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Thermal composition fluctuations in binary homopolymer mixtures as a function of pressure and temperature

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Abstract

Thermal composition fluctuations were studied by SANS in two d-PB/PS binary polymer mixtures as a function of temperature and pressure. The difference between both blends is related to the microstructure. The structure factor at scattering vector $Q = 0$ was analyzed by a crossover function from which the critical temperature, the Ginzburg number and the entropic term of the Flory–Huggins interaction parameter were obtained. Our experiments show that Gi is influenced by the microstructure and is connected to the packing of the polymers. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Small-angle scattering; Polymer blends; Ginzburg criterion

1. Introduction

It is common practice to describe the thermodynamic behavior of polymer blends by the Flory–Huggins model which is a mean-field theory neglecting thermal composition fluctuations [1,2]. This procedure is justified by an universal Ginzburg criterion ($Gi \propto N^{-1}$, N the degree of polymerization [1]) which predicts a small Ginzburg number Gi and, therefore, a small region close to the critical point where fluctuations are important [1–3]. This Ginzburg criterion, however, contradicts recent scattering experiments [4–8]

where a non-universal and an appreciably larger Gi is observed. It is the aim of the present paper to give an interpretation of these experimental results.

Thermal composition fluctuations are measured by the structure factor $S(Q)$ whose extrapolated value at scattering vector $Q = 0$ is a susceptibility. In the one-phase region, $S(0)$ can be described by a crossover function [9] from which the characteristic parameters of the system, namely T_c , Gi and Γ_σ can be determined. Γ_σ is the entropic term of the Flory–Huggins parameter Γ according to $\Gamma = \Gamma_h/T - \Gamma_\sigma$ (Γ_h enthalpic term) and the Ginzburg parameter $Gi := (T^* - T_c)/T^*$ (T_c critical temperature). It is the reduced transition temperature T^* separating the region of weak and of strong fluctuations. From the crossover function one gets for polymer blends the Ginzburg criterion

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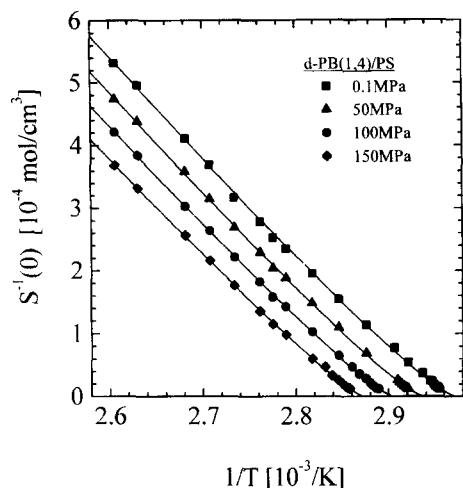


Fig. 1. Inverse susceptibility versus inverse temperature of the d-PB(1,4)/PS blend for pressures between 0.1 and 150 MPa. The solid lines are a fit of a crossover function from which the critical temperature, the Ginzburg number and the entropic term of the Flory–Huggins parameter is obtained.

[8] $Gi \propto [N^{(2-\gamma)}(2/N + \Gamma_\sigma)]^{1/(\gamma-1)}$ with $\gamma \cong 1.24$ the critical exponent of the 3D-Ising model [3]. In the limit $\Gamma_\sigma \ll 2/N$ one finds the conventional form $Gi \propto N^{-1}$. This suggests that the entropic term Γ_σ and the large exponent $1/(\gamma-1) \cong 4.17$ are the reason for the observed non-universal and large Gi . It can furthermore be concluded that, according to equation of states theories, Γ_σ is related to the compressibility or packing of the polymers [10]. These connections between Gi , Γ_σ and compressibility in polymer blends can be experimentally proved by pressure- and temperature-dependent studies of thermal composition fluctuations.

2. Experimental results

The experiments were performed with the small-angle neutron scattering (SANS) diffractometer KWS1 at the FRJ2 research reactor in Jülich, Germany [11]. The pressure/temperature cell allows measurements in the ranges between $0.1 < P < 200$ MPa and $-20 < T < 200$ °C with a stability better than ± 0.1 K. The two investigated homopolymer blends d-PB/PS consist of polysty-

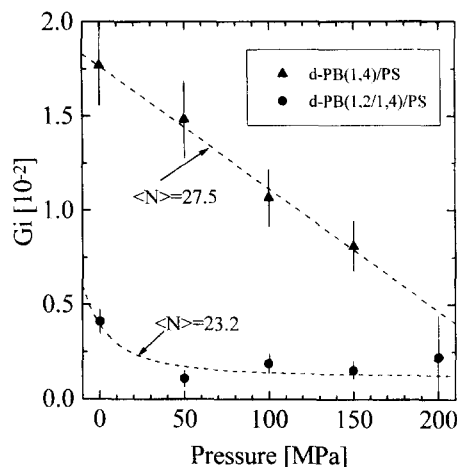


Fig. 2. Ginzburg number Gi versus pressure of two d-PB/PS blends with a similar average degree of polymerization $\langle N \rangle$ but with a PB polymer of different microstructure. In both blends the value of Gi decreases by applying pressure. An overall smaller Gi is found for the blend with the PB(1,2; 1,4) polymer.

rene (degree of polymerization $N = 18$) and of deuterated polybutadiene, in one case with monomers of 1,4 microstructure ($N = 37$) and in the other case with equal amounts of statistically distributed monomers of 1,4 and 1,2 microstructure ($N = 33$). The composition was always chosen to be close to the critical one.

In Fig. 1 the inverse susceptibility of the d-PB(1,4)/PS blend has been plotted versus the inverse temperature for four different pressures between 0.1 and 150 MPa. The measurements were always performed in the homogeneous state of the samples. $S(0)$ measures the degree of thermal composition fluctuations and diverges at the critical point. The solid lines in Fig. 1 represent a fit of the crossover function [8]. The Ginzburg number of the two investigated blends has been plotted versus pressure in Fig. 2. In both cases Gi decreases with increasing pressure. The blend with the PB(1,4) always shows the larger Gi which linearly decreases with pressure by a factor of two at 150 MPa. The blend with PB(1,4; 1,2) shows a quite different behavior: at 0.1 MPa, Gi is three times smaller than for the other blend. It shows a two times larger decrease already at 50 MPa and then remains constant within the error bars.

3. Discussions

The essential result of this work is the pressure-induced decrease of the Ginzburg number Gi in the two d-PB/PS blends which are different only by the microstructure of the PB component. In both cases an about two times decrease of Gi is observed at higher pressure. The values of Gi are different in both blends; in the PB(1,2; 1,4) blend a roughly three times smaller Gi is found which remains constant above 50 MPa. Our results deliver a non-universal Gi , e.g. it is not solely determined by the degree of polymerization. Our Gi is consistent with the Ginzburg criterion obtained from the crossover function and with equation of states theories [10].

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