Temperature Gradients Induce Phase Separation in a Miscible Polymer Solution

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Phase separation occurred up to 20 °C above the coexistence temperature in a polymer solution (polystyrene-polybutadiene-dioctylphthalate) to which small temperature gradients (≈2 °C) were applied. Before convection began, spinodal-like patterns with characteristic spacing that grew in proportion to time elapsed persisted for times up to hours. The cause appears to be thermally driven concentration gradients normal to the surface, large enough to induce phase separation parallel to the surface, although temperatures throughout the mixture exceeded the thermodynamic coexistence temperature. [S0031-9007(96)01078-2]

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Temperature inhomogeneity is common in nature and technology—yet physical studies of the origins of phase transitions and the resulting morphologies generally concern systems whose temperature is constant everywhere, the contrary situation being viewed as too applied. Indeed, temperature gradients have interesting applications. They can be exploited for controlled crystal growth in zone refining of metals and semiconductors [1], can underly a rich physics of convection [2], and can generate chemical differentiation in an otherwise homogeneous geological mantle [3]. This issue also pertains to a more general intellectual problem, to understand the structure and phase behavior of mixtures when the thermodynamic variables are inhomogeneous [4–12]. We report below a connection between temperature inhomogeneity and the actual occurrence of a phase transition above the thermodynamic coexistence temperature. Phase separation induced by temperature gradients has previously been observed when one portion of a sample is below the critical temperature and another portion above it [7,8], but, to our knowledge, not previously when the entire sample is above this temperature, with the possible exception of the cryptic allusion by Lesher and Walker to certain "failed experiments" with geological magmas [13]. Reasons are given to expect such behavior to be especially common for macromolecular mixtures in the vicinity of phase transitions.

The experiments show that small temperature gradients (2 °C) resulted in clear-cut phase separation at temperatures up to 20 °C above the critical temperature. The resulting structure was investigated; spinodal-like structures grew for minutes to hours before convection intervened. Phase separation occurred, although temperatures throughout the mixture exceeded the thermodynamic phase transition temperature. We conclude by discussing the significance of this effect.

The ternary polymer solution, PS/PB/DOP (polystyrene/polybutadiene/dioctylphthalate) at its critical composition (see Fig. 4), was mounted on a hot stage and heated from below to produce a temperature difference of 2 °C. A control experiment showed no difference when the bottom surface was cooler than the top. The weight-average molecular weights of the polymers were $M_w = 2.14 \times 10^5$ for PS and 3.13×10^5 for PB (ratio of weight-average to number-average weights $M_w/M_n = 1.05$ and 1.90, respectively). The PS and PB were present in equal mass concentration with total polymer composition 3.3 wt. %. The bulk critical temperature was $T_c = 76$ °C. The sample was selected because of extensive prior study of its equilibrium and shear-induced phases [14,15]. In the absence of convection, it has long been understood that a temperature gradient in solution induces concentration gradients of solute in opposite directions (the Soret effect [4]). In a linear temperature gradient this gives, at steady state,

$$(d/dz)\ln c = -[\alpha]\Delta T/H\,, \qquad (1)$$

where c denotes concentration, z distance, H sample thickness, T temperature, ΔT temperature difference, and α is a constant of proportionality which we discuss below. Macromolecules, the larger species, typically migrate toward the cooler surface [9–12]. Therefore, Soret-driven polymer concentrations at the cooler surface should be expected to increase in proportion to the sample thickness, i.e., $c(z = H) \sim H$. The sample geometry is illustrated in the inset of Fig. 2.

Initially we were concerned about potential wetting effects, and therefore compared responses using polar and hydrophobic glass to contain the sample [clean glass or a methyl-terminated organic monolayer of octadecyl chains (OTE) [16] on glass]. No difference was observed, indicating that wetting effects played no significant role. The findings reported below refer to OTE-coated glass surfaces for which the temperature difference between top and bottom plates was 2 °C.

Figure 1 shows images obtained by optical microscopy after the sample was quenched from 105 to 85 °C. The critical temperature was $T_c = 76$ °C as indicated in Fig. 4. The temperature gradient was -6 °C/mm. These data refer to the region within several tens of micrometers

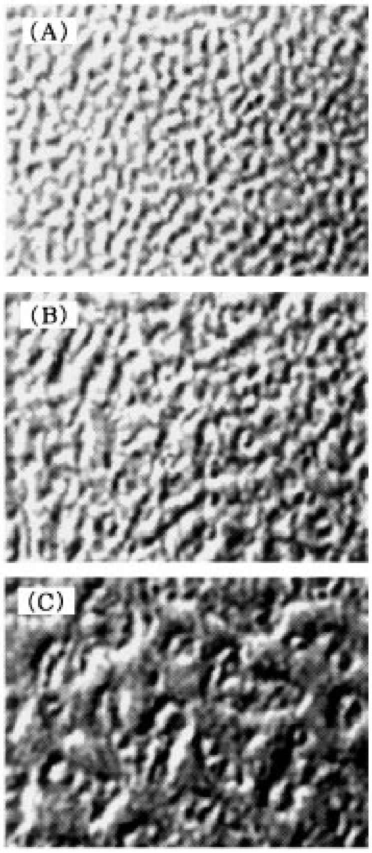

FIG. 1. Optical images (differential interference contrast microscopy) of Soret-induced phase separated structures in PS/PB/DOP. Vertical temperature gradient was $-6\,^{\circ}\mathrm{C/mm}$ (film thickness 327 μm). Microscope was focused just below the cooler (upper) plate. The sample was quenched from 105 to 85 °C (9 °C above the critical temperature of 76 °C). The computer contrast-enhanced images, at elapsed times of (a) 3 min, (b) 5 min, and (c) 10 min, show interconnected spinodal-like structures. Size of cross section, 250×188 μm. Note that temperatures throughout the sample were in the one-phase region of the isothermal phase diagram (shown in Fig. 4).

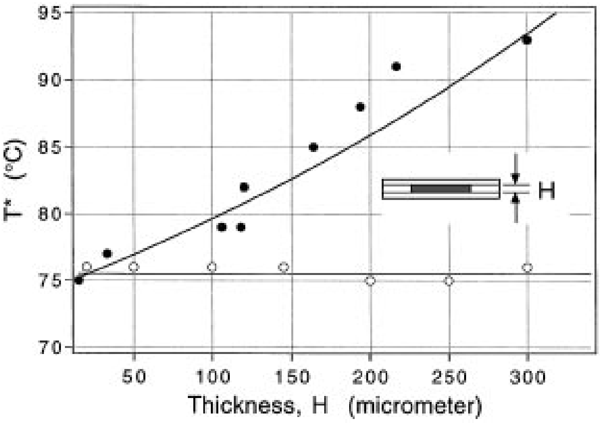

FIG. 2. Temperature (T^*) at onset of visibly phase-separated structure, plotted against the sample thickness (H). Conditions same as for Fig. 1. Some experiments involved plates at fixed separation, H. In other experiments it was convenient to incline the plates to form a wedge (angle 0.86°) in order to investigate a wide range of H in the same experiment. Both setups gave the same result. Symbols: $-6\,^{\circ}\mathrm{C/mm}$ (filled circles); $\Delta T = 0\,^{\circ}\mathrm{C}$ (open circles). Inset shows a schematic diagram (not to scale) of the sample mounted between two plates with variable spacing, H. Lateral length of the plates was 3 cm.

of the cooler plate, where Eq. (1) leads one to expect the highest thermally driven polymer concentration. The region below was clear and appeared to remain in the one-phase region. A control experiment showed that when the temperature gradient was eliminated, the sample became clear everywhere. In these images one observes domains whose characteristic size grew with elapsed time. The domains formed an interconnected structure with relatively homogeneous spacing, typical of spinodal decomposition.

Again reasoning from Eq. (1), we sought to vary the polymer concentration at the cooler plate by changing the sample thickness. The thicker the sample, the broader the temperature range above T_c over which phase-separated structures could be detected. In Fig. 2, the temperature (T^*) above which no structure was visible is shown for a range of sample thickness. Scatter probably reflects difficulties in accurately determining the onset of phase separation by light microscopy. Nonetheless, one observes that T^* grew in rough proportion to sample thickness up to the highest temperatures investigated, 20 °C above T_c. This suggested the hypothesis that the difference, $T^* - T_{\mathrm{exp}}$ (T_{exp} denotes experimental temperature), might be regarded as undercooling by analogy with well-known phase separation kinetics of isothermal mixtures [17–19], Indeed we found that the smaller the undercooling ($T^* - T_{\mathrm{exp}}$), the slower the growth of spinodal-like structures.

To further explore parallels with isothermal phase separation, the time dependence of growth was analyzed quantitatively at fixed undercooling. Characteristic spacings of the spinodal-like structures were quantified by Fourier transform of many images obtained during the experiment depicted in Fig. 1. In Fig. 3, these spacings are plotted against elapsed time on log-log scales. The data show linear dependence over a considerable time, one decade. Linear dependence would be typical of late stage spinodal decomposition in binary mixtures when hydrodynamic effects dominate [17–19], and also has been observed near isothermal surfaces [20]. It is tempting to conjecture a similar hydrodynamic origin in the present nonisothermal system.

What of behavior at longer times? Parenthetically, we note that saturation of domain spacing in Fig. 3 was probably related to thickness of the polymer-enriched layer within which phase separation occurred. It provides a rough estimate of that thickness. Saturation of domain spacing was accompanied by the emergence of new, smaller circular-shaped domains [barely visible in Fig. 1(c)], so that both types of domains coexisted near the cooler surface, as indicated in Fig. 3. This presumably reflected a second stage of phase separation within the phase-separated structure formed originally. Also we note

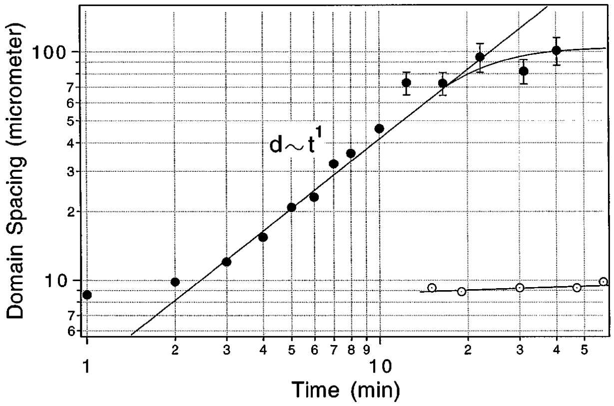

FIG. 3. Domain spacing of spinodal-like structures (filled circles) and small circular domains visible during a second stage of phase separation (open circles) plotted against elapsed time. Conditions same as for Fig. 1. To improve the statistics, the areas analyzed were larger than shown in Fig. 1.

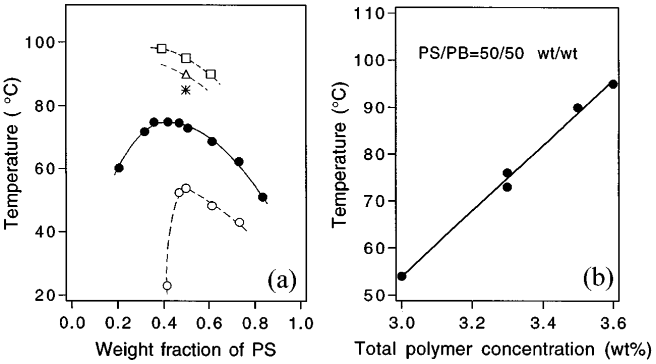

FIG. 4. (a) Phase diagram of PS/PB/DOP systems with PS and PB present at equal mass concentrations and total polymer concentration of 3.0 wt. % (open circles), 3.3 wt. % (filled circles), 3.5 wt. % (triangle), and 3.6 wt. % (squares). Note that Figs. 1–3 concern the 3.3 wt. % system. Star symbol indicates 85 °C, the temperature at which experiments in Figs. 1–3 were performed. (b) Isothermal phase separation temperature at equal mass concentration of PS and PB, plotted against total polymer concentration. Note the large slope.

that hexagonal-shaped convection rolls eventually became visible (1 h for the experiment in Fig. 1). The temperature gradient in this experiment was two orders of magnitude smaller than that required for classical Rayleigh-Bénard convection; convection was enhanced by phase separation because phase separation enhances density variations in space. The main point is that before convection began, seemingly classical patterns of phase separation persisted for extended periods of time.

Related questions have been addressed in the literature [7,8,13,21], in particular, in a seminal study in which one portion of a binary mixture was held below the critical temperature and another portion held above it [7,8].

It will be interesting, in future work, to determine from direct measurement the vertical thickness over which the Soret-driven phase-separated structures evolved. However, with the light microscopy methods at our disposal, it was possible to estimate, from the isothermal phase diagrams, the thermally driven concentration changes. Figure 4(a) shows that phase diagrams of the isothermal PS/PB/DOP system displayed striking sensitivity to the total polymer concentration. Figure 4(b) quantifies this dependence and shows that a modest increase of total polymer concentration (roughly 10%) sufficed to raise the phase separation temperature by the 20 °C observed for the thickest samples in Fig. 2. The comparison is admittedly rough because we do not expect the Soret-driven concentration gradients of PS and PB to be the same, but does show that the observed large enhancement of phase separation temperature could be explained by modest enhancements of the local polymer concentration near the cooler plate.

Why is the magnitude of the Soret effect so large in this system, whereas historically [2,11] it has been reported to be so much weaker in other systems? The magnitude is set by the parameter α in Eq. (1). Over the years the magnitude of α has been variously modeled though without definitive conclusion, as reviewed in Ref. [11]. But as Douglas has emphasized [22], enhancement of α for macromolecules as against small molecules follows when one reflects on the fact that α is the ratio of the thermal and cooperative diffusion coefficients [4,9]. While the former appears to be independent of molecular size [9,10], it is known in polymer physics that the latter decreases strongly with increasing molecular weight in predictable fashion for solutions of low concentration [23], implying that α also increases predictably. The quantitative dependence on solute concentration is also understood [23]. This simple consideration clarifies the common observation that α is many times higher for solutions of polymers than for ordinary liquids [9–12], by a factor of up to order 100. By Eq. (1), this implies an effect 100-fold stronger.

For binary mixtures, similar arguments would apply. At temperatures below the critical temperature but still in the one-phase region, it is logical to expect that thermal gradients should induce enhancements of local concentration, such that two phases would be more stable than one, and therefore phase separation of the kind described here.

In summary, we have shown that phase separation, resulting from locally enriched solution concentrations, can occur although temperatures throughout the sample are in the one-phase region of the phase diagram. This has immediate practical bearing on the nonequilibrium structures and phases to be expected in many situations. In polymer processing [24] thermal gradients are common and the large value of α discussed above may have prominent consequences. The phases in quenched geological magmas may be influenced [13]. As Navrotsky has noted [25], the dependence on molecular size implies that similarly strong effects should also be expected in mixtures containing protein and nucleic acid macromolecules in a biological environment.

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