Phase equilibria in mixtures of block copolymer and homopolymer

Deog Man Baek, Chang Dae Han* and Jin Kon Kim
Department of Chemical Engineering, Polytechnic University, Brooklyn, NY 11201, USA
(Received 15 October 1991; revised 17 February 1992; accepted 19 March 1992)

Phase diagrams were constructed experimentally for mixtures of a polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) copolymer and a homopolymer polystyrene. For the study, two SIS triblock copolymers having spherical and cylindrical microdomain structures, respectively, and a series of homopolymer polystyrenes were synthesized via anionic polymerization. In constructing phase diagrams, we combined the results of dynamic viscoelastic measurement (i.e. logarithmic plots of dynamic storage modulus *versus* dynamic loss modulus), which allowed us to determine the boundary between the mesophase and homogeneous phase, and turbidity measurement, which allowed us to determine cloud point curves for liquid–liquid (macrophase) separation. Experimental results are compared with predictions made by the theory of Hong and Noolandi. We have found that predicted results are at variance with experimental results.

(Keywords: mixture; block copolymers; anionic polymerization)

INTRODUCTION

In recent years, block copolymers have received the increasing attention of polymer scientists for various industrial applications, such as for pressure-sensitive adhesives and compatibilizing agents. In the preparation of pressure-sensitive adhesives, polydiene-based block copolymers, such as polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) and polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) copolymers, are widely used[1]. Since block copolymer alone is not sufficient to give the desired adhesion and tack, a low molecular weight resin(s), often referred to as a 'tackifying resin', is usually added in order to improve its ability to wet the surface and to form a bond of measurable strength upon contact. Tackifying resins come with a variety of chemical structures and physical properties. It is generally believed that in order to have the desired performance, pressure-sensitive adhesive formulas (i.e. mixtures of an SIS (or SBS) block copolymer and a tackifying resin) must not undergo macrophase separation, meaning that added tackifying resin must be solubilized in the block copolymer[2]. This suggests that, in the development of pressure-sensitive adhesives, it is very important to have information on the phase diagram for mixtures of an SIS (or SBS) block copolymer and a tackifying resin.

One of the very active research areas in the polymer industry today is the development of polymer blends consisting of two chemically dissimilar structures. In such endeavours, more often than not, a lack of compatibility is found between the two homopolymers chosen. In order to impart (or improve) compatibility between homopolymer A and homopolymer B, it is tempting to employ an AB-type diblock copolymer, such that block A may be compatible with homopolymer A, and block B may be compatible with homopolymer B. In such an instance, the block copolymer functions as a compatibilizer. It should be mentioned that the chemical structure of the constituent blocks in a diblock copolymer, which is to be used as compatibilizer, can be different from the chemical structure of the two homopolymers that are to be blended. It is important to realize that, in mixing a block copolymer with a homopolymer, one must have information on the phase diagram, because the extent of compatibility (i.e. miscibility window) between the two would depend, among many other factors, on the molecular weights of the constituent polymers.

Previously, using the combined results of small-angle X-ray scattering and turbidity measurements, Roe and co-workers[3,4] reported that when a homopolymer polystyrene (PS) was added to an SB diblock copolymer, the spinodal temperature of the block copolymer was raised or lowered, depending upon the molecular weight of added homopolymer PS. They showed further that the phase diagram for mixtures of a block copolymer and a homopolymer could become very complicated, depending upon the molecular weight of added homopolymer. Subsequently, using the combined results of dynamic viscoelastic measurement (i.e. logarithmic plots of dynamic storage modulus *versus* dynamic loss modulus) and turbidity measurement, Han and co-workers[5–7] reported phase diagrams for mixtures of an SIS (and SBS) triblock copolymer and a midblock-associating resin (i.e. tackifying resin) or an endblock-associating resin.

On the theoretical side, Krause[8] developed a thermodynamic theory for microphase separation in a mixture of block copolymer and homopolymer, and predicted that the addition of homopolymer A to a

---

*To whom correspondence should be addressed

0032-3861/92/224821-11

symmetric AB-type diblock copolymer would enhance microphase separation, unless the degree of polymerization of homopolymer A was equal to or less than one-quarter the degree of polymerization of the block copolymer. Later, Leibler and Benoit[9] extended the earlier theory of Leibler[10] in order to predict the spinodal temperature (T_s) for a mixture of AB-type diblock copolymer and homopolymer whose structure is identical to that of one of the blocks.

Using a density functional formalism on the basis of mean-field theory and employing the fourth-order expansion of the free energy of the microphase, Hong and Noolandi[11] developed a statistical thermodynamic theory that enables one to predict T_s for a mixture of diblock copolymer and homopolymer whose chemical structure can be different from that of both blocks. It should be mentioned that the second-order term of the free energy in the Hong–Noolandi theory reduces to the Leibler–Benoit theory in the limit that all Kuhn statistical lengths and all reference (pure component) densities are equal, and when the chemical structure of added homopolymer is identical to that of one of the blocks. Hong and Noolandi[11] and Whitmore and Noolandi[12] have shown further how to construct a phase diagram for mixtures of an AB-type diblock copolymer and a homopolymer, in terms of the ratio of the molecular weights of homopolymer and corresponding block, block copolymer composition, and the Flory–Huggins interaction parameters for the polymer pairs involved. It should be pointed out, however, that this theory has so far been implemented for block copolymers having a lamellar microdomain structure.

To date, there appear to be no reports in the literature that compare the phase diagram for mixtures of a block copolymer and a homopolymer obtained from experiment with that predicted from the Hong–Noolandi theory[11]. In this paper, we shall present experimental results of phase diagrams for mixtures of an SIS triblock copolymer and a homopolymer PS and then compare them with predictions made by the Hong–Noolandi theory.

EXPERIMENTAL

Materials

Two SIS triblock copolymers, having spherical and cylindrical microdomain structures, respectively, and a series of homopolymer PSs were synthesized via anionic polymerization. *Tables 1* and *2* summarize the molecular characteristics of the polymers employed in this study. The block copolymers, SIS-A and SIS-B, are identical to those used in our previous study[13], except that in the present study the 'dead' homopolymer PS in the respective block copolymers was removed by fractionation. Note that SIS-A has spherical microdomain structure and SIS-B has cylindrical microdomain structure[13].

Table 1 Molecular characteristics of the block copolymers

Sample code	M_w (S–I–S)	M_w/M_n
SIS-A	7400–99 000–7400	~1.5
SIS-B	5850–27 300–5850	~1.5

Table 2 Molecular characteristics of the homopolymers

Sample code	M_w	M_w/M_n
PS15	1500	<1.1
PS20	2000	<1.1
PS30	3000	<1.05
PS37	3700	<1.05

Sample preparation

We prepared mixtures of a block copolymer (SIS-A and SIS-B) and a homopolymer (PS15, PS20, PS30 and PS37), with various proportions for dynamic viscoelastic measurements and turbidity measurements, as described below.

Various mixtures were prepared by first dissolving the block copolymer and a homopolymer in toluene (10% solid in solution) in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Co.) and then slowly evaporating the solvent. The evaporation of solvent was carried out initially in open air at room temperature for 1 week and then in a vacuum oven at 40°C for 3 days. The last trace of solvent was removed by drying the sample in a vacuum oven at elevated temperature by gradually raising the oven temperature up to 110°C. Drying of the sample was continued until there was no further change in weight. Finally, the sample was annealed at 130°C for 10 h.

Measurement of dynamic viscoelastic properties

A Model R16 Weissenberg rheogoniometer (Sangamo Control Inc.) in the cone-and-plate mode (25 mm diameter plate and 4° cone angle with a 160 μm gap) was used to measure, in the oscillatory shear mode, the dynamic storage modulus (G') and dynamic loss modulus (G'') as functions of angular frequency (ω) at various temperatures. These measurements were used later to determine the boundary between the mesophase and homogeneous phase, following the procedure described elsewhere[5–7]. In the oscillatory measurements a fixed strain of 0.003, which was well within the linear viscoelastic range of the materials investigated, was used. All experiments were conducted in the presence of nitrogen in order to preclude oxidative degradation of the sample. Data acquisition was accomplished with the aid of a microcomputer interfaced with the rheometer. Rheological measurements were made at various temperatures in the range 80–200°C, to within ±1°C.

Turbidity measurements

A He–Ne laser ($\lambda = 632.8$ nm) light scattering apparatus constructed in our laboratory was used to determine the turbidity of mixtures of a block copolymer and a homopolymer. The turbidity measurements were used to construct cloud point curves for the mixtures. The light scattering apparatus was attached to a programmable temperature controller. Samples were placed between two glass plates and optimum scattering angles were chosen in the range of 5–10°, depending upon the sample.

RESULTS AND DISCUSSION

Phase diagram constructed from experiment

In constructing the phase diagram from experiment, we combined the results of two methods, namely dynamic viscoelastic measurements, which enabled us to determine the boundary between the mesophase and the homogeneous phase, and turbidity measurements, which enabled us to obtain the cloud point curve for the liquid–liquid (i.e. macrophase) separation between block copolymer and homopolymer. In the use of dynamic viscoelastic measurements, plots of log *G′ versus* log *G″* were prepared to determine the order–disorder transition temperature (T_r) of the block copolymer SIS-A (or SIS-B), and mixtures of the block copolymer and homopolymer PS. Details of the procedures employed are described elsewhere[5–7,14,15].

Phase diagrams constructed from experiment are given in *Figure 1a* for the SIS-A/PS15 system, in *Figure 2a* for the SIS-A/PS20 system, and in *Figure 3a* for the SIS-A/PS30 system. Phase diagrams predicted with the Hong–Noolandi theory[11] are given in *Figures 1b–3b*, but comparison between experimental results and predictions will be discussed after all other experimental results are presented.

With reference to *Figures 1a–3a*: curve AB separating the mesophase (M_1) and the homogeneous phase (H) was obtained by dynamic viscoelastic measurements and the cloud point curve was obtained using turbidity measurements; the region denoted by ($M_1 + L_2$) represents the mixture consisting of the mesophase (M_1) and the macrophase-separated PS (L_2); the region denoted by ($L_1 + L_2$) represents the mixture consisting of the disordered block copolymer (L_1) and the macrophase-separated PS (L_2). It should be pointed out that the mesophase M_1 contains part of the added PS that has been solubilized. Thus the morphology of the mesophase M_1 inside the cloud point curve in *Figures 1a–3a* may be different from that on the left-hand side of the cloud point curve, because a morphological transition (e.g. from cylindrical to lamellar microdomains or a phase inversion) may take place as the amount of added homopolymer PS is increased[16–18]. The horizontal broken line BC (denoted by square symbols) within the cloud point curve in *Figures 1a–3a* indicates the phase boundary at which the microdomains in the block copolymer SIS-A become disordered (i.e. homogeneous) as the temperature is increased. This was determined by a sudden change in scattered light intensity observed during turbidity measurements. It should be noted that Roe and co-workers[3,4] used small-angle X-ray scattering (SAXS) to determine the spinodal curves for microphase separation in mixtures of a block copolymer and a homopolymer.

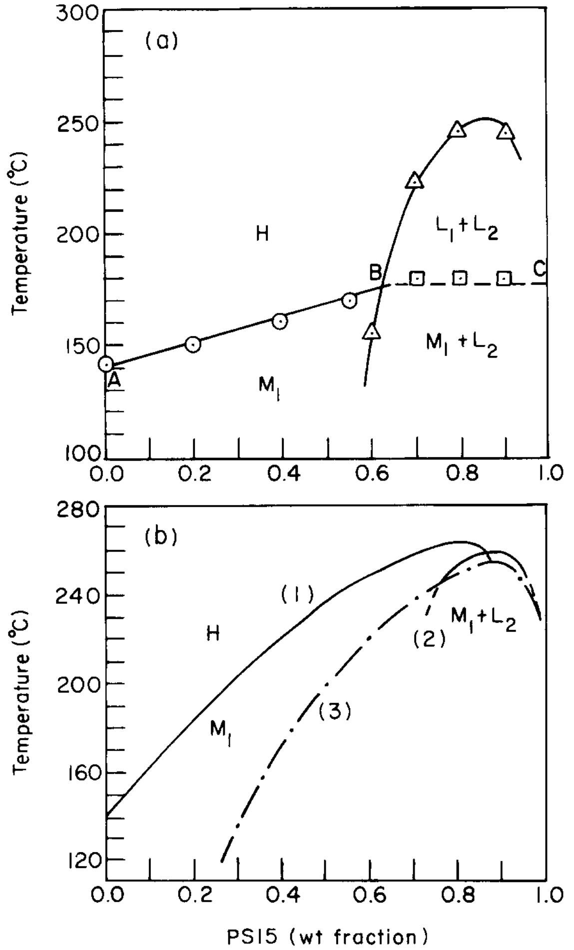

Figure 1 Phase diagram for block copolymer SIS-A/homopolymer PS15 mixtures: (a) experimental phase diagram; (b) theoretical phase diagram. 1, Spinodal curve for microphase separation based on the Hong–Noolandi theory; 2, binodal curve for macrophase separation based on the Hong–Noolandi theory; 3, binodal curve for macrophase separation based on the Flory–Huggins theory

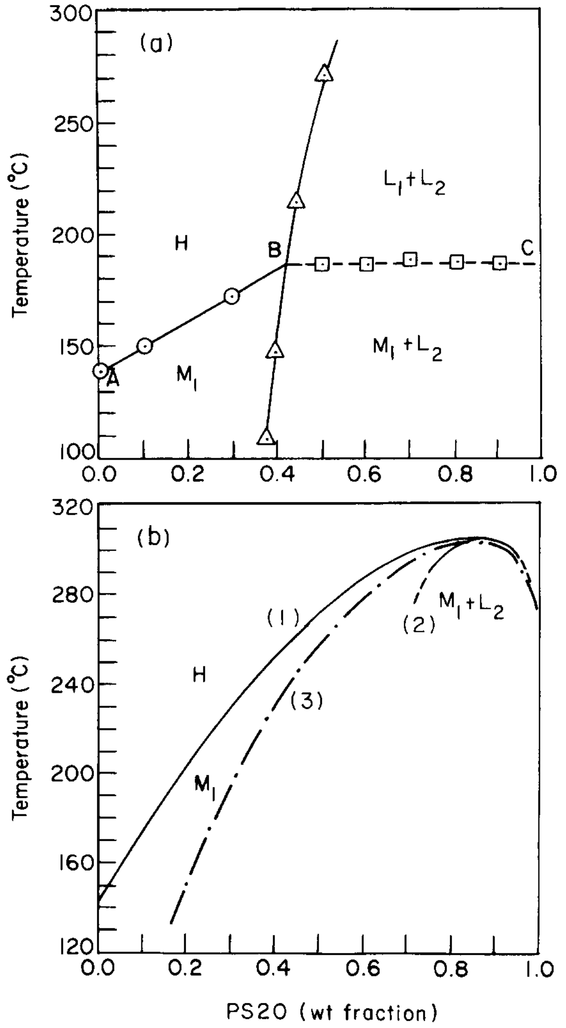

Figure 2 Phase diagram for block copolymer SIS-A/homopolymer PS20 mixtures: (a) experimental phase diagram; (b) theoretical phase diagram. 1, Spinodal curve for microphase separation based on the Hong–Noolandi theory; 2, binodal curve for macrophase separation based on the Hong–Noolandi theory; 3, binodal curve for macrophase separation based on the Flory–Huggins theory

The following observations are worth noting in *Figures 1a–3a*: (1) the solubility limit of homopolymer PS in the block copolymer SIS-A decreases as the molecular weight of homopolymer PS (M_H) increases from 1500

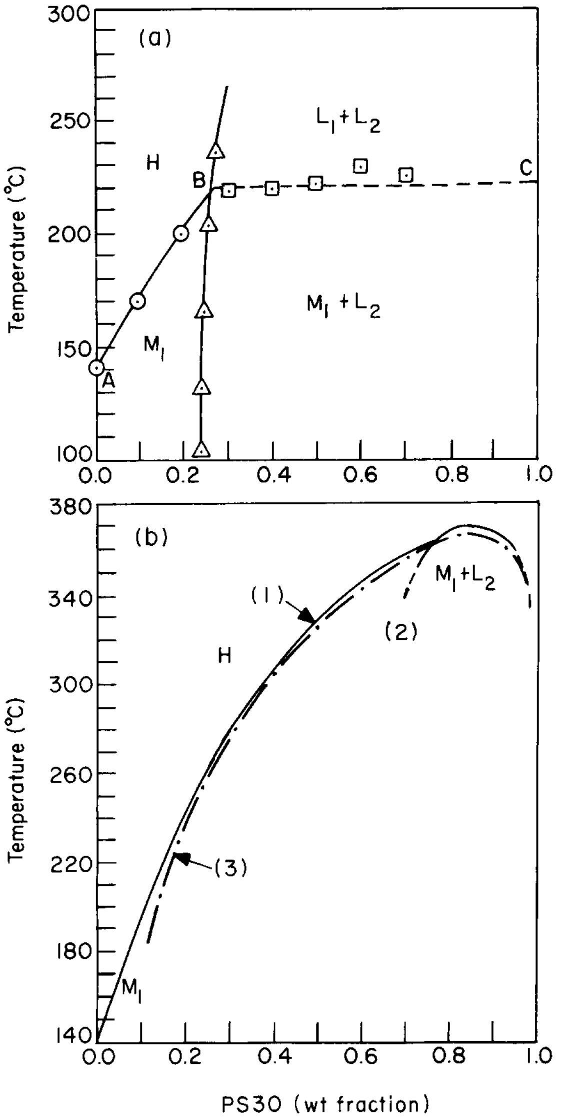

Figure 3 Phase diagram for block copolymer SIS-A/homopolymer PS30 mixtures: (a) experimental phase diagram; (b) theoretical phase diagram. 1, Spinodal curve for microphase separation based on the Hong–Noolandi theory; 2, binodal curve for macrophase separation based on the Hong–Noolandi theory; 3, binodal curve for macrophase separation based on the Flory–Huggins theory

to 2000 and to 3000; (2) the slope of the phase boundary separating region H and region M_1 becomes steeper as M_{H} increases from 1500 to 2000 and to 3000.

Phase diagrams constructed from experiment are given in *Figure 4a* for the SIS-B/PS15 system, in *Figure 5a* for SIS-B/PS20 system, in *Figure 6a* for the SIS-B/PS30 system and in *Figure 7a* for the SIS-B/PS37 system. Symbols H, M_1, L_1 and L_2 in *Figures 4a–7a* have the same meanings as in *Figures 1a–3a*. The following observations are worth noting in *Figures 4a–7a*: (1) the solubility limit of homopolymer PS in the block copolymer SIS-B decreases as M_{H} increases from 1500 to 3700; (2) the slope of the phase boundary separating region H from region M_1 becomes steeper as M_{H} increases from 1500 to 3700; (3) at a fixed $M_{\mathrm{H}}/M_{\mathrm{A}}$ ratio, M_{A} being the molecular weight of PS in the block copolymer, the solubility limit of homopolymer PS is greater in the block copolymer SIS-B having cylindrical microdomains than in the block copolymer SIS-A having spherical microdomains; (4) at a fixed $M_{\mathrm{H}}/M_{\mathrm{A}}$ ratio, the slope of the phase boundary separating region H and region M_1 is lower in the block copolymer SIS-B/homopolymer PS system than in the block copolymer SIS-A/homopolymer PS system.

Comparison with prediction

Using the Hong–Noolandi theory[11], phase diagrams were constructed for each block copolymer/homopolymer system studied experimentally, and they are given in *Figures 1b–7b*. Note in *Figures 1b–7b* that curve 1 represents the spinodal for *microphase* separation and curve 2 represents the binodal for *macrophase* separation. For comparison, in *Figures 1b–7b* we have added curve 3, representing the binodal for *macrophase* separation, which was obtained using the Flory–Huggins theory. It should be mentioned that in the use of the Flory–Huggins theory, the block copolymers SIS-A and SIS-B were treated as random copolymers. It can be seen in *Figures 1b–7b* that phase separation behaviour in mixtures of a block copolymer and a homopolymer is quite different from that in mixtures of a random copolymer and a homopolymer. The Appendix contains a summary of the procedures for constructing the phase diagram, and for further details reference should be made to the original paper of Hong and Noolandi[11].

In predicting the phase diagrams presented in *Figures 1b–7b*, we treated the SIS triblock copolymer as an SI

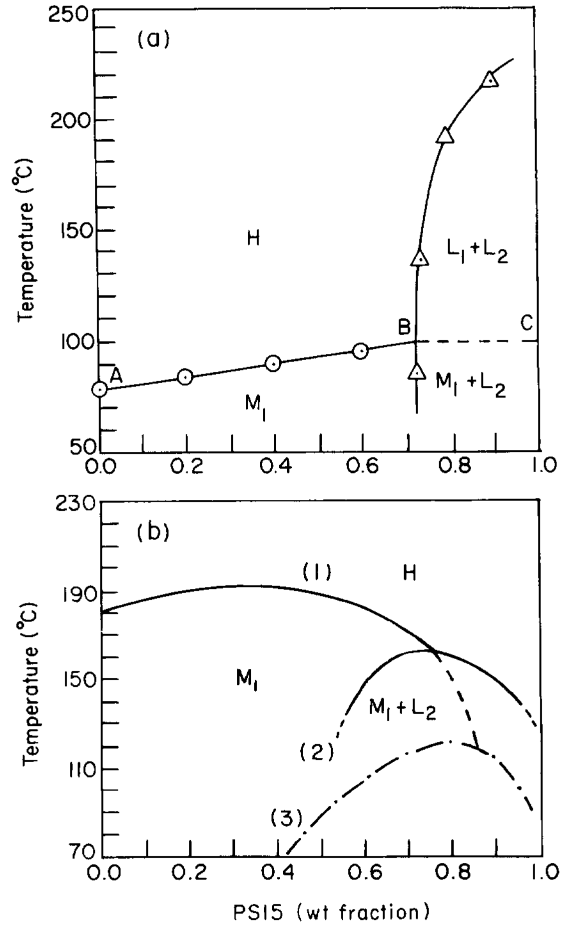

Figure 4 Phase diagram for block copolymer SIS-B/homopolymer PS15 mixtures: (a) experimental phase diagram; (b) theoretical phase diagram. 1, Spinodal curve for microphase separation based on the Hong–Noolandi theory; 2, binodal curve for macrophase separation based on the Hong–Noolandi theory; 3, binodal curve for macrophase separation based on the Flory–Huggins theory

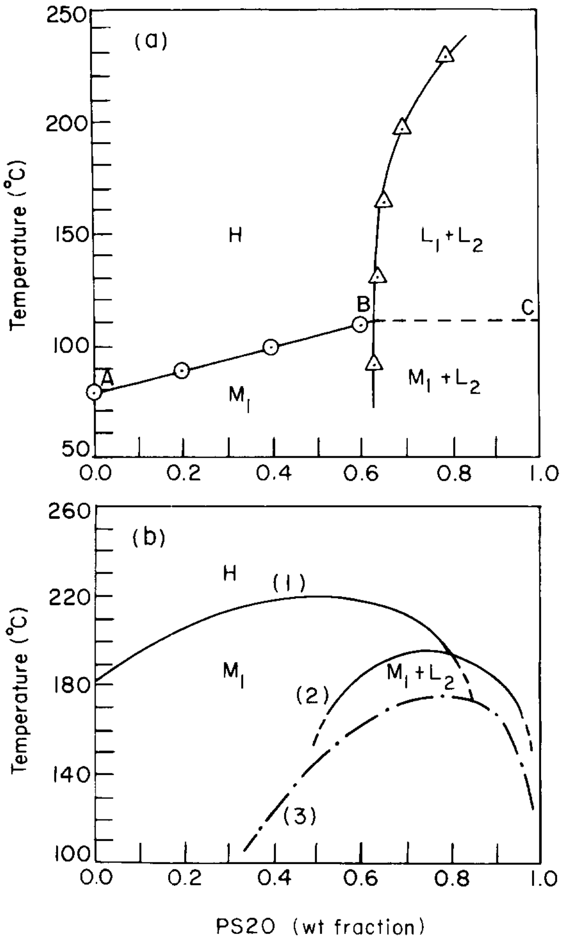

Figure 5 Phase diagram for block copolymer SIS-B/homopolymer PS20 mixtures: (a) experimental phase diagram; (b) theoretical phase diagram. 1, Spinodal curve for microphase separation based on the Hong–Noolandi theory; 2, binodal curve for macrophase separation based on the Hong–Noolandi theory; 3, binodal curve for macrophase separation based on the Flory–Huggins theory

diblock copolymer by dividing the molecular weight of the midblock polyisoprene (PI) in half. This was done because the Hong–Noolandi theory[11] is based on an AB-type diblock copolymer. However, we compared the predicted spinodal temperatures T_s for mixtures of SI diblock copolymer and homopolymer PS with those for mixtures of SIS triblock copolymer and homopolymer PS. In determining the T_s of the triblock copolymer and its mixtures with homopolymer PS, we employed the expressions for the density correlation functions S_{ij} for an ABA-type triblock copolymer presented by Mori *et al.*[19] (see equations (A20)–(A22) in the Appendix). We have found that the predicted values for T_s for the block copolymer SIS-A (also for SIS-B) and its mixtures with homopolymer PS are about 10°C higher than those for the corresponding diblock copolymer and its mixtures with homopolymer PS. Therefore we conclude that the shape of the predicted phase diagram for the SI diblock copolymer would not be much different from that for the SIS triblock copolymer.

In constructing the theoretical phase diagrams, the following expression for the interaction energy density Λ (cal cm^{-3}) for the PS/PI pair was used[20]:

$$\Lambda_{PS/PI} = 1.490 - 0.00179T \tag{1}$$

The specific volume v (cm^3 g^{-1}) for PS was obtained from[21]:

$$v_{PS} = 0.9199 + 5.098 \times 10^{-4}(T\text{-}273) + 2.354 \times 10^{-7}(T\text{-}273)^2 + [32.46 + 0.1017(T\text{-}273)]/M_{w,PS} \tag{2}$$

and for PI from[15]:

$$v_{PI} = 1.0771 + 7.22 \times 10^{-4}(T\text{-}273) + 2.46 \times 10^{-7}(T\text{-}273)^2 \tag{3}$$

where T is the absolute temperature and $M_{w,PS}$ is the molecular weight of PS. Note that the Flory–Huggins interaction parameter χ is related to the interaction energy density Λ by $\chi = \Lambda V_r/RT$, where V_r is the molar volume of a reference component. In the present study, styrene monomer was chosen as the reference component in computing values of χ for the PS/PI pair.

We have found that for the block copolymer SIS-A, the predicted value for T_r (138°C) on the basis of the Leibler theory[10] is very close to the measured value (140°C) (see *Figures 1–3*); however, for the block copolymer SIS-B the predicted value for T_r (180°C) is much higher than the measured value (80°C) (see *Figures 4–7*). The reason for such a large discrepency between the two values for the block copolymer SIS-B is not known at present. It should be mentioned that the

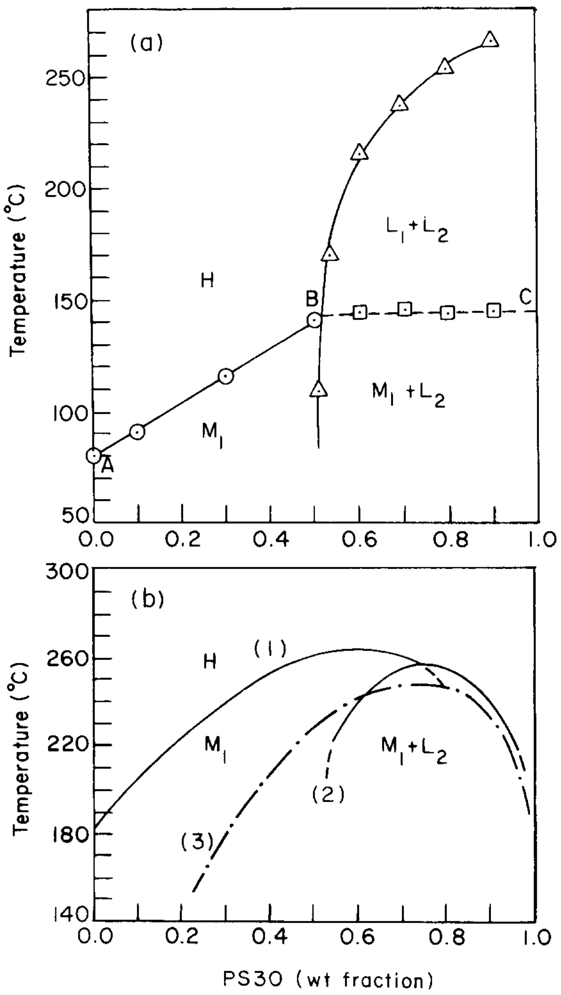

Figure 6 Phase diagram for block copolymer SIS-B/homopolymer PS30 mixtures: (a) experimental phase diagram; (b) theoretical phase diagram. 1, Spinodal curve for microphase separation based on the Hong–Noolandi theory; 2, binodal curve for macrophase separation based on the Hong–Noolandi theory; 3, binodal curve for macrophase separation based on the Flory–Huggins theory

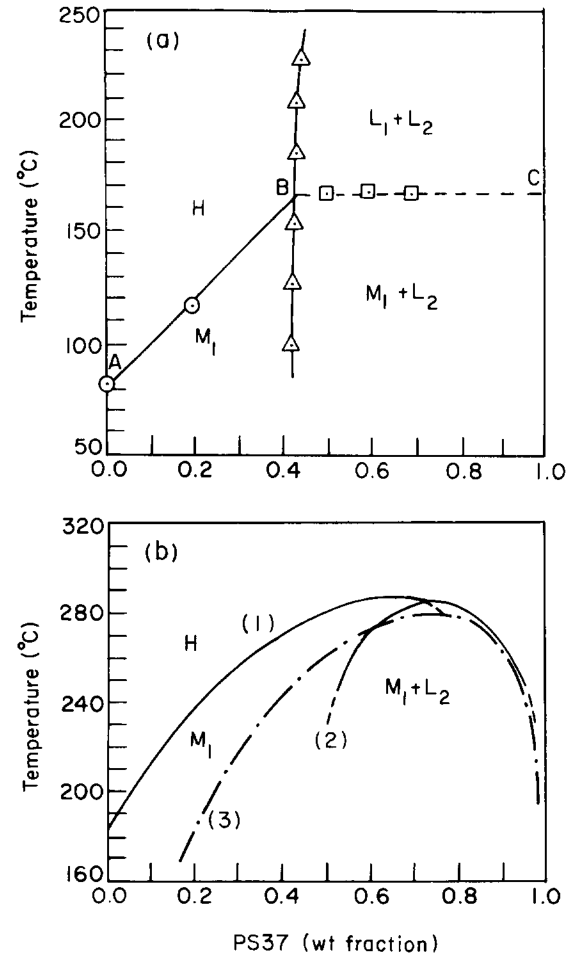

Figure 7 Phase diagram for block copolymer SIS-B/homopolymer PS37 mixtures: (a) experimental phase diagram; (b) theoretical phase diagram. 1, Spinodal curve for microphase separation based on the Hong–Noolandi theory; 2, binodal curve for macrophase separation based on the Hong–Noolandi theory; 3, binodal curve for macrophase separation based on the Flory–Huggins theory

measured values of T_r obtained in this study for the block copolymers SIS-A and SIS-B are somewhat lower than the respective values reported in our previous paper[13], owing to the fact that the 'dead' homopolymer PS, which had been present in the samples used in the previous study, was removed by fractionation.

Using SAXS measurements to determine the T_r of a block copolymer and turbidity measurements to determine the cloud point curve, Roe and Zin[3] constructed phase diagrams for (1) mixtures of a polystyrene-*block*-polybutadiene copolymer (here designated as SB-R) having $M_w = 7560$ for the PS block and $M_w = 20\,440$ for the polybutadiene (PB) block and a homopolymer PS having $M_w = 2400$ (PS24), and (2) mixtures of SB-R and a homopolymer PB having $M_w = 26\,000$ (PB260). Their experimental results are reproduced in *Figure 8a* for the SB-R/PS24 system and in *Figure 9a* for the SB-R/PB260 system. For comparison, we used the Hong–Noolandi theory to construct phase diagrams for both systems and they are displayed in *Figures 8b* and *9b*. In predicting the phase diagrams given in *Figures 8b* and *9b*, we used the following expression for the interaction energy density $\Lambda_{PS/PB}$ for the PS–PB pair[22]:

$$\Lambda_{PS/PB} = 1.573 + 0.09\phi_{PS} - 0.0021T \qquad (4)$$

where ϕ_{PS} denotes the volume fraction of PS, and for the specific volume of PB[23]:

$$v_{PB} = 1.1138 + 8.24 \times 10^{-4}(T\text{-}273) \qquad (5)$$

It should be noted in *Figures 8* and *9* that the shape of the phase diagrams predicted with the Hong–Noolandi theory is quite different from the experimental results; there are several potential sources for these discrepancies. The Hong–Noolandi theory assumes that the morphology of ordered microdomains in a block copolymer remains as lamellae even after a homopolymer is added. However, it has been reported[16,18,24–26] that the transformation of microdomain morphology in a block copolymer may take place from spheres to cylinders and to lamellae as the amount of added homopolymer is increased, until phase inversion takes place. It should be remembered that block copolymer SIS-A has a spherical microdomain structure and block copolymer SIS-B has a cylindrical microdomain structure. In this regard, perhaps a comparison of phase diagrams between experiment and prediction may not be warranted. On the other hand, according to Whitmore[27], who employed the fourth-order expansion of the free energy of the microphase given in terms of the local density of A monomers in an AB-type diblock copolymer except very near to the order–disorder transition, the difference

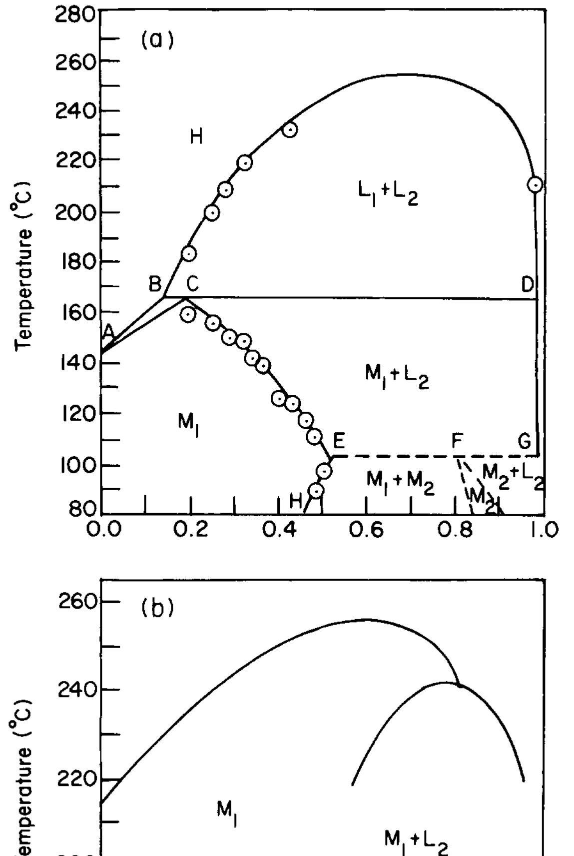

Figure 8 Phase diagram for block copolymer SB-R/homopolymer PS24 mixtures: (a) experimental results taken from ref. 3; (b) theoretical prediction based on the Hong–Noolandi theory

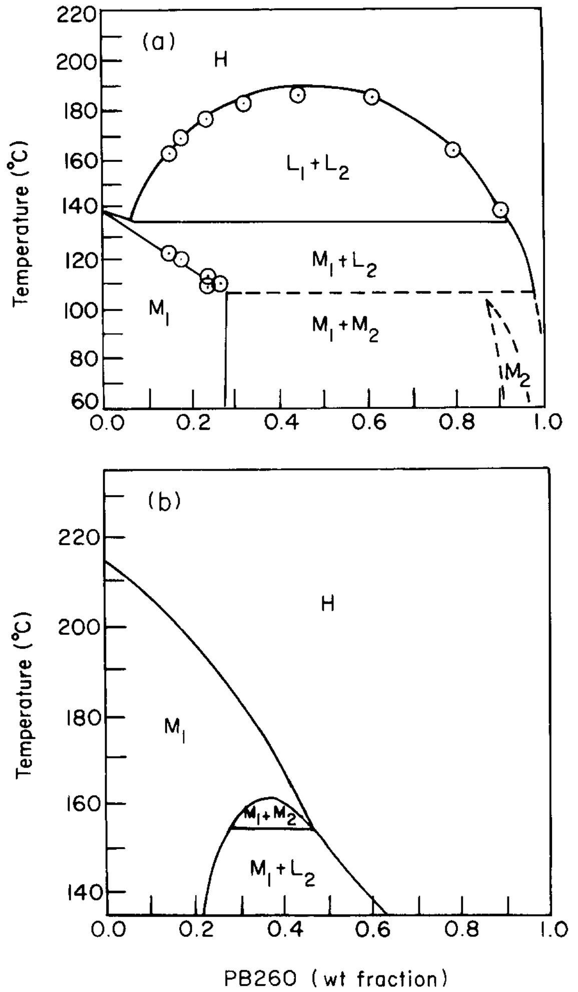

Figure 9 Phase diagram for block copolymer SB-R/homopolymer PB260 mixtures: (a) experimental results taken from ref. 3; (b) theoretical prediction based on the Hong–Noolandi theory

between the free energies of any two morphologies is generally much smaller than the difference between the free energies of any microphase and the homogeneous phase. This seems to suggest that the morphological transition taking place, for instance from cylinders to lamellae, by the addition of a homopolymer to the block copolymer may play a small role in explaining the discrepancies observed above between experiment and prediction. However, more recently, by performing fully self-consistent calculations for neat block copolymers, Whitmore[27] found that there is a considerable difference in the free energies between spheres on a body-centred cubic lattice and lamellae. This seems to suggest that in the context of a mean-field theory, different morphologies of microdomains might indeed affect the shape of the phase diagram for mixtures of a block copolymer and a homopolymer if fully self-consistent calculations, rather than the fourth-order expansion of the free energy of the microphase, are carried out. This is a subject for further investigation.

The Hong–Noolandi theory makes use of a perturbation near the spinodal point. This implies that the theory would not be accurate at temperatures far away from the spinodal point. The computer programs used in this work do not calculate the binodal lines arbitrarily close to compositions corresponding to ϕ_H equal to 0 or 1, ϕ_H being the volume fraction of added homopolymer. In our calculations they were terminated on the right side at $\phi_H = 0.95$. This is why in all the predicted phase diagrams (*Figures 1b–7b*) the binodal curve was not drawn at compositions where $\phi_H > 0.95$. This suggests that the Hong–Noolandi theory must be extended to be able to predicrt phase diagrams for mixtures of a block copolymer and a homopolymer at temperatures far away from the spinodal point. It should also be noted that the Hong–Noolandi theory assumes a single sinusoidal function to represent composition fluctuations near the spinodal point. This assumption might be too restrictive and thus multiple sinusoidal functions may better be able to represent composition fluctuations near the spinodal point. The use of the Flory–Huggins expression in constructing binodal curves for mixtures of a microphase-separated block copolymer and a homopolymer may not be warranted.

Note that, like the Leibler theory for neat block copolymers, the Hong–Noolandi theory[11] for mixtures of a block copolymer and a homopolymer is a mean-field theory, i.e. an approximation which is rigorously valid only for an infinite molecular weight block copolymer. More recently, Fredrickson and Helfand[28] took into account a finite-sized diblock copolymer and improved the Landau-type mean-field prediction, yielding:

$$(\chi N)_t = 10.495 + 41.022N^{-1/3} \qquad (6)$$

for a symmetric diblock copolymer with equal block lengths ($f = 0.5$) and also equal Kuhn statistical lengths, with $(\chi N)_t$ referring to the location of the transition induced by composition fluctuations, Flory interaction parameter χ, and degree of polymerization N. Note that the derivation of equation (6) includes the effect of composition fluctuations on the microphase separation transition (MST), which was neglected in Leibler's final equation, $(\chi N)_t = 10.495$, although the importance of this effect was pointed out by Leibler. In view of the fact that χ is inversely proportional to temperature, it can be seen in equation (6) that the presence of the second term, $41.022N^{-1/3}$, will lower the predicted value of the transition temperature below the value based on the first term alone.

For asymmetric block copolymers having unequal block lengths ($f \neq 0.5$) and also unequal Kuhn statistical lengths, such as SIS-A and SIS-B under consideration, the following general expression[28] should be used instead of equation (6):

$$(\chi N)_t = (\chi N)_s - (1/2)c^2\tau^*(d\lambda)^{2/3}\tilde{N}^{-1/3} \qquad (7)$$

where $(\chi N)_s$ is the value of χN at the spinodal point; $\tilde{N}$ is the reduced degree of polymerization defined by

$$\tilde{N} = N[(b^6/v^2)_{PS}(b^6/v^2)_{PI}]^{1/2}$$

in which b is the Kuhn statistical length and v is the statistical segment volume; c is defined by

$$c = \left[\frac{x}{3}\frac{\partial^2 F(x,f)}{\partial x^2}\right]^{1/2}_{x=x^*} \qquad (8)$$

where $F(x,f)$ is defined by

$$F(x,f) = g(1,x)/\{g(f,x)g(1-f,x) - (1/4)[g(1,x) - g(f,x) - g(1-f,x)]^2\} \qquad (9)$$

in which $g(f,x)$ is the Debye function defined by

$$g(f,x) = (2/x^2)[fx + \exp(-fx) - 1] \qquad (10)$$

and x is defined by

$$x = q^2Nb^2/6 = q^2R_g^2 \qquad (11)$$

where q is the magnitude of the wave vector and R_g is the radius of gyration of an ideal chain. It should be mentioned that x^* in equation (8) denotes the value of x, defined by equation (11), at the spinodal point. τ^* in equation (7) is a dimensionless parameter defined by[29]

$$\tau^* = \tau(d\lambda)^{-2/3}\tilde{N}^{1/3}$$

where τ is defined by[28]

$$\tau = [F(x^*, f) - 2\chi N]/c^2$$

Note that τ^* is a constant (-2.0308) for lamellar microdomains, but varies with $\tilde{N}$ for spherical and cylindrical microdomains. Note further that τ and λ in equation (7) are related to Leibler's[10] coefficients α_n and β_n, and d is given by

$$d = 3x^*/2\pi \qquad (12)$$

Since SIS-A ($f = 0.111$) and SIS-B ($f = 0.256$) are triblock copolymers, in using equation (7), which was derived for an AB-type diblock copolymer, we treated the triblock copolymers SIS-A and SIS-B as SI diblock copolymers by dividing the molecular weight of the midblock PI in half, and then evaluated the parameters c, τ^*, d, λ and $\tilde{N}$, appearing in equation (7). For SIS-A we obtained:

$$(\chi N)_t = 62.252 + 735.961\tilde{N}^{-1/3} \qquad (13)$$

and for SIS-B:

$$(\chi N)_t = 17.635 + 100.629\tilde{N}^{-1/3} \qquad (14)$$

Using $N = 798$, which is based on one-half of the molecular weight of SIS-A, $\tilde{N}$ was calculated to be 3133, yielding $735.97\tilde{N}^{-1/3} = 50.298$; using $N = 257$, which is based on one-half of the molecular weight of SIS-B, $\tilde{N}$ was calculated to be 1008, yielding $100.629\tilde{N}^{-1/3} = 10.038$. In carrying out numerical computations, however, we learned that the Fredrickson–Helfand theory did *not* predict the existence of spherical microdomains for $\tilde{N} = 3133$ (i.e. SIS-A) and for $\tilde{N} = 1008$ (i.e. for SIS-B); this confirmed the observation reported earlier[28] that, owing to the nature of the Hartree approximation employed, the use of equation (7) is only valid for $\tilde{N} \geqslant 10^4$. Therefore, it can be concluded that equation (7) is not directly applicable to predicting correct values of T_r for SIS-A and SIS-B.

Very recently, Burger *et al.*[29] considered the polydispersity effect on composition fluctuations in the MST of diblock copolymers and, for a diblock copolymer having a broad molecular distribution, predicted the existence of spherical microdomains even when the value of $\tilde{N}$ is about 10^4. In the present study we applied the analysis of Burger *et al.* to the block copolymers, SIS-A and SIS-B, each having a polydispersity index (M_w/M_n) of about 1.5. We found that the existence of spherical microdomains was *not* predicted for both block copolymers, suggesting that the values of $M_w/M_n = 1.5$ and $\tilde{N} = 3133$ for SIS-A, and the values of $M_w/M_n = 1.5$ and $\tilde{N} = 1008$ for SIS-B, were not sufficiently large. Note that since the values of $(\chi N)_{s,\mathrm{poly}}$ for polydisperse block copolymers are smaller than the values of $(\chi N)_{s,\mathrm{mono}}$ for monodisperse block copolymers, the inclusion of the polydispersity effect will predict higher values of T_r than the Liebler theory, which considers monodisperse block copolymers. Thus, the inclusion of the polydispersity effect counterbalances the contribution of composition fluctuations to $(\chi N)_t$, with regard to predicting the order–disorder transition temperature of a block copolymer.

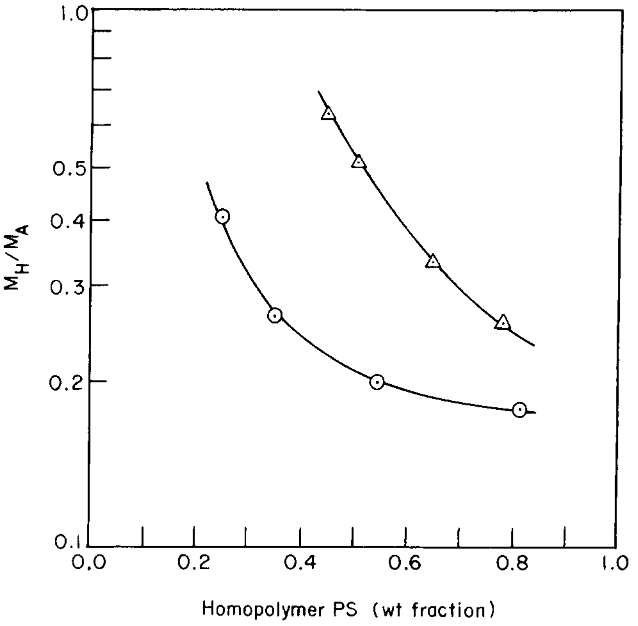

Figure 10 Solubility limits of homopolymer polystyrene in SIS block copolymer determined at 50°C: ⊙, block copolymer SIS-A/homopolymer PS mixtures; △, block copolymer SIS-B/homopolymer PS mixtures

Solubility limits of homopolymer in block copolymer

Figure 10 gives a summary of the solubility limits of homopolymer PS at 50°C, determined via light scattering, in the block copolymers SIS-A and SIS-B. In obtaining the results, we varied the concentration of homopolymer PS with an interval of 10 wt% and measured turbidity. Therefore, the data points (i.e. the phase boundary) in *Figure 10* should not be construed as exact values. The solid curves in *Figure 10* were drawn through the data points. It can be seen in *Figure 10* that for a fixed M_H/M_A ratio, a greater amount of PS is solubilized in SIS-B than in SIS-A. This indicates that the block length ratio (i.e. composition) of block copolymer dictates solubility limits of added homopolymer.

CONCLUDING REMARKS

In this paper we have presented experimentally determined phase diagrams for mixtures of an SIS triblock copolymer and a homopolymer PS and compared them with predictions made by the theory of Hong and Noolandi. We have found that predicted results are at variance with experimental results. We have described several plausible reasons that might explain the observed discrepancies between experiment and theory.

We feel that the following three factors, among others, are worth consideration in future theoretical developments.

(1) In general, the Leibler theory predicts the order–disorder transition temperature T_r (also referred to

as the microphase separation transition temperature) of a block copolymer to be much higher than the measured value, as was the case for the block copolymer SIS-B considered in this study (see also ref. 13). Since the theory of Hong and Noolandi is based, like the Leibler theory, on an infinite molecular weight block copolymer, it seems necessary to develop a theory for microphase separation in block copolymers with finite molecular weight. In this paper we have shown that a correction due to composition fluctuations for predicted transition temperature T_r, suggested by Fredrickson and Helfand, is not applicable to such block copolymers as those considered in this study, which have a degree of polymerization N of the order of hundreds.

(2) In view of the experimental fact that when a homopolymer A (or homopolymer B) is added to an AB- or ABA-type block copolymer the resulting microdomain morphology changes from spheres to cylinders and to lamellae until a reverse morphology occurs[18], we feel that this experimental aspect must be incorporated in future theoretical efforts, in predicting the phase diagram for mixtures of block copolymer and homopolymer. The theory of Hong and Noolandi in the present form assumes lamellar microdomain structure for the block copolymer as well as its mixtures with a homopolymer.

(3) Owing to the fact that a perturbation technique was applied near the spinodal point, the theory of Hong and Noolandi in the present form cannot predict binodal curves at temperatures far from the spinodal point (see *Figures 1b–7b*). We feel that higher order terms in the expansion of the free energy functional or a fully self-consistent method may be necessary in order to predict phase equilibria in mixtures of a block copolymer and a homopolymer at temperatures far from the spinodal point.

However, more experimental study, especially with AB-type diblock copolymers, is needed to establish the effects of microdomain morphology (spheres, cylinders, lamellae) on the nature of phase equilibria in mixtures with a homopolymer and on the solubility limits of such homopolymers.

It should be pointed out that the accuracy of the theoretical predictions presented in this paper is very sensitive to the accuracy of the Flory–Huggins interaction parameter χ. In the present study we used values of χ based on equation (1), which was obtained from cloud point measurements and then curve-fitting the data to the Flory–Huggins theory. Very recently, using experimental results from SAXS and the random phase approximation (RPA) method, Hashimoto and co-workers[30] investigated the effect of the molecular weight of added homopolymer on χ in mixtures of an SI diblock copolymer and a homopolymer PS, in addition to investigating the effect of temperature. They concluded that as low-molecular weight homopolymer PS was added, the values of χ increased, and that the values of χ depended on the degree of polymerization of the block copolymer. However, a recent series of papers by Freed and co-workers[31–33] warn that the values of χ obtained from RPA calculation may not be accurate, since the RPA method is based on the assumption of incompressibility, which may be not valid for polymer blends and block copolymer melts. It should be pointed out that in the use of the Flory–Huggins theory, the value of χ is independent of molecular weight.

REFERENCES

1 Schaldeman, J. A. in 'Handbook of Pressure-Sensitive Adhesive Technology' (Ed. D. Santos), Van Nostrand Reinhold, New York, 1982, p. 360
2 Sheriff, M., Knibbs, R. W. and Langely, P. G. *J. Appl. Polym. Sci.* 1973, **17**, 3423
3 Roe, R. J. and Zin, W. C. *Macromolecules* 1984, **17**, 189
4 Nojima, S. and Roe, R. J. *Macromolecules* 1987, **20**, 1866
5 Kim, J., Han, C. D. and Chu, S. G. *J. Polym. Sci., Polym. Phys. Edn* 1988, **26**, 677
6 Han, C. D., Kim, J. and Baek, D. M. *J. Adhesion* 1989, **28**, 201
7 Han, C. D., Kim, J., Baek, D. M. and Chu, S. G. *J. Polym. Sci., Polym. Phys. Edn* 1990, **28**, 315
8 Krause, S. in 'Colloidal and Morphological Behavior of Block and Graft Copolymers' (Ed. G. E. Molau), Plenum, New York,, 1971, p. 223
9 Leibler, L. and Benoit, H. *Polymer* 1981, **22**, 195
10 Leibler, L. *Macromolecules* 1980, **13**, 1602
11 Hong, K. M. and Noolandi, J. *Macromolecules* 1983, **16**, 1083
12 Whitmore, M. D. and Noolandi, J. *Macromolecules* 1985, **18**, 2486
13 Han, C. D., Baek, D. M. and Kim, J. K. *Macromolecules* 1990, **23**, 561
14 Han, C. D. and Kim, J. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1741
15 Han, C. D., Kim, J. and Kim, J. K. *Macromolecules* 1989, **22**, 383
16 Toy, L., Ninomi, M. and Shen, M. *J. Macromol. Sci. Phys.* 1975, **B11**(3), 281
17 Ninomi, M., Akovali, G. and Shen, M. *J. Macromol. Sci. Phys.* 1977, **B13**(1), 133
18 Han, C. D., Baek, D. M., Kim, J., Kimishima, K. and Hashimoto, T. *Macromolecules* 1992, **25**, 3052
19 Mori, K., Tanaka, H. and Hashimoto, T. *Macromolecules* 1987, **20**, 381
20 Rounds, N. A. Doctoral Disseratation, University of Akron, 1971
21 Richardson, M. J. and Savill, N. G. *Polymer* 1977, **18**, 3
22 Zin, W. C. and Roe, R. J. *Macromolecules* 1980, **13**, 1221
23 Rigby, D. and Roe, R. J. *Macromolecules* 1986, **19**, 721
24 Molau, G. E. in 'Block Copolymers' (Ed. S. L. Aggarwal), Plenum Press, New York, 1970, p. 79
25 Hashimoto, T., Tanaka, H. and Hasegawa, H. in 'Molecular Conformation and Dynamics of Macromolecules in Condensed Systems' (Ed. M. Nagasawa), Elsevier, Amsterdam, 1988, p. 257
26 Hashimoto, T., Tanaka, H. and Hasegawa, H. *Macromolecules* 1990, **23**, 4378
27 Whitmore, M. D. personal communication, 1991
28 Fredrickson, G. H. and Helfand, E. *J. Chem. Phys.* 1987, **81**, 697
29 Burger, C., Ruland, W. and Semenov, A. N. *Macromolecules* 1990, **23**, 3339
30 Tanaka, H., Hasegawa, H. and Hashimoto, T. *Macromolecules* 1991, **24**, 240
31 McMullen, W. E. and Freed, K. F. *Macromolecules* 1990, **23**, 255
32 Dudowicz, J. and Freed, K. F. *Macromolecules* 1990, **23**, 1519
33 Tang, H. and Freed, K. F. *Macromolecules* 1991, **24**, 958
34 Olabisi, O., Robseon, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979

APPENDIX

Using density functional formalism on the basis of mean-field theory which employs the fourth-order expansion of the free energy of the microphase, Hong and Noolandi[11] derived an expression for the free energy of an inhomogeneous mixture of an AB-type diblock copolymer and a homopolymer, and suggested that the spinodal temperature (T_s) for the mixture can be determined by satisfying the following relation:

$$\lambda_-(q^*) = 0 \qquad \text{(A1)}$$

where q^* is the value of the wave vector $\mathbf{q}$ that minimizes λ_-, which is defined by

$$\lambda_-(q) = (1/2)[c(q) + a(q) - \Delta(q)] \qquad \text{(A2)}$$

where

$$\Delta(q) = \{[c(q) - a(q)]^2 + 4b^2(q)\}^{1/2} \qquad \text{(A3)}$$

$$a(q) = \frac{g_{\mathrm{AA}}^{-1}(q)}{r_{\mathrm{C}}\phi_{\mathrm{C}}} + \frac{1}{r_{\mathrm{H}}\phi_{\mathrm{H}}g_{\mathrm{H}}(q)} - 2\chi_{\mathrm{AH}} \qquad \text{(A4)}$$

$$b(q) = \frac{g_{\mathrm{AB}}^{-1}(q)}{r_{\mathrm{C}}\phi_{\mathrm{C}}} + \frac{1}{r_{\mathrm{H}}\phi_{\mathrm{H}}g_{\mathrm{H}}(q)} + \chi_{\mathrm{AB}} - \chi_{\mathrm{AH}} - \chi_{\mathrm{BH}} \qquad \text{(A5)}$$

$$c(\mathrm{q}) = \frac{g_{\mathrm{BB}}^{-1}(q)}{r_{\mathrm{C}}\phi_{\mathrm{C}}} + \frac{1}{r_{\mathrm{H}}\phi_{\mathrm{H}}g_{\mathrm{H}}(q)} - 2\chi_{\mathrm{BH}} \qquad \text{(A6)}$$

where subscripts A, B, C and H refer to block A, block B, copolymer and homopolymer, respectively; χ_{AB}, χ_{AH} and χ_{BH} are interaction parameters; r_{C} is equal to $V_{\mathrm{C}}/V_{\mathrm{r}}$ and r_{H} is equal to $V_{\mathrm{H}}/V_{\mathrm{r}}$, where V_{r} is the reference volume and V_{C} and V_{H} are the molecular volumes of the block copolymer and homopolymer, respectively; ϕ_{C} and ϕ_{H} are the volume fractions of the block copolymer and homopolymer, respectively, in the mixture; $g_{\mathrm{H}}(q)$ is equal to $g(x_h)$, which is defined by

$$g(x_j) = (2/x_j^2)[x_j + \exp(-x_j) - 1] \qquad \text{(A7)}$$

in which x_j ($j = 1, 2, h$) are defined by

$$x_1 = q^2R_1^2/6 \qquad x_2 = q^2R_2^2/6 \qquad x_h = q^2R_{\mathrm{H}}^2/6 \qquad \text{(A8)}$$

where R_1, R_2 and R_{H} are the root-mean-square end-to-end distances of block A, block B and homopolymer, respectively. In equations (A4)–(A6), $g_{\mathrm{AA}}^{-1}(q)$, $g_{\mathrm{BB}}^{-1}(q)$ and $g_{\mathrm{AB}}^{-1}(q)$ are elements of the inverse of matrix $\|g\|$, defined by

$$\left\|\begin{matrix} g_{\mathrm{AA}}(q) & g_{\mathrm{AB}}(q) \\ g_{\mathrm{BA}}(q) & g_{\mathrm{BB}}(q) \end{matrix}\right\| = \left\|\begin{matrix} S_{11}(q)/N_{\mathrm{C}} & S_{12}(q)/N_{\mathrm{C}} \\ S_{12}(q)/N_{\mathrm{C}} & S_{22}(q)/N_{\mathrm{C}} \end{matrix}\right\| \qquad \text{(A9)}$$

For an AB-type diblock copolymer, the expressions for $S_{11}(q)$, $S_{12}(q)$ and $S_{22}(q)$ appearing in equation (A9) are given by[10]

$$S_{11} = N_{\mathrm{C}}g_1(f_1, x) \qquad \text{(A10)}$$

$$S_{22} = N_{\mathrm{C}}g_1(1 - f_1, x) \qquad \text{(A11)}$$

$$S_{12} = (N_{\mathrm{C}}/2)[g_1(1, x) - g_1(f_1, x) - g_1(1 - f_1, x)] \qquad \text{(A12)}$$

where f_1 is the fraction of block A (or block B) in an AB-type diblock copolymer for which $f_1 + f_2 = 1$ and N_{C} is the total number of statistical segments. Note that if the monomeric volume and the Kuhn statistical length of each block are the same as those of homopolymer, N_{C} becomes the polymerization index of the block copolymer, which was the situation dealt with in the Leibler and Leibler–Benoit theories, respectively. But since the monomeric volume and the Kuhn statistical length of each block of the block copolymer SIS-A (or SIS-B) and the homopolymers, which are under consideration in this study, are different, N_{C} must be regarded as being the same as r_{C} appearing in equations (A4)–(A6) (i.e. $N_{\mathrm{C}} = r_{\mathrm{C}} = V_{\mathrm{C}}/V_{\mathrm{r}}$). $g_1(f_1, x)$ appearing in equations (A10)–(A12) is the Debye function, which is equal to $f_1^2 g(x_1)$, $g(x_1)$ being defined by equation (A7). Note that $x = x_1 + x_2$; $x = x_1/f_1 = x_2/f_2$; x_1 and x_2 are defined by equation (A8).

It should be noted that equations (A1)–(A6) contain three interaction parameters, χ_{AB}, χ_{AH} and χ_{BH}, which in turn depend on temperature. Therefore, one must find the temperature which satisfies the condition given by equation (A1).

The spinodal temperature (T_{s}) of microphase separation for mixtures of an AB-type diblock copolymer and a homopolymer can be determined as follows. We must first determine the value of the wave vector q^* which satisfies equation (A1). Note that from equations (A2) and (A3) we have

$$a(q^*)c(q^*) = b^2(q^*) \qquad \text{(A13)}$$

where a, b and c are defined by equations (A4)–(A6), respectively. The components of the inverse of matrix $\|g\|$, g_{AA}^{-1}, g_{AB}^{-1} and g_{BB}^{-1}, which appear in equations (A4)–(A6), are defined by

$$g_{\mathrm{AA}}^{-1} = g_{\mathrm{BB}}/D \qquad g_{\mathrm{AB}}^{-1} = -g_{\mathrm{AB}}/D \qquad g_{\mathrm{BB}}^{-1} = g_{\mathrm{AA}}/D \qquad \text{(A14)}$$

where D is defined by

$$D = g_{\mathrm{AA}}g_{\mathrm{BB}} - g_{\mathrm{AB}}^2 \qquad \text{(A15)}$$

and g_{AA}, g_{BB} and g_{AB} are given by equations (A10)–(A12), respectively.

Substitution of equations (A4)–(A6) into equation (A13) gives

$$\begin{aligned} &[(1 - a_0 - b_0)^2 - 4a_0b_0](\chi_{\mathrm{AB}}r_{\mathrm{C}}\phi_{\mathrm{C}})^2 \\ &\quad + 2\left[\left(g_{\mathrm{AB}}^{-1} + \frac{1}{A}\right)(1 - a_0 - b_0) + a_0\left(g_{\mathrm{BB}}^{-1} + \frac{1}{A}\right)\right. \\ &\quad \left. + b_0\left(g_{\mathrm{AA}}^{-1} + \frac{1}{A}\right)\right]\chi_{\mathrm{AB}}r_{\mathrm{C}}\phi_{\mathrm{C}} \\ &\quad + \left[\left(g_{\mathrm{AB}}^{-1} + \frac{1}{A}\right)^2 - \left(g_{\mathrm{AA}}^{-1} + \frac{1}{A}\right)\left(g_{\mathrm{BB}}^{-1} + \frac{1}{A}\right)\right] = 0 \qquad \text{(A16)} \end{aligned}$$

where

$$A = \frac{r_{\mathrm{H}}\phi_{\mathrm{H}}}{r_{\mathrm{C}}\phi_{\mathrm{C}}}\,g_{\mathrm{H}}$$

$$a_0 = \frac{\chi_{\mathrm{AH}}}{\chi_{\mathrm{AB}}} \qquad \text{(A17)}$$

$$b_0 = \frac{\chi_{\mathrm{BH}}}{\chi_{\mathrm{AB}}}$$

Note that the interaction parameters χ_{AB}, χ_{AH} and χ_{BH} depend on temperature. Therefore, one must find the temperature T_{s} which satisfies equation (A16), using an iterative procedure. It can be seen from equation (A16) that for a given copolymer composition, $\chi_{\mathrm{AB}}r_{\mathrm{C}}$ ($= \chi_{\mathrm{AB}}N_{\mathrm{C}}$) is dependent upon $V_{\mathrm{H}}/V_{\mathrm{C}}$, ϕ_{H}, $\chi_{\mathrm{AH}}/\chi_{\mathrm{AB}}$ and $\chi_{\mathrm{BH}}/\chi_{\mathrm{AB}}$.

When the chemical structure of the homopolymer is identical to that of block A (i.e. $\chi_{\mathrm{AH}} = 0$ and $\chi_{\mathrm{BH}} = \chi_{\mathrm{AB}}$), equation (A16) reduces to

$$2(\chi_{\mathrm{AB}})_{\mathrm{s}}r_{\mathrm{C}} = \frac{\phi_{\mathrm{H}}(r_{\mathrm{H}}/r_{\mathrm{C}})g_{\mathrm{H}} + \phi_{\mathrm{C}}(g_{\mathrm{AA}} + g_{\mathrm{BB}} + 2g_{\mathrm{AB}})}{\phi_{\mathrm{C}}\phi_{\mathrm{H}}(r_{\mathrm{H}}/r_{\mathrm{C}})g_{\mathrm{H}}g_{\mathrm{BB}} + \phi_{\mathrm{C}}^2(g_{\mathrm{AA}}g_{\mathrm{BB}} - g_{\mathrm{AB}}^2)} \qquad \text{(A18)}$$

where the subscript s on the variable χ_{AB} refers to the transition condition. On the other hand, when the chemical structure of the homopolymer is identical to that of block B (i.e. $\chi_{BH} = 0$ and $\chi_{AH} = \chi_{AB}$), equation (A16) reduces to

$$2(\chi_{AB})_s r_C = \frac{\phi_H (r_H/r_C) g_H + \phi_C (g_{AA} + g_{BB} + 2g_{AB})}{\phi_C \phi_H (r_H/r_C) g_H g_{AA} + \phi_C^2 (g_{AA} g_{BB} - g_{AB}^2)} \tag{A19}$$

In this study we used the following composition correlation functions S_{ij}, given by Mori *et al.*[19], to predict the T_s of an ABA-type triblock copolymer:

$$\begin{aligned} S_{11} = N_C[&g_1(f_1, x) + g_1(f_2, x) + g_1(f_3, x) + g_1(1, x) \\ &- g_1(1 - f_3, x) - g_1(1 - f_1, x)] \end{aligned} \tag{A20}$$

$$S_{22} = N_C g_1(f_2, x) \tag{A21}$$

$$\begin{aligned} S_{12} = (N_C/2)[&g_1(1 - f_1, x) + g_1(1 - f_3, x) \\ &- g_1(f_1, x) - g_1(f_3, x) - 2g_1(f_2, x)] \end{aligned} \tag{A22}$$

where $g_1(f, x)$ is equal to $f^2 g(x_j)$, $g(x_j)$ being defined by equation (A7); f_1, f_2 and f_3 are the volume fractions of each block sequence in the ABA-type triblock copolymer, for which $f_1 = f_3$ and thus $2f_1 + f_2 = 1$; $x = x_1 + x_2 + x_3$ and $x = x_1/f_1 = x_2/f_2 = x_3/f_3$; and x_{1c} and x_{3c} are defined by

$$\begin{aligned} x_{1c} &= q^2(R_c^2 - R_1^2)/6 \\ x_{3c} &= q^2(R_c^2 - R_3^2)/6 \end{aligned} \tag{A23}$$

in which R_c is the root-mean-square end-to-end distance of the block copolymer, and N_C is the total number of statistical segments.

Note that the spinodal curve for microphase separation is constructed by solving equations (A1)–(A6), namely, by calculating q^* (or x^*) at various compositions of block copolymer, until the condition given by equation (A1) is satisfied.

The construction of a binodal curve for an inhomogeneous system is much more difficult than the construction of a spinodal curve, but the basic concept is the same as that used in the Flory–Huggins theory, i.e. the chemical potential of each component in one phase, $\Delta\mu_1'$, must be the same as that in the other phase, $\Delta\mu_1''$. The procedure for constructing binodal curves using the Flory–Huggins theory is described in ref. 34.

However, in the present study, which deals with mixtures of a block copolymer and a homopolymer which is not a solvent (i.e. $r_H \neq 1$), equation (2.60) in ref. 34 was modified as follows:

$$\frac{\Delta\mu_H}{kT} = \ln \phi_H + \left(1 - \frac{1}{r}\right)(1 - \phi_H) + \chi r_H (1 - \phi_H)^2 \tag{A24}$$

$$\frac{\Delta\mu_C}{kT} = \ln(1 - \phi_H) + (1 - r)\phi_H + \chi r_C \phi_H^2 \tag{A25}$$

where $\Delta\mu_H$ and $\Delta\mu_C$ are the chemical potentials for homopolymer (H) and copolymer (C), respectively, k is the Boltzmann constant, T is the absolute temperature, $r_H = V_H/V_r$ and $r_C = V_C/V_r$. Note that r in equations (A24) and (A25) is given by

$$r = r_C/r_H = V_C/V_H \tag{A26}$$

It should be mentioned that the interaction parameter χ between the homopolymer and copolymer is given by

$$\chi = f_A \chi_{AH} + f_B \chi_{BH} - f_A f_B \chi_{AB} \tag{A27}$$

where $f_A = f_1 + f_3$ and $f_B = f_2$ for an ABA-type triblock copolymer. Therefore ϕ_H' for phase 1 and ϕ_H'' for phase 2 can be obtained from:

$$\begin{aligned} &\ln \phi_H' + \left(1 - \frac{1}{r}\right)(1 - \phi_H') + \chi r_H (1 - \phi_H')^2 \\ &\quad = \ln \phi_H'' + \left(1 - \frac{1}{r}\right)(1 - \phi_H'') + \chi r_H (1 - \phi_H'')^2 \end{aligned} \tag{A28}$$

$$\begin{aligned} &\ln(1 - \phi_H') + (1 - r)\phi_H' + \chi r_C (\phi_H')^2 \\ &\quad = \ln(1 - \phi_H'') + (1 - r)\phi_H'' + \chi r_C (\phi_H'')^2 \end{aligned} \tag{A29}$$

Briefly, the following steps were taken to construct a binodal curve for an inhomogeneous system: (1) The contribution of the free energy from the homogeneous system was calculated; (2) the contribution of the free energy from the inhomogeneous system was calculated; (3) curves were drawn for the total free energy computed at various compositions for a given temperature; (4) the common slope was found from the free-energy curves by drawing a line through two different compositions; (5) the temperature was changed, and steps 1–4 were repeated.