with  $\Gamma_S$  (shown as a solid line). The value of  $\Gamma_{\sigma}$  decreases with pressure as expected from its relationship to the free volume [11], they are within  $\pm 40\%$  the same as the calculated values of  $\Gamma_S$ .

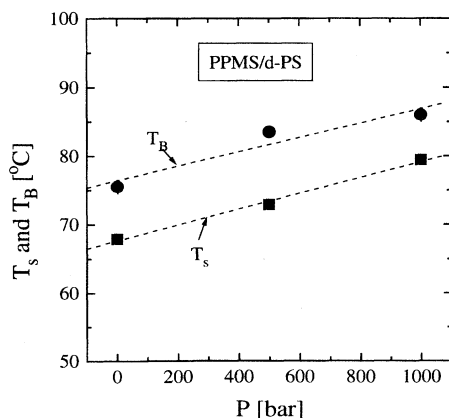


FIG. 2. Spinodal and binodal temperature vs pressure.  $T_c$  and  $T_B$  increase with pressure. Their increment is the same within the error bars (Table II). The increase of the phase transition temperatures with  $P$  can be understood from the decrease of free volume with increasing pressure and from its correlation with the segmental entropy  $\Gamma_{\sigma}$  (Fig. 4).

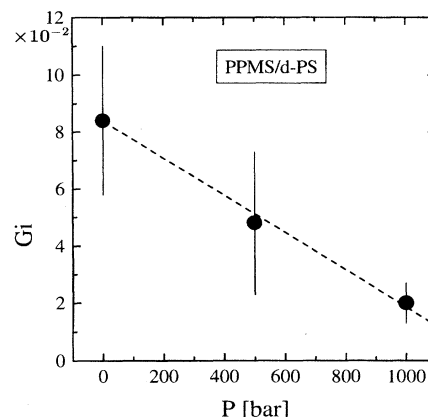


FIG. 3. Ginzburg number vs pressure as obtained from the fit in Fig. 1. A decrease of  $G_i$  with  $P$  is clearly observed indicating that the Ginzburg criterion in Eq. (1) is *incorrect*. In order to achieve smaller error bars the blend had to be closer to critical temperature and composition. From these results we expect that, at pressures roughly above 1500 bar,  $G_i$  should become universal as soon as  $\Gamma_{\sigma} \ll \Gamma_c$ .

The following conclusions can be drawn from our experiments. (i) One basic result is the observed decrease of  $G_i$  with  $P$ , as presented in Fig. 3. This coincides with the prediction of Eq. (2) while it is an experimental proof that the criterion of Eq. (1) is incorrect. This observation is plausible: Eq. (2) has been derived from the more fundamental crossover function [9], whereas Eq. (1) was derived using the Flory-Huggins theory [2]. (ii) Another basic result is related to the segmental entropic term of the Flory-Huggins parameter  $\Gamma_{\sigma}$  plotted in Fig. 4 and to the anomalous high  $G_i$  values of polymer blends. As demonstrated in Ref. [11]  $\Gamma_{\sigma}$  is related to the packing or free volume of the sample. Our analysis yields  $\Gamma_{\sigma} \cong \Gamma_c$ . In the case of  $\Gamma_{\sigma} = 0$  we calculate

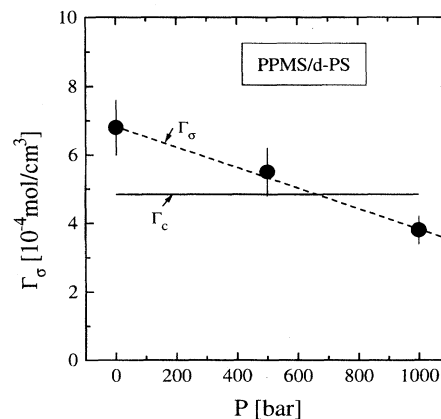


FIG. 4. The segmental entropic term  $\Gamma_{\sigma}$  vs  $P$ .  $\Gamma_{\sigma}$  decreases about 50% for a pressure increase of 1000 bar.  $\Gamma_c$  is shown by the solid line. There is always roughly  $\Gamma_{\sigma} \cong \Gamma_c$ . Therefore,  $G_i$  does not fulfill the condition of universality. The conventional analysis of the SANS data in Fig. 1 using  $S^{-1}(0) \propto \tau$  for the temperatures above  $\cong 100$   $^{\circ}\text{C}$  would give  $\Gamma_{\sigma}$  values smaller by a factor of 3, compared to the values from the crossover function.

$Gi \cong 0.002$  from Eq. (2) and the parameters in Table II. From this value we can extrapolate the  $Gi$  number for low molecular liquids because under this condition  $Gi \propto 1/V$ . A value  $Gi \cong 0.01$  is found as expected [4,9]. This means that the estimation of the Ginzburg number and thereby the validity range of the Flory-Huggins theory by de Gennes [2] is valid only in the case of  $\Gamma_\sigma \cong 0$ . According to the finite value of  $\Gamma_\sigma$  we find a value of  $Gi$  more than one order of magnitude larger than in case of  $\Gamma_\sigma \cong 0$  and nearly one order of magnitude higher than  $Gi$  of low-molecular-weight liquids. This is consistent with the SANS results in Refs. [4,5] and with lattice cluster theory calculations [6]. Furthermore, it is known that the dilution of binary polymer mixtures with a solvent as a third component increases  $Gi$  [14]. In this respect we can treat the influence of the free volume as if there were a third component [6]. At high pressure, on the other hand, the condition  $\Gamma_\sigma \ll \Gamma_c$  will be fulfilled. Under this condition (for our system seems to be at about 1500 bar), the Flory-Huggins theory becomes valid as originally proposed for polymer blends.

A final remark is related to the general validity of the presented results. The crossover function for the susceptibil-

ity  $S(0)$  in Eq. (3) and the Ginzburg criterion in Eq. (2) are valid for systems of the universality classes of the 3D Ising model and the mean-field approximation. The critical amplitudes  $C$  and  $C_{MF}$  of  $S(0)$  in the respective Ising and mean-field range are the system-dependent parameters. In our case  $C_{MF}$  increases with pressure by  $\cong 35\%$  while within the error bars no change with pressure is observed for  $C$  (Table II). These results might be characteristic for polymer blends but may also inspire similar experiments on other systems than polymer blends.

#### ACKNOWLEDGMENTS

The experiments were supported by the commission of the EC through the large installation. We would like to thank Professor T. Springer for a critical reading of the manuscript and various suggestions, H. Feilbach and M. Heiderich of IFF for design and technical assistance of the pressure cell, and H. Frielinghaus, G. Müller, and S. Janßen (all IFF) for the help during the SANS experiments and for various discussions.

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