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Coexistence in a Binary Isotopic Polymer Mixture.

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Abstract. – We have measured directly the phase coexistence characteristics in a high-molecular- weight binary isotopic polymer mixture over a range of temperatures around the critical point, using nuclear-reaction analysis. Our results reveal an equilibrium phase diagram with an upper critical solution temperature, in fair quantitative accord with the simplest form of the Flory-Huggins mean-field model. Deviations may be due to a mild compositional dependence of the monomeric interaction parameter.

Binary liquid mixtures demix into two coexisting phases when taken into the thermodynamically unstable regime. This demixing or spinodal process has been extensively studied: microscopic compositional fluctuations grow in time to an interpenetrated random array of domains tending to the coexisting compositions (often associated with a macroscopic «cloudiness» when accompanied by refractive differences). In due course, surface-energy–driven ripening, mediated by diffusion, diminishes the smaller domains and enlarges the bigger ones; and in the fullness of time, one expects two adjacent macroscopic phases to coexist [1, 2].

For a large and technologically important class of complex fluids—that of binary high polymer mixtures [3]—such coexistence has rarely been directly observed. Characterization of the onset of demixing in these systems has come mostly from scattering studies [4-11] which probe the growth of compositional fluctuations near the critical point in the one-phase regime, and by extensive determinations of cloud-point loci [5, 10]. The difficulty in directly observing true coexistence between partly-miscible polymeric phases is due to the extremely low molecular mobility in entangled polymer melts, which implies unacceptable waiting times for equilibrium to be attained over macroscopic dimensions. At the same time, the phase equilibrium behaviour provides very direct information regarding the thermodynamics of mixing of long polymeric chains [11]. The advent of high-resolution,

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direct composition-profiling methods in mixtures of bulk polymers [12] has enabled the investigation of samples with microscopic dimensions, and has led to some very recent studies of coexistence between bulk polymer phases. Bruder *et al.* [13], using elastic-ion recoil detection, studied the coexistence of polystyrene and its brominated analogue. Chaturvedi *et al.* [14], and Steiner *et al.* [15] used Nuclear Reaction Analysis (NRA) [16] to investigate coexisting phases of regular (hydrogenous) polystyrene (pPS) and its deuterated analogue (dPS), and the structure of the interface between them. The use of such isotopic pairs as model binary systems presents attractive features when comparing with theoretical models, due especially to the high degree of local structural symmetry between the two types of monomers. We have extended our earlier measurements [14, 15] and report here the determination of the locus of coexisting phases about the critical point in the model isotopic pPS/dPS blend.

In our experiments a uniform film (thickness ca. 500 nm) of pPS (monomer structure -(CH_2-$CH(C_6H_5)$)-, weight-averaged degree of polymerization $DP \equiv N_B = 2.78 \cdot 10^4$) is spin-cast on a polished silicon substrate and a similar film of perdeuterated polystyrene, dPS (-(CD_2-$CD(C_6D_5)$)-, $DP \equiv N_A = 9.20 \cdot 10^3$) is spin-cast, floated off on water, and mounted on top of the pPS film to form a bilayer, which is then sealed under vacuum in a glass ampoule prior to annealing. This pPS/dPS system has an upper critical solution temperature T_c much higher than its glass transition temperature $T_g \approx 100\,°C$. Thus, on heating the bilayer to a temperature $T_c > T > T_g$, molecular transport takes place across the interface between the initially pure pPS and dPS layers, driving their compositions towards their coexisting values. The concentration profile of dPS across the sample is determined directly to yield the overall composition profile as shown in fig. 1, using nuclear reaction analysis, as recently described [12, 14, 16], based on the reaction $^3He + {}^2H \rightarrow {}^4He + {}^1H + 18.352\,MeV$.

With time, transport of the pPS and dPS chains takes place across the interface, until limiting values of the plateau compositions ϕ_1 and ϕ_2, corresponding to the dPS

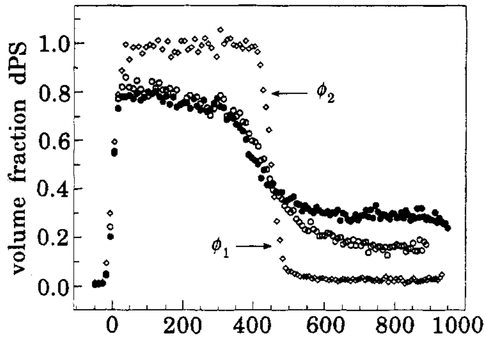

Fig. 1.

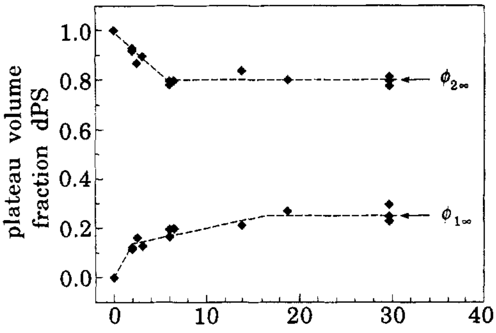

Fig. 2.

Fig. 1. – Typical concentration distance profiles of the region about the interface for a pPS/dPS bilayer annealing for different times, 6.0 d (○) and 29.7 d (●) (nonannealed (◇)) at 170 °C. Profiles are determined by nuclear-reaction analysis [12, 16] (see text for reaction) at a forward angle of 30° and an incident ^3He beam energy of 1.2 MeV. The absolute values of the volume fractions are determined by mounting a pure dPS layer on top of the annealed bilayer in order to establish the 100% dPS level. Values of the plateau volume fractions ϕ_1 and ϕ_2 for a 6.0 d annealing time are indicated. DP of the pPS and dPS samples are given in the text, while their weight average/number average ratios are 1.09 and 1.03, respectively.

Fig. 2. – Variation of the plateau volume fractions ϕ_1 and ϕ_2 as a function of annealing time, shown for an annealing temperature 170 °C. Data correspond to ratios of pPS/dPS film thickness varying from 1 to 1.2. Values of the limiting plateau volume fractions $\phi_{1\infty}$ and $\phi_{2\infty}$ for this temperature are indicated.

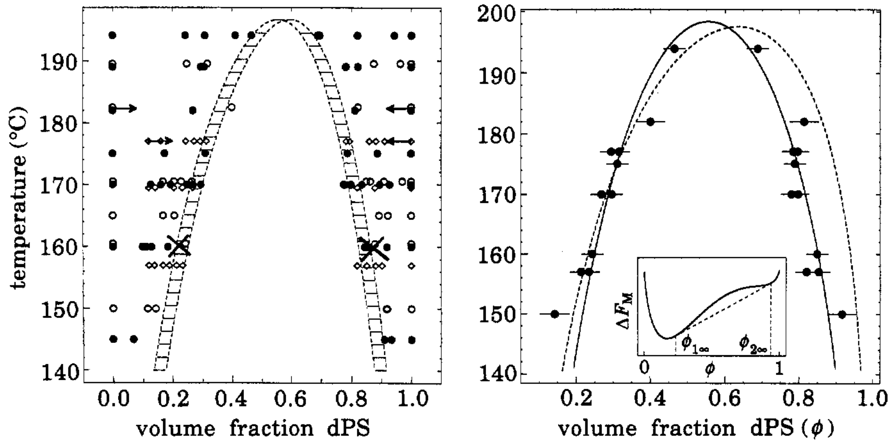

Fig. 3. – *a*) The variation of plateau compositions ϕ_1 and ϕ_2 with time in the temperature-composition plane. Compositions at all temperatures were initially at dPS volume fraction $\phi_1 = 0$ and $\phi_2 = 1$ or at initial compositions $\phi_1 = 0.12 \div 0.15$, $\phi_2 = 1$, and moved at increasing times (in the sense of the arrows) towards their limiting values $\phi_{1\infty}$ and $\phi_{2\infty}$, as indicated in fig. 2. The shaded band is a guide to the eye defining the locus of $\phi_{1\infty}$ and $\phi_{2\infty}$ and indicating the estimated uncertainty in determining their values from plots as in fig. 1. The different initial dPS and pPS film thickness ratios are: ○ r (pPS/dPS) = $0.4 \div 0.7$; ● r (pPS/dPS) = $0.8 \div 1.2$; ◇ r (pPS/dPS) = $1 \div 1.8$. × coexisting compositions from ref. [14]. *b*) Comparison of our experimental coexistence data (showing limiting values of $\phi_{1\infty}$ and $\phi_{2\infty}$) with prediction of the FH model. The broken curve represents the locus of contacts of the common tangent to the mixing-free-energy profile (as indicated in the inset) based on eq. (1), using a ϕ-independent $\chi(T)$ from ref. [7] as described in the text. The solid curve was generated in the same way but using an interaction parameter with both a temperature dependence and a weak linear compositional dependence (^{1}) $\chi(T, \phi) = (0.124T^{-1} - 1.06 \cdot 10^{-4})(1 - 0.18\phi)$.

concentrations in the two phases, are attained. This is clearly seen in fig. 2, where these long-time limits of ϕ_1 and ϕ_2 define the coexisting values $\phi_{1\infty}$ and $\phi_{2\infty}$, while the region ($\phi_{1\infty}$-$\phi_{2\infty}$) defines the miscibility gap at that temperature. Values of ϕ_1 and ϕ_2 were determined in this way at increasing times for temperatures in the range $(145 \div 194)$ °C ($\pm$ 0.5 °C), and are presented in fig. 3*a*), together with data for 160 °C from the earlier study by Chaturvedi *et al.* [14]. The limiting interfacial widths do not exceed $(20 \div 25)\%$ of the overall bilayer thickness in any of our experiments, thereby providing clear plateaus (at ϕ_1 and ϕ_2) and avoiding problems associated with finite-size effects. The locus of $\phi_{1\infty}$ and $\phi_{2\infty}$ as a function of temperature is the coexistence curve in the composition-temperature plane for this binary polymer blend. We note that in experiments carried out at a slightly higher temperature (215 °C) the two layers fully interdiffused to a homogeneous concentration, resulting in a flat profile in which no interface could be differentiated. Moreover, varying the relative thicknesses of the as-cast dPS and pPS layers in the bilayer within a factor three, as well as varying the starting compositions of the two films (within values outside the miscibility gap, see fig. 3*a*)) resulted—within the scatter—in the same limiting compositions $\phi_{1\infty}$ and $\phi_{2\infty}$. These observations confirm that the magnitudes of the limiting plateau compositions in fig. 3 are indeed close to their coexistence values. We observe at once that the locus of the coexistence compositions qualitatively resembles a classic phase equilibrium diagram [7] with an upper critical solution temperature (UCST) estimated—from fig. 3—as

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(^{1}) A χ parameter with a weak parabolic ϕ-dependence can also be made to provide a good fit to our data.

$T_c = (197 \pm 3)\,^\circ\mathrm{C}$. This directly determined coexistence curve must be compared with molecular models and with other studies on the same isotopic mixture.

A good starting point for the understanding of phase equilibrium in polymer mixtures is the Flory-Huggins (FH) mean-field lattice model of polymer mixing [17, 18], where the normalized free energy ΔF_{M} is given by

$$\Delta F_{\mathrm{M}}/(k_{\mathrm{B}}T) = (\phi_A/N_A)\ \ln \phi_A + (\phi_B/N_B)\ \ln \phi_B + \chi \phi_A \phi_B . \tag{1}$$

Here ϕ_A, N_A and ϕ_B, N_B are the mean volume fractions and degrees of polymerization of the two species ($\phi_A + \phi_B = 1$), while χ is a segmental interaction parameter; k_{B} and T have their usual meaning. In the present study, by working in the bulk (and using very long chains) we expect mean-field behaviour to hold everywhere except in the extreme vicinity (within $|(T - T_c)/T_c| < N_A^{-1}$) of the critical temperature [4, 6, 18]; in particular, however, use of an isotopic polymer pair ensures that the requirement of structural symmetry between the monomeric species—one of the basic assumptions of the original FH model formulated in eq. (1)—is well obeyed. We therefore examine the coexistence curve of fig. 3 initially with reference to eq. (1). For an interaction parameter χ which is independent of composition (as assumed in the original FH model), this equation predicts that the critical point occurs at a composition corresponding to a volume fraction of component A given by $\phi_c = N_B^{1/2} \cdot (N_B^{1/2} + N_A^{1/2})^{-1}$; and at a temperature T_c corresponding to a value of the interaction parameter given by [18] $\chi_c = (N_B^{1/2} + N_A^{1/2})^2/(2N_A N_B)$.

To make a detailed comparison between our coexistence curve and the FH theory, we need to have an explicit relation between χ and T. For the dPS/pPS binary mixture the interaction parameter has been determined in a number of studies, both via small-angle neutron scattering (SANS) [7, 9], using the random phase approximation [18, 19], and from thermodynamic slowdown of the mutual diffusion coefficient [20]. $\chi(T)$ can also be extracted from our earlier investigations [14, 15] of the interfacial structure between coexisting pPS/dPS phases and its variation with temperature. We use eq. (1), together with the value of the interaction parameter $\chi(T) = (0.20 \pm 0.01)\,T^{-1} - (2.9 \pm 0.4) \cdot 10^4$, determined from SANS by Bates and Wignall [7] for the pPS/dPS pair (with $N_A \approx N_B \approx 10^4$ and $\phi \equiv N_A = 0.5$), to generate the coexistence (or binodal) curve; this is shown in fig. 3*b*).

Comparison of the calculated and experimentally determined binodals in fig. 3*b*) reveals two main features. Firstly, the coexistence curve deduced from the classic FH model in its basic form does a very respectable job of predicting—quantitatively—the directly measured behaviour. It is noteworthy that the predicted value of T_c, which is 198 °C based on the mean value of $\chi(T)$ as determined [7] by SANS (though this value is associated with a large uncertainty of some ± 60 °C resulting from the quoted uncertainty limits), is close to the experimental T_c estimated from fig. 3*a*). Secondly, we find that it is not possible to improve the predicted fit to the overall shape of the experimental coexistence curve in any significant manner using the FH model with a χ of the form $(AT^{-1} + B)$, which is the ϕ-independent form used in the interpretation of the earlier studies [7, 14, 20]. Notably, the critical composition corresponding to a volume fraction $\phi_c = 0.58 \pm 0.02$ of dPS estimated from the experimental data in fig. 3 appears to differ (even within the scatter) from the value $\phi_c = 0.64$ expected from our N_A and N_B values. It is of interest to consider the reasons for this.

We recall that the SANS studies yield (in the limit of small-scattering wave vector) the second derivative $\partial^2 \Delta F_{\mathrm{M}}/\partial \phi^2$ of the mixing free energy: this is only identical with χ in eq. (1) for the case of a ϕ-independent interaction parameter, so that the value derived from the scattering studies need not equal that which best fits the coexistence curve [10]. More significantly, the expression for ϕ_c given above, derived from the condition $\partial^3 \Delta F_{\mathrm{M}}/\partial \phi^3 = 0$, also holds only for a ϕ-independent interaction parameter. In fact it has long been known that in polymer solutions and mixtures this is not generally true, an effect which has been attributed to differences between the structure of the monomers [11]. Recent SANS studies have shown that even for the near-ideal case of isotopic mixtures, where such local structural asymmetry is absent, there is a marked composition dependence of χ. A parabolic dependence has been found, with a minimum in χ at $\phi \approx 0.5$ in two of the cases [8], while the very recent study by Schwann *et al.* on the pPS/dPS system [9] has been interpreted as showing a maximum in χ at $\phi \approx 0.5$ (with $N_A \approx N_B$ in all three cases). Several recent theoretical approaches [8, 21-23] which extend the FH model to the case of isotopic mixtures, but treat effects not included in the original model—such as monomer correlations, compositional fluctuation, finite compressibilities and corrections arising when the constraints of a lattice model are relaxed—also indicate an effective interaction parameter which has a ϕ (and for that matter, N) dependence. While we do not feel that the accuracy of our data is sufficient to warrant explicit comparison with the studies indicating a $\chi(\phi)$ variation, we note that a good quantitative fit to the data is possible by introducing a weak dependence of χ on ϕ (see caption to fig. 3*b*)). The most likely reason for the (slight) deviation of the measured coexistence curve in fig. 3 from the predictions of the original FH model, therefore, is likely to be a mild compositional dependence of the interaction parameter.

To conclude: we have determined directly the phase coexistence diagram in a model binary isotopic polymer mixture over a temperature range about the critical point. Our findings reveal a coexistence curve with a well-defined upper critical solution point, in qualitative accord with expectations based on scattering experiments. Within the range of our experimental parameters, slight deviations from the predictions of the original Flory-Huggins mean-field lattice theory are probably due to a weak compositional dependence of the monomeric interaction parameter not included in the original model.

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