Communications to the Editor

Order–Disorder Transition in Binary Mixtures of Nearly Symmetric Diblock Copolymers

Block copolymers are fascinating materials that have attracted both academic and industrial interest for over three decades. In recent years considerable theoretical[1-3] and experimental[4-11] effort has been focused on the ordering process in bulk and concentrated solutions of block copolymers. Central to our understanding of block copolymer phase behavior is the order–disorder transition (ODT). The seminal mean-field theory of Leibler,[1] augmented by the elegant incorporation of fluctuation effects by Fredrickson and Helfand,[2] currently represents the most advanced treatment dealing with the ODT; we refer to this as the BLFH theory.[7] Recent experiments on model, nearly monodisperse, diblock copolymers indicate that the BLFH theory captures many of the essential features characterizing the ODT. In particular, the ODT has been demonstrated to be a weak first-order transition, as evidenced by discontinuities in low-frequency rheological properties[4,6] and in the small-angle neutron scattering response.[7] Although the BLFH theory has been developed for ideal (i.e., monodisperse) block copolymers, corrections for modest amounts of polydispersity based on a Schultz–Zimm (monomodal) distribution, have been incorporated into this class of predictions with reasonable success.[5,12-14] However, to the best of our knowledge neither theoretical nor experimental assessments of the influence of nonideal (nonmonomodal) distributions of block copolymers on the nature of the ODT have been reported. In this paper we present the initial results of a rheological study of the phase behavior of block copolymer mixtures in which a bimodal distribution of equal composition chains has been deliberately created.

The synthesis and characterization of the materials used in this study have been described earlier;[15] characterization data are given in Table I. Samples PEP–PEE-1, PEP–PEE-2, PEP–PEE-3, and PEP–PEE-5 (where PEP = poly(ethylenepropylene) and PEE = poly(ethylethylene)) are relatively narrow molar mass distribution (MMD), monomodal polymers, containing 55 ± 2% by volume PEP. In order to evaluate the effects of polydispersity, we have prepared three mixtures of samples PEP–PEE-1 and PEP–PEE-3 by dissolving the components in cyclohexane followed by vacuum drying at 80 °C. Sample identification, the mass-average degree of polymerization, N_w, and the polydispersity, N_w/N_n, for these mixtures are listed in Table I.

Rheological measurements were conducted using a Rheometrics RSAII solids analyzer equipped with a shear-sandwich fixture (0.5-mm gap). Samples for the rheometer were prepared by heating the polymer on a glass plate to remove air bubbles and subsequently compressing the sample to a thickness of 0.5 mm between the glass plate and a Teflon sheet. The entire procedure was carried out in a vacuum oven.

For narrow MMD monomodal samples the ODT is characterized by a discontinuous drop in the low-frequency dynamic elastic shear modulus, G', consistent with the first-order character of the transition.[2,6,7] Such data are shown in Figure 1 for PEP–PEE-5. Also shown in Figure 1 are comparable data for the bimodal sample P1P3-B (see Table I), where the frequencies were chosen such that the overall magnitude of the change in G' is similar for the two samples. At sufficiently low frequencies the width of the ODT is frequency independent.[6,7] Both of the chosen frequencies are in this range. These measurements indicate that the sharp nature of the transition, characteristic of the narrow MMD monomodal sample, is lost in the bimodal sample.

Table I
Molecular Characterization Data (55% by Volume PEP)

	volume fraction PEP–PEE-1	$10^{-3}N_w$[a]	N_w/N_n	T_{ODT},[b] °C
PEP–PEE-1	1	0.59	1.05	−41[c]
P1P3-A	0.505	1.05	1.30	57–75
P1P3-B	0.423	1.16	1.29	111–128
P1P3-C	0.265	1.28	1.25	168–183
PEP–PEE-3	0	1.52	1.05	291[d]
PEP–PEE-2	0	0.96	1.07	96[d]
PEP–PEE-5	0	1.03	1.05	125[e]

[a] The degree of polymerization data is based on a repeat unit molar mass of 56 g/mol. [b] Two values correspond to T_s and T_l as indicated in Figure 1. [c] Calculated based on eq 1–5. [d] Reference 6. [e] Reference 7.

The full-frequency response of sample P1P3-B as a function of temperature is shown in Figure 2, where the data have been time–temperature superposed by using the high-frequency portion of the spectra.[4,6,7] Both above and below the transition region (T_s to T_l in Figure 1), the low-frequency behavior of the block copolymer mixture resembles that for monomodal diblock copolymer,[4,6,7] $G' \sim \omega^2$ and $G' \sim \omega^{1/2}$, respectively. In the disordered state the effects of composition fluctuations, evidenced by thermorheological complexity,[4,6,7] are apparent up to aproximately 50 °C above the ODT. As with the isochronal data (Figure 1), the transition from terminal to nonterminal behavior occurs continuously, in contrast with the discontinuous response displayed by sample PEP–PEE-5 over a comparable range of temperatures and frequencies.[6,7]

The ODT has been examined in three different mixtures of PEP–PEE-1 and PEP–PEE-3, as indicated in Table I. In all three cases the nature of the transition is similar to that shown for sample P1P3-B. In Figure 3 the ODT temperatures for the three mixtures are plotted versus the mass-average degree of polymerization, N_w. The solid curve in Figure 3 represents the BLFH fluctuation theory[2,7] evaluated with $N = N_w$, based on the following equations, developed for the PEP–PEE diblock copolymers:[7]

$$\chi = 4.69/T + 4.44 \times 10^{-4} \qquad (1)$$

$$(\chi N)_{ODT} = 10.698 + 43.16\bar{N}^{-1/3} \qquad (2)$$

$$\bar{N} = Na^6/v^2 \qquad (3)$$

$$\ln a^2 = -2.21 \times 10^{-3}T + 4.84 \qquad (4)$$

$$\ln v = 6.5 \times 10^{-4}T + 4.489 \qquad (5)$$

Here χ is the conventional Flory–Huggins segment-

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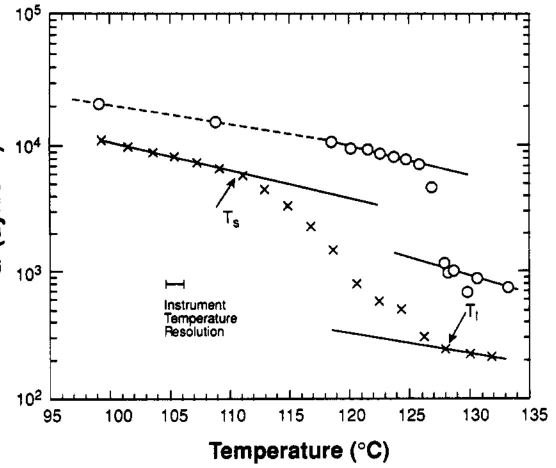

Figure 1. G' plotted versus temperature for PEP–PEE-5 (○) and P1P3-B (×). Measurements were obtained by using a 2% strain amplitude and at ω = 2.5 rad/s for PEP–PEE-5 and ω = 0.6309 rad/s for P1P3-B. T_s and T_l indicate the speculated solidus and liquidus temperatures, respectively.

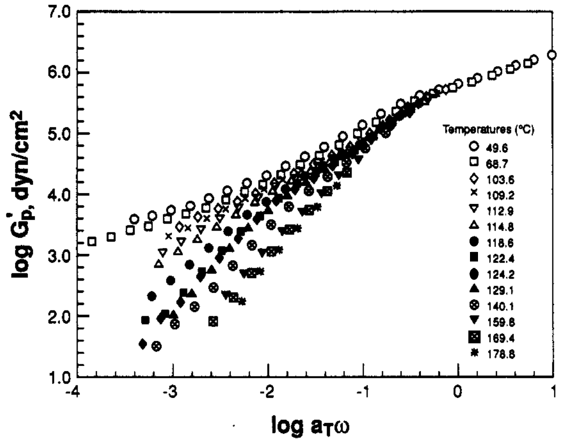

Figure 2. Reduced dynamic storage modulus, G_p', versus reduced frequency for P1P3-B. The data were shifted by using the following WLF parameters: T_0 = 35 °C, C_1^0 = 6.491 K^{-1}, C_2^0 = 141.4, $\rho(T)/\rho(35\ °C) = \exp(-6.5 \times 10^{-4}(T - 308.15))$.

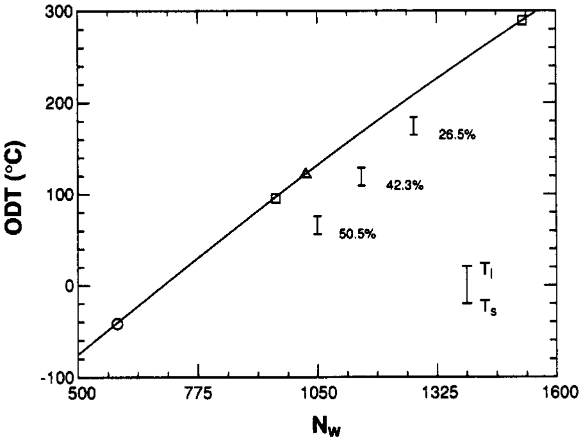

Figure 3. ODT temperature versus mass-average degree of polymerization for samples PEP–PEE-2 and PEP–PEE-3 (□),[6] PEP–PEE-5 (△),[7] and PEP–PEE-1 (○) (calculated using eqs 1–5). The line is calculated from eqs 1–5. The bars represent the range of the ODT for the three mixtures studied in this work as indicated by T_s and T_l in Figure 1. Percentages indicate the PEP–PEE-1 content by volume.

segment interaction parameter, T the absolute temperature, a the effective statistical segment length for the block copolymer, and v the reference (segment) volume. The line calculated from these equations gives the ODT temperature for narrow monomodal polymers. Corrections for small polydispersities as discussed earlier will not significantly alter the form of the curve. It is noticeable that the theory cannot predict the ODT temperatures for the mixtures even though the polydispersities involved are relatively small.

A quantitative description of the different nature of the ODT in bimodal block copolymer samples as opposed to narrow monomodal samples is not presently available. Nevertheless, the continuous character of the ODT observed in the rheological data presented here can be rationalized in the context of classic two-component, liquid–solid, phase behavior.[16] For the present situation we consider the class of phase diagrams characterized by regions of complete liquid-state and solid-state miscibility, separated by a biphasic region, bounded by liquidus and solidus lines (e.g., see the dichlorobenzene–p-dibromobenzene phase diagram[16]). Such a phase diagram for the mixtures studied in this work can be obtained by replacing N_w with the volume fraction of PEP–PEE-1, in Figure 3. However, because PEP–PEE-1 and PEP–PEE-3 have essentially equal densities, these two quantities are proportional, and the form of Figure 3 is not affected.

Within the biphasic region a high molar mass rich ordered phase will exist in equilibrium with a low molar mass rich disordered phase. Increasing or decreasing the temperature produces a continuous shift in the volume fractions of the disordered and ordered phases; pure solid and pure liquid phases are present below and above the solidus and liquidus lines, respectively. As a consequence, the transition from the ordered (solid) state to the disordered (liquid) state will be manifested as a continuous drop in G' at low frequencies. The width of the rheological transition will reflect the temperature range of the biphasic region; i.e., T_s and T_l in Figure 1 correspond to the solidus and liquidus temperatures, respectively. Here we note that Fredrickson and Leibler[17] have considered the related case of a binary mixture of diblock copolymer and nonselective good solvent and predict the existence of a narrow biphasic region between the ordered and disordered states.

At present our interpretation of the ODT in bimodal, nearly symmetric, block copolymers is speculative. Nevertheless, these experimental results demonstrate that the identification of the ODT by rheological measurements can be complicated by the presence of even modest degrees of polydispersity or nonideal (e.g., bimodal) molar mass distributions.

Acknowledgment. We have benefited from discussion of this work with Glenn Fredrickson, particularly regarding the speculated phase behavior. This work was supported by the Center for Interfacial Engineering (CIE), an NSF-funded engineering research center at the University of Minnesota. Additional assistance has been provided to K.A. by the NATO Science Fellowship Programme, the Danish Natural and Technical Science Councils, and Knud Højgaards Fond and to F.S.B. from the NSF under PYI Grant DMR-8957386.

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Received May 23, 1990
Revised Manuscript Received July 20, 1990