ELSEVIER

Physica A 314 (2002) 411–418

PHYSICA A

www.elsevier.com/locate/physa

Critical phenomena in binary and ternary polymer blends

Petr Štěpánek[a,*], Terry L. Morkved[b], Kasiraman Krishnan[b], Timothy P. Lodge[b], Frank S. Bates[b]

[a] *Department of Supramolecular Polymer Systems, Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Square 2, 16206, Prague, Czech Republic*

[b] *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN, USA*

Abstract

We have studied the dynamic and static properties of binary and ternary polymer blends in temperature and concentration domains that include the critical temperature. The ternary blends consisted of A and B homopolymers and an A–B diblock copolymer. In binary blends and in ternary blends with lower content of the diblock copolymer, we have observed critical divergence of dynamic and static correlation lengths and of static susceptibility, as measured by dynamic light scattering and small-angle neutron scattering. The critical divergence for the binary blends could be analyzed in terms of a crossover between a mean-field and a nonclassical, Ising-type critical behavior. For ternary blends, the addition of a block copolymer stabilizes the system by decreasing the extent of composition fluctuations and by lowering the critical temperature. At a particular composition of the ternary blend, the appearance of a bicontinuous microemulsion was established by small-angle neutron scattering. It was shown that a maximum in the dynamic correlation length derived from dynamic light scattering and observed under these conditions is a characteristic signature of the microemulsion structure.

PACS: 83.80.Es; 61.25.H; 83.10.Nn; 83.70.Hq

Keywords: Polymer blends; Polymer dynamics; Block copolymers; Microemulsions; Critical behavior

---

[*] Corresponding author. Tel.: +1-420-2-20403211; fax: +1-420-2-35357981.
E-mail address: stepan@imc.cas.cz (P. Štěpánek).

PII: S0378-4371(02)01140-8

1. Introduction

Critical phenomena have long been of exceptional interest to the physicist's community as they occur naturally in connection with many phase transitions [1,2]. In binary mixtures of low-molecular-weight systems, these phenomena have been studied extensively. The results have contributed to understanding the effects of fluctuations on the validity of mean-field (classical) theory, and to the development of nonclassical theories describing the behavior of a system very close to critical conditions. It was recognized some time ago that polymer mixtures offer a unique opportunity to study critical phenomena in detail [3,4]. The characteristically large molecular dimensions, and the correspondingly slow molecular dynamics, combine to make a variety of behavioral regimes experimentally accessible.

In general, most polymer pairs are not miscible, yet different polymers have properties that are desirable to combine in a stable mixture. Consequently, it is often advantageous to stabilize a dispersion of one polymer in another by using a macromolecular surfactant, such as a diblock copolymer. It is then possible to direct the system to adopt more controlled and varied morphologies [5] that depend especially on concentration, temperature, interfacial tension and molecular size of the constituents. Various ordered and disordered phases have been observed in these systems, such as lamellae, hexagonally packed cylinders and cubic phases. Of particular interest in this work is the bicontinuous microemulsion [6] existing in a specific domain of composition and temperature of the mixture that has the property of being microscopically segregated but macroscopically disordered. In such a ternary polymer system, homopolymer-rich domains are separated by a block copolymer-rich interface. Furthermore, this composition range coincides with the regime where the mean-field theory predicts an isotropic Lifshitz point [7,8], i.e., a point in the phase diagram where disordered, uniformly ordered and periodically ordered phases meet. We use dynamic light scattering (DLS) and small-angle neutron scattering (SANS) to study the critical properties of binary and ternary polymer blends.

2. Background

From the experimental point of view, the quantities of interest in the present study of critical behavior of a polymer blend are the static susceptibility S, the correlation length ξ and the decay rate of composition fluctuations Γ. The reduced temperature for polymer mixtures can be defined as [9]

$$\varepsilon = \frac{\chi - \chi_s}{\chi_s} , \qquad (1)$$

where $\chi = (A/T + B)$ represents the segment–segment interaction parameter, T is the absolute temperature, A and B are system-specific constants and χ_s corresponds to the thermodynamic stability limit at temperature T_s. Thus,

$$\varepsilon \sim (T_s^{-1} - T^{-1}) \quad \text{or} \quad \varepsilon \sim T^{-1} . \qquad (2)$$

In the vicinity of T_s these quantities behave as power laws,

$$S \sim \varepsilon^{-\gamma}, \quad \xi \sim \varepsilon^{-\nu}, \quad \Gamma \sim \varepsilon^{-x}, \tag{3}$$

where γ and ν are standard critical exponents. The exponent x depends on the ratio of the scattering vector q to various length scales of the system. For the common case characterized [10] by $q\xi < 1$ and $\xi < R_g N^{0.5}$ and considered here (R_g is the radius of gyration of the polymer), $x = \nu$. S is a static quantity obtainable form scattering experiments (e.g., the static structure factor $S(q)$ from SANS) in the $q=0$ limit. Γ is a dynamic quantity obtainable from dynamic light scattering (DLS). The static correlation length ξ can be obtained [10] from SANS using the Ornstein–Zernicke equation

$$S(q) = \frac{S(0)}{1 + \xi^2 q^2} \tag{4}$$

and the dynamic correlation length from DLS using the Kawasaki–Stokes equation

$$\Gamma = Dq^2 = \frac{k_B T}{6\pi\eta\xi_d} q^2 \tag{5}$$

but ξ and ξ_s are not necessarily identical. Mean-field theory predicts [1] that the critical exponents should have values $\gamma = 1$ and $\nu = 0.5$, whereas in the nonclassical region, they should adopt the (Ising) values $\gamma = 1.26$ and $\nu = 0.63$. The crossover between these two regions, i.e., the change in the values of the exponents as temperature is changed occurs at a reduced temperature ε_x (the Ginzburg criterion [11]). Assuming that both polymers in the binary mixture have the same polymerization degree N and radius of gyration R_g, it is predicted [12] that $\varepsilon_x \sim N^{-1}$.

For ternary blends, we consider symmetric systems where $N_A = N_B = N$, $\phi_A = \phi_B$ and $f_A = \frac{1}{2}$. Here, N_i and ϕ_i are the degrees of polymerization and volume fractions of homopolymer i and f_A is the fraction of polymer A in the diblock copolymer; $\phi_H = \phi_A + \phi_B$ is the total volume fraction of the homopolymers. For $\alpha = N/N_{AB} < 1$, the (longer) copolymer is effective in compatibilizing the homopolymer blend and capable of forming mesophases [8]. Fig. 1 represents a mean-field phase diagram [13] of such symmetric ternary mixture. Experimentally, fluctuations destroy the lamellar structure in the vicinity of the unbinding transition, leading to the appearance of a bicontinuous microemulsion in an approximately vertical channel of width of a few percent around the theoretical unbinding transition.

The static structure factor of the ternary polymer blend is predicted to have the form [14]

$$S(q) = \frac{S(0)}{a_2 + c_1 q^2 + c_2 q^4}, \tag{6}$$

where a_2, c_1 and c_2 are the coefficients in the expansion of the Landau free energy to second order in the order parameter; $c_1 < 0$ indicates the appearance of a microemulsion structure. In the homogeneous and microemulsion phases, the decay rate Γ obtained by DLS can be again converted to a correlation length ξ_d using Eq. (5).

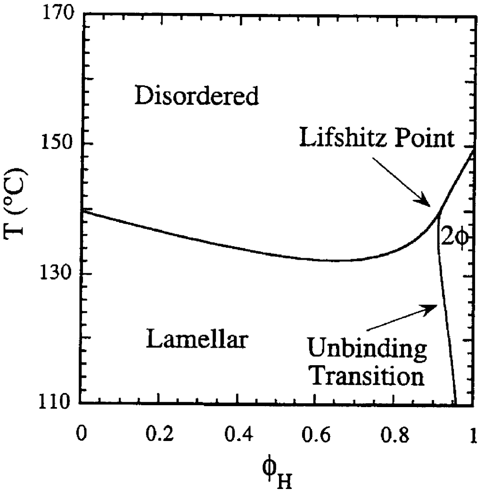

Fig. 1. Theoretical mean-field phase diagram for a symmetric homopolymer/homopolymer/diblock copolymer blend with equal volume fractions of each homopolymer, with $\alpha = 0.2$. The unbinding transition separates the lamellar and two-phase (2ϕ) regions and meets the order-to-disorder transition and stability lines at an isotropic Lifshitz point.

3. Experimental

Polymer samples were prepared by living anionic polymerization following standard procedures, as described elsewhere [15]. The following polymers were synthesized: polyisoprene (PI, molecular weight $M_n = 2000$ and 5000), poly(ethylene-*alt*-propylene) (PEP, $M_n = 5000$), poly(dimethyl siloxane) (PDMS, $M_n = 2130$), poly(ethyl ethylene) (PEE, $M_n = 1710$) and a diblock copolymer PDMS–PEE (52% PDMS, $M_n = 10\,400$).

The dynamic light scattering instrument used was described elsewhere [16]. The autocorrelation functions of the scattered intensity were analyzed either by fitting to a single exponential function or by the regularized nonlinear inverse Laplace transformation REPES [17]. Small-angle neutron scattering experiments were conducted at the 30 m Exxon/Minnesota/NIST instrument at NIST as described in more detail earlier [18].

4. Results and discussion

The crossover from mean-field to nonclassical critical dynamics was studied on a binary blend of PI(5000)/PEP(5000) for which the critical composition is $\phi_{c,PI} = 0.605$ and the critical temperature is $T_c = 130.6^\circ C$. The dynamic correlation length ξ_d was derived from the decay rate of composition fluctuations measured by DLS using Eq. (5) as a function of temperature in a large range above T_c. In virtue of Eqs. (2) and (3) we should have $\xi^{-1/v} \sim T^{-1}$. Fig. 2 shows that we indeed obtain a linear

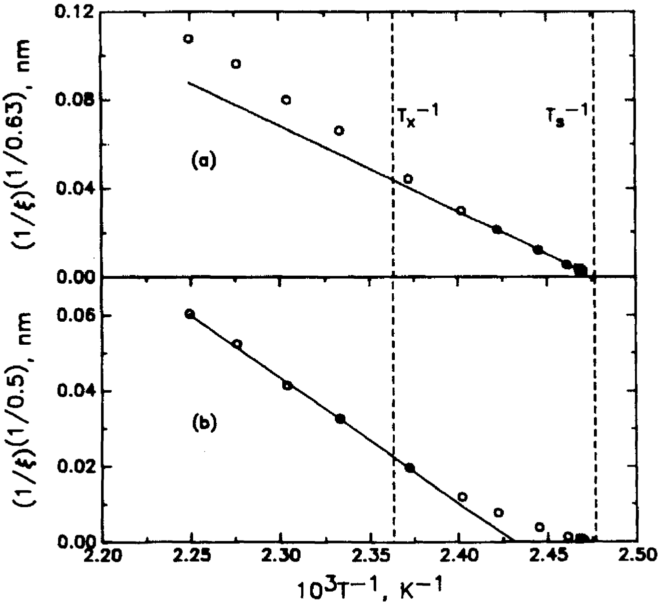

Fig. 2. Inverse correlation length ξ (a) raised to the power 1/0.5 vs. inverse temperature T. The linear regions below and above $T_x = 150^\circ$C correspond to nonclassical and mean-field regions, respectively.

regime in such representation, both with the mean-field value of the critical exponent $\nu=0.5$ (where the linear regime is at high temperatures) and with the nonclassical value $\nu = 0.63$ (where the linear regime is in the vicinity of the critical temperature T_c). The crossover between the mean-field and nonclassical regimes occurs progressively in a temperature interval around the Ginzburg temperature $T_x = T_s + 20^\circ$C. The extent of the nonclassical critical regime is very large for a polymer system, which is due to the rather low molecular weight of the constituents. Fig. 3 reproduces data obtained earlier [10] by SANS on the same polymer system with a slightly smaller molecular weight, PI(2000)/PEP(5000). A similar behavior is observed, namely a crossover from mean-field to nonclassical critical behavior, at $T_x = T_s + 34^\circ$C.

The effect of a diblock copolymer on critical fluctuations was studied on a similar mixture consisting of equal amounts of homopolymers (described above) PDMS and PEE and a variable fraction of diblock copolymer PDMS–PEP, in the range of the block copolymer content $\phi_{ED} = 0$–15%. Fig. 4 displays the temperature dependence of the dynamic correlation length ξ_d for various values of ϕ_{ED}. For the lowest three concentrations, ξ_d still diverges but as the fraction of block copolymer increases the critical temperature decreases. This describes the stabilizing effect of the block copolymer on the polymer mixture: at a given temperature the correlation length of composition fluctuations is smaller for a larger content of block copolymer. For the four higher concentrations, ξ_d exhibits a clear maximum before decreasing as temperature is further decreased. This indicates a dramatic change in behavior of the polymer mixture which can be explained by considering the SANS data obtained on the same

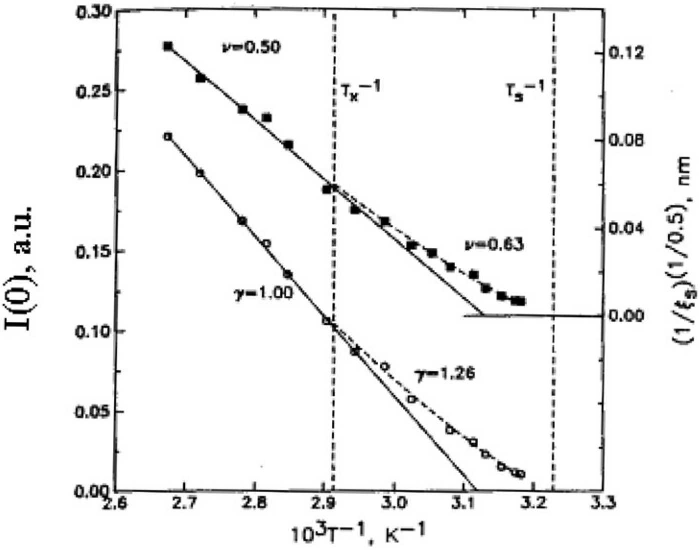

Fig. 3. SANS intensity $I(0)$ and inverse correlation length as a function of temperature for the mixture PI(2000)/PEP(5000). T_x corresponds to the mean-field–nonclassical crossover temperature, T_s is the stability limit. The dashed lines correspond to the Ising theory.

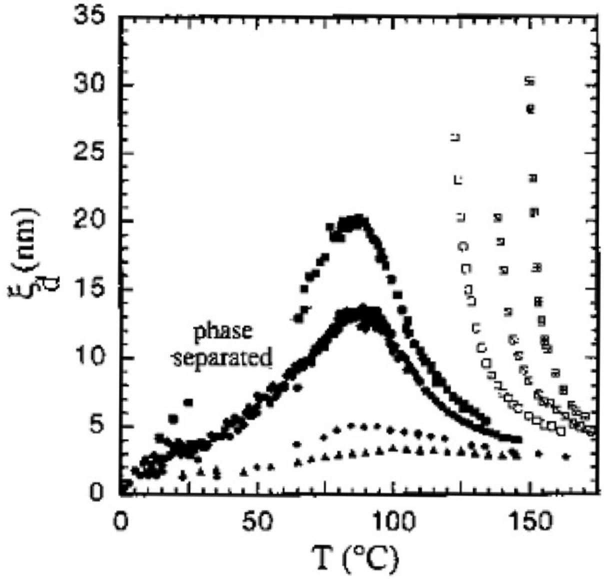

Fig. 4. Dynamic correlation length for the system PEE/PDMS/PEE–PDMS as a function of temperature for several volume fractions of the block copolymer ϕ_{ED}, from right to left: 0%, 4%, 7.1%, 9.2%, 10%, 12%, and 15%. The 9.2% mixture has a phase-separated region surrounded by microemulsion regions.

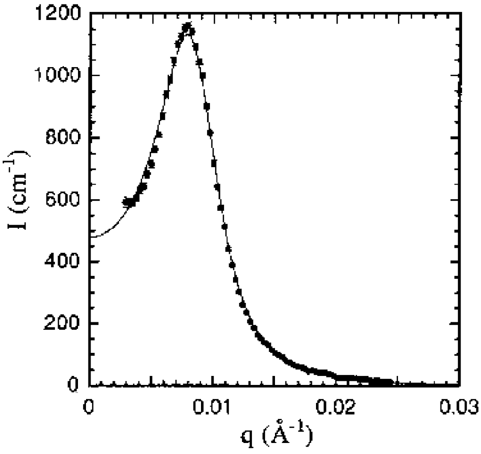

Fig. 5. SANS intensity as a function of scattering vector for the 10% mixture at 25°C. The line is a fit to Eq. (6).

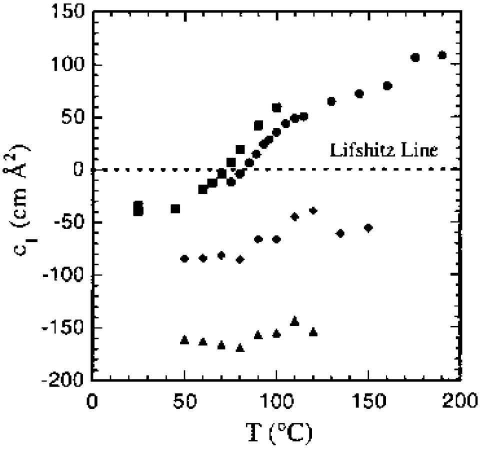

Fig. 6. Temperature dependence of the coefficient c_1 for mixtures with increasing content of the diblock copolymer, from top to bottom: 9.2%, 10%, 12%, and 15%.

system. A typical plot of SANS intensity as a function of scattering vector is shown in Fig. 5. These data were fitted with Eq. (6) to obtain the parameters a_2, c_1 and c_2. As mentioned earlier, negative values of the parameter c_1 indicate a microemulsion structure of the polymer mixture. Fig. 6 shows that c_1 becomes negative for temperatures $T \leqslant 85^\circ$C, which is just the temperature of the maxima of the dynamic correlation length in Fig. 4. This maximum is a very distinctive experimental indication of the formation of a bicontinuous microemulsion. It occurs because the dynamics of spontaneous concentration fluctuations are very sensitive to the underlying fluid structure. On cooling from the fully disordered phase, the dynamic correlation length increases due to the longer-range, larger-amplitude fluctuations, until the formation of the microemulsion arrests the divergence.

5. Conclusions

The crossover from mean-field to nonclassical, Ising-type critical behavior in binary polymer blends was observed at a rather large distance from the critical temperature, $T_x - T_c = 20$–30°C. This distance is larger for lower molecular weights of the polymers. The addition of a diblock copolymer decreases the temperature of phase separation and reduces the extent of composition fluctuations. For a content of copolymer corresponding to the appearance of bicontinuous microemulsion, the critical divergence is arrested and the temperature dependence of the dynamic correlation length exhibits a characteristic maximum.

Acknowledgements

We gratefully acknowledge support for this work by the Academy of Sciences of the Czech Republic (grant No. K4050111), by the MRSEC program of the National Science Foundation (Award No. DMR-9809364) and by the Center for Interfacial Engineering, a NSF-sponsored Engineering Research Center at the University of Minnesota.

References

[1] H.E. Stanley, Introduction to Phase Transitions and Critical Phenomena, Oxford University Press, Oxford, 1971.
[2] S.K. Ma, Modern Theory of Critical Phenomena, Benjamin, New York, 1976.
[3] D. Schwahn, K. Mortensen, Y. Yee-Madeira, Phys. Rev. Lett. 58 (1987) 1544.
[4] F.S. Bates, J.H. Rosedale, P. Štěpánek, T.P. Lodge, P. Wiltzius, G.H. Fredrickson, R.P. Hjelm Jr., Phys. Rev. Lett. 65 (1990) 1893.
[5] S. Jeon, J.H. Lee, N.P. Balsara, Phys. Rev. Lett. 79 (1977) 3274.
[6] F.S. Bates, W.W. Maurer, P.M. Lipic, M.A. Hillmyer, K. Almdal, K. Mortensen, G.H. Fredrickson, T.P. Lodge, Phys. Rev. Lett. 79 (1977) 849.
[7] D. Brosetta, G.H. Fredrickson, J. Chem. Phys. 93 (1990) 2927.
[8] R. Holyst, M. Schick, J. Chem. Phys. 93 (1992) 7728.
[9] K. Binder, J. Chem. Phys. 79 (1983) 6387.
[10] P. Štěpánek, T.P. Lodge, C. Kedrowski, F.S. Bates, J. Chem. Phys. 94 (1991) 8289.
[11] V.L. Ginzburg, Sov. Phys. Solid State 1 (1960) 1824.
[12] P.G. de Gennes, J. Phys. Lett. (Paris) 38 (1977) L–441.
[13] P.K. Janert, M. Schick, Macromolecules 30 (1997) 3916.
[14] M. Teubner, R. Strey, J. Chem. Phys. 87 (1987) 3195.
[15] A. Cumming, P. Wiltzius, F.S. Bates, Phys. Rev. Lett. 65 (1990) 863;
M.A. Hillmyer, W.W. Maurer, T.P. Lodge, F.S. Bates, K. Almdal, J. Phys. Chem. B 103 (1999) 4814.
[16] T.P. Lodge, P. Markland, Polymer 28 (1987) 1377.
[17] J. Jakeš, Czech. J. Phys. B 38 (1988) 1305.
[18] T.L. Morkved, P. Štěpánek, K. Krishnan, F.S. Bates, T.P. Lodge, J. Chem. Phys. 114 (2001) 7247.