Phase Equilibria and Transition in Mixtures of a Homopolymer and a Block Copolymer. 2. Phase Diagram

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ABSTRACT: The phase relationship in mixtures containing a block copolymer and a homopolymer has been studied by means of light scattering. The copolymer employed is a styrene–butadiene block copolymer of molecular weight (M_w) 28 000, containing 27% styrene. The homopolymer in the mixture is either (1) polystyrene of $M_w = 2400$, (2) polystyrene of $M_w = 3500$, or (3) polybutadiene of $M_w = 26\,000$. The first system containing the lower molecular weight polystyrene was previously studied in detail also by means of small-angle X-ray scattering. The observed cloud points show a change with temperature in the limit of solubility of the homopolymers in the block copolymer, which has an ordered, microdomain structure at low temperatures but a disordered, homogeneous structure at high temperatures. The observed solubility limits at low temperatures turn out to be greater, by an order of magnitude, than the prediction based on an earlier block copolymer theory. The phase diagram, constructed on the basis of the light and X-ray scattering data, is rich in features and resembles the complex phase diagrams often observed with binary metal alloys. The possibility of observing a critical phenomenon at a certain ratio of the homopolymer chain length to the block chain length is pointed out.

I. Introduction

When a small amount of a homopolymer A is added to a block copolymer A–B possessing ordered microdomain structure, the homopolymer is readily accommodated in the microdomains consisting of A blocks of the copolymer. As more of the homopolymer is added, a solubility limit is eventually reached, and a phase consisting mainly of the homopolymer separates out. The solubility limit is governed by the relative lengths of the homopolymer A and the block A in the copolymer as well as by the microdomain structure of the latter.

When a change in the microdomain structure is induced by heating such a mixture, the solubility limit is altered accordingly. A pronounced change in the thermodynamic behavior of the mixture can occur in particular when the block copolymer structure undergoes a transition, on heating, to a homogeneous, disordered structure. Such a transition can be observed, in the experimentally accessible temperature range, if the block lengths are relatively short or the two blocks of the copolymer are only moderately incompatible.

Part 1[1] of the present series of papers reported the result of a small-angle X-ray scattering study on a system of mixtures of a low molecular weight polystyrene with a styrene–butadiene block copolymer and described the change in their structure observed as a function of polystyrene concentration and temperature. The present article reports the result of a light scattering study on the same system and also on two other related systems of mixtures. The observed cloud point reveals the onset of separation into phases that are much larger than the microphases detected by the small-angle X-ray technique. The three systems investigated are as follows: One of the components of all the mixtures is a styrene–butadiene diblock copolymer containing about 25% styrene. The second component is a homopolymer which is either a polystyrene of $M_w = 2400$, a polystyrene of $M_w = 3500$, or a polybutadiene of $M_w = 26\,000$.

The microdomains are of sizes much smaller than the wavelength of light, and therefore the mixtures having a microdomain structure at low temperatures remain transparent to light as long as the amount of the homopolymer is within the solubility limit. When the mixture is heated and the microdomain structure is disrupted, the resulting disordered block copolymer is often no longer compatible with the homopolymer, unless the temperature is very high. Thus, when such a mixture is heated from room temperature, it is at first clear but becomes suddenly turbid at a certain temperature and remains so until, at an even higher temperature, it becomes clear again. The temperatures of transition from clear to turbid and then back to clear states of course depend on the concentration of the homopolymer. The observed cloud point curves, obtained as a function of the temperature and the composition, and the phase diagram deduced from them exhibit interesting complexities resembling those obtained frequently with binary metal alloys.

The solubility limits of homopolymers in the block copolymer microdomains are found to decrease as the ratio of the homopolymer chain length to the corresponding block sequence length is increased. This is in accord with the expectation based on one of the early block copolymer theories. Quantitatively, however, the observed solubility limits turn out to be greater than the prediction by an order of magnitude.

With the temperature, the concentration, and the molecular weights of the components as the variables at our disposal, the mixtures containing block copolymers can be made to exhibit a wealth of features of theoretical and practical interest. The light scattering and small-angle X-ray scattering techniques are complementary to each other for the study of these systems, as they provide structural information on different size scales.

II. Experimental Section

Materials. The styrene–butadiene diblock copolymer contains 27% (by weight) of styrene, as determined by NMR, and its M_w and M_n (determined by GPC) are 28 000 and 27 000, respectively. This is the same material studied in our previous work.[1-3] Characterization data of this polymer have also been reported by Krause et al.[4] The polybutadiene has M_w and M_n (determined by GPC) equal to 26 000 and 25 000, respectively. The diblock copolymer and the polybutadiene were kindly synthesized for us by Dr. H. L. Hsieh of Philips Petroleum Co. The two polystyrenes used were of $M_w = 2400$ and 3500 and were obtained from Pressure Chemical Co. These three homopolymers were also used in our previous work[2] and more detailed characterization data were given there.

Method. Construction of the light scattering apparatus and the method of measurements were described in the previous publication.[2] In particular, the polymer mixtures were prepared, without solvent, in a glass tube, which was subsequently sealed

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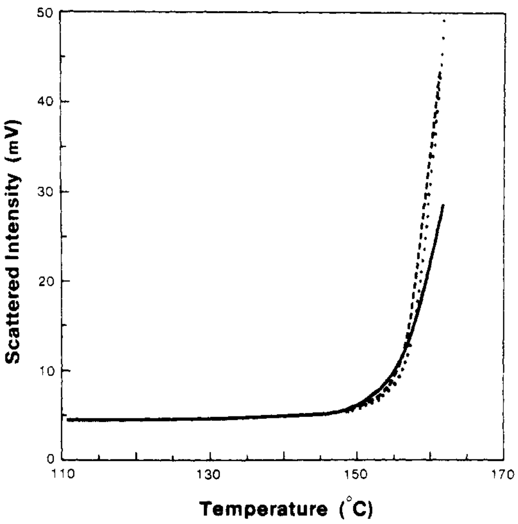

Figure 1. Scattered intensity (or the output of the photodiode detector in mV) obtained from the mixture containing 25% of polystyrene (M_w = 2400) at various heating rates. Solid line, 4 °C/min; dotted line, 2 °C/min; broken line, 0.5 °C/min.

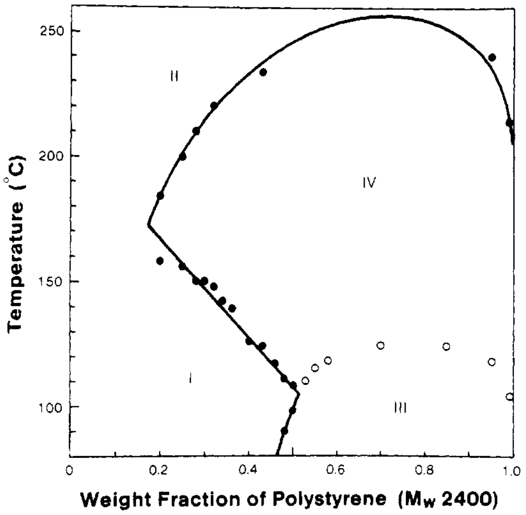

Figure 2. Cloud points obtained with mixtures containing polystyrene (M_w = 2400). In regions I and II the mixture is transparent, while in regions III and IV it is turbid. The turbidity increases sharply on crossing from region III to region IV at the temperatures indicated by open circles.

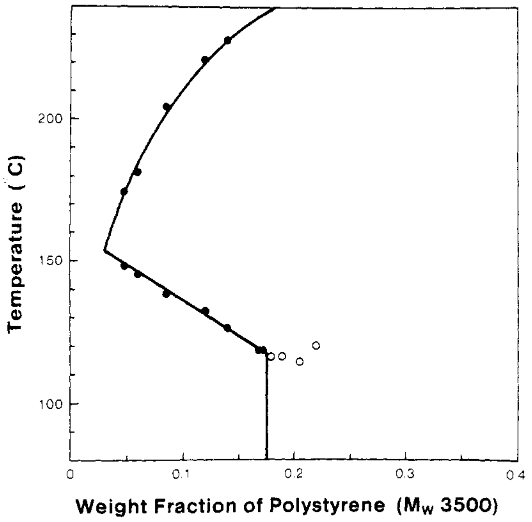

Figure 3. Cloud points obtained with mixtures containing polystyrene (M_w = 3500).

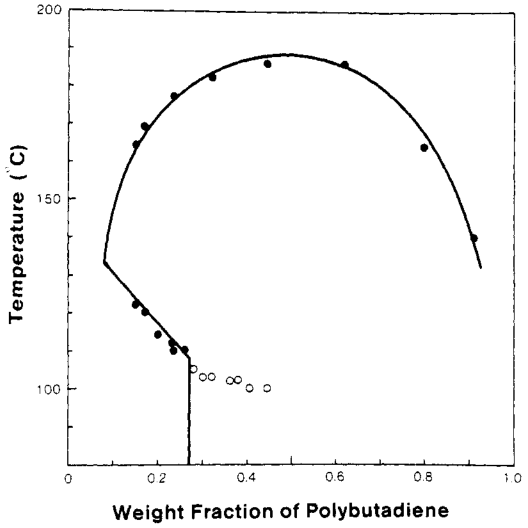

Figure 4. Cloud points obtained with mixtures containing polybutadiene (M_w = 26 000).

under vacuum. A magnetically activated glass stirrer, also sealed in the tube, was used to mix the components at high temperatures at which they are compatible. A low-power He–Ne laser was used as the light source, and the intensity of light scattered at a 90° angle was measured with a photodiode.

After a preliminary determination of the approximate cloud point, the temperature of the sample was cycled up and down over a 40–60 °C interval around the cloud point by means of a temperature programmer, and the outputs of the thermocouple and the light detector were continuously recorded on a chart recorder. A heating/cooling rate of 1 °C/min was used ordinarily, except at temperatures above 180 °C, where a 2 °C/min rate was used to minimize the possibility of thermal degradation. The effect of different heating rates is illustrated in Figure 1, where the intensity (or the output of the photodiode in mV) of light scattered from a mixture containing the block copolymer and 25% of 2400 molecular weight polystyrene is plotted against temperature. The three curves were obtained at 4, 2, and 0.5 °C/min, and only a minor difference is noted between the last two cases. A downward extrapolation of the steep linear increase beyond 150 °C intersects with the base line at about 156 °C, which is taken as the cloud point. The element of subjective judgement in the extrapolation procedure appears to introduce an uncertainty of not more than 4 °C in the cloud point thus determined. The reproducibility on duplicate runs is withini 2 °C. The cloud points determined on heating and cooling are usually found to differ by a few degrees. Those determined on a temperature change in the direction of decreasing turbidity are reported in this paper.

III. Results

The cloud point curves obtained with the three mixture systems are given in Figures 2–4. The system containing the block copolymer and the polystyrene (M_w = 2400) was studied in more detail than the other two. This system was also examined by small-angle X-ray scattering as reported in part 1.

In region I in Figure 2, the mixture is visually transparent, although there is a tendency for the scattered intensity to increase slightly with inccreasing temperature as seen in Figure 1. In crossing from region I to region IV, the turbidity increases very steeply, and the mixture becomes opaque, giving all the appearance of macroscopic phase separation. In region II the mixture is again transparent and behaves as a homogeneous liquid of moderate viscosity. In crossing from region I to region II, no change in the intensity of scattered light is detected. From the small-angle X-ray scattering study[1] it is, however, known that the ordered structure of block copolymer microdomains present in region I gives way to a homogeneous disordered structure as the mixture is brought to

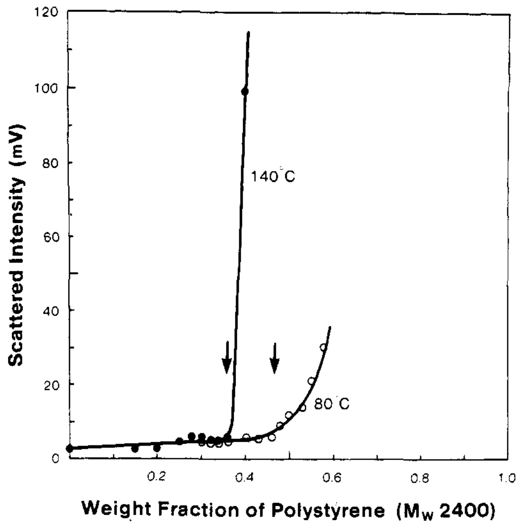

Figure 5. The scattered intensity, initially obtained as a function of temperature, is replotted as a function of the weight fraction of polystyrene (M_w = 2400) in the mixture. The difference in the rate of change of the turbidity with composition between the data at two temperatures, 80 and 140 °C, is illustrated.

region II. In region III the mixture remains moderately cloudy throughout, with its turbidity tending to increase somewhat as the temperature is lowered toward room temperature. Region III is considered to arise as a result of the mixture separating into two phases, the one consisting of the block copolymer swollen with the polystyrene but still maintaining the microdomain structure, and the other of the polystyrene with suspended block copolymer micelles. The boundary between regions I and III in Figure 2 is slightly inclined from the temperature axis. Thus, when a mixture containing 48% of the polystyrene, which is in region III at room temperature, is heated, it becomes clear on crossing into region I at 90 °C and then sharply cloudy again on crossing into region IV at 110 °C. The opaqueness in region IV is much greater than in region III. As a result, on heating a mixture containing, for example, 60% polystyrene, the scattered intensity sharply increses as it crosses from region III to region IV at around 120 °C. This suggests, therefore, that although both regions III and IV represent conditions for coexistence of macroscopic phases, the nature of the phahses that separate out are different. In both cases, one of the phases is the ordered block copolymer swollen with polystyrene. The second phase which coexists with it in region III and in region IV will be discussed in the next section.

To illustrate the degree of sharpness of the transitions between different regions, the scattered intensities observed at 80 and 140 °C are replotted as a function of the composition of the mixture in Figure 5. The arrows denote the cloud points determined from the original chart recordings of the intensity against temperature. At 80 °C the cloudy mixture is in region III and at 140 °C it is in region IV, and the difference between these two regions is illustrated by the widely different levels of scattered intensity.

The features observed with the other two systems, shown in Figures 3 and 4, are generally similar to those described above, but some minor differences are to be noted. With these two systems, the boundary between regions I and III is parallel with the temperature axis within the experimental uncertainty. Also, the turbidity in region III is generally much higher than is observed with the first system, and as a result it is difficult to determine the boundary between regions III and IV except when the concentration of the homopolymer is only moderately in excess of the solubility limit, as seen in Figures 3 and 4.

Table I
Solubility of Homopolymer in Block Copolymer

	homopolymer		
	PS	PS	PBD
1. M_w of homopolymer H, M_H	2400	3500	26 000
2. MW of the block A,[a] M_A	7600	7600	20 400
3. M_H/M_A	0.32	0.46	1.27
4. wt fr of homopolymer, w	0.48[b]	0.18	0.27
5. wt fr of monomer A	0.62	0.37	0.80
6. wt fr of H in (H + A), p	0.77	0.44	0.34
7. vol ratio of H to A, q	3.4	0.79	0.51
8. vol ratio q, theoretical[5]	0.23	0.12	0.03

[a] The block having the same monomer as the homopolymer is designated A. [b] At 90 °C.

IV. Discussion

The experimentally obtained solubility limits of the three homopolymers in the styrene–butadiene block copolymer at low temperatures are given in Table I. The solubility limits are expressed in four different ways. Row 4 gives the weight fraction of the homopolymer in the mixture, as read off directly from Figures 2–4. Row 5 gives the weight fraction of monomer A belonging both to the homopolymer and to the block A of the copolymer. Row 6 gives the volume fraction, p, of the homopolymer in the microdomains in which it is dissolved. Row 7 gives the ratio, q, of the volume of dissolved homopolymer to the volume of the solubilizing block; $q = p/(1 - p)$. The solubility is seen to decrease as the relative size of the dissolving homopolymer becomes larger and the molecular weight ratio, M_H/M_A, of the homopolymer to the solubilizing block of the copolymer increases.

The only theory available for comparison with our solubility data is the one due to Meier.[5] The values calculated from his theory for the case of diblock copolymers having equal lengths of A and B blocks and forming a lamellar microdomain structure are given in row 8 of Table I. The trend of change in the solubility as a function of the molecular weight ratio is correctly predicted, but the theory underestimates the solubility by an order of magnitude. In his theory, five factors affecting the free energy of mixing are considered. They are (a) the microdomain interfacial energy, (b) the entropy of junction confinement, (c) constraints and distortions to the block copolymer chain conformation, (d) constraints to the homopolymer conformation, and (e) the entropy of mixing. Factor c accounts for the entropy loss associated with the confinement of copolymer blocks within their respective microdomains and also with the distortion to their conformation out of the necessity of maintaining a constant density throughout the microdomain. Meier defines a chain perturbation parameter α to represent the degree of extension of the block chain end-to-end distance and equates it to the ratio of the thickness of the lamellar microdomain to the unperturbed end-to-end distance of the block chain. As the microdomain becomes swollen with solubilized homopolymers, according to the theory, α becomes larger and therefore the conformational entropy of the block chain is further reduced. It is likely, however, that α becomes smaller, rather than larger, as more homopolymer is dissolved. The requirement of maintaining a constant density can now be satisfied more easily by placing more of the homopolymer molecules toward the central part of the lamellae which otherwise had to be filled by highly stretched block chains. The conformational entropy of the block chains is thus increased with homopolymer solubilization and provides the additional driving force which

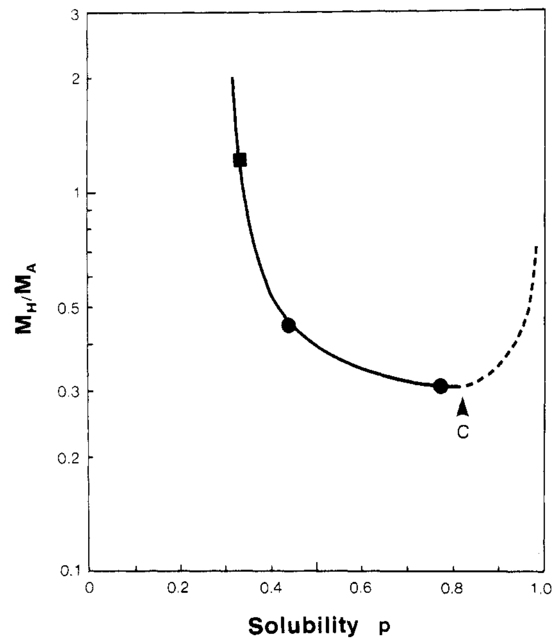

Figure 6. Solubility of homopolymer in the block copolymer, expressed as the weight fraction p of the homopolymer in the microdomain in which it is solubilized, plotted against M_H/M_A, where M_H is the molecular weight of the homopolymer and M_A is that of the block in the copolymer having the same type of monomers. See the text for the explanation of the curve drawn in broken line. Point C represents a critical point which is closely analogous to the critical consolute point in the composition–temperature phase diagram of a binary liquid mixture.

probably accounts for the observed solubility much greater than predicted by the original theory.

The data given in Figure 2–4 show that the solubility of the homopolymers at low temperatures is fairly insensitive to the temperature variation. This means that the solubility limits are determined, to a first approximation, solely by an entropy effect. This should be particularly true at temperatures low enough to make the assumption of thin interfaces valid. The solubility limit is then a function of three parameters defining the systems: the molecular weight M_H of the homopolymer and the molecular weights M_A and M_B of the two blocks of the copolymer. (A denotes the block having the same monomer as the homopolymer.) Since changing the three molecular weights by equal factors does not alter the geometry of the system, the solubility limit can actually be given as a function of two variables

$$p = (M_H/M_A, M_B/M_A) \qquad (1)$$

In Figure 6, the values of p in row 6 of Table I are plotted against M_H/M_A. The value of M_B/M_A for the third point (with polybutadiene) is actually different from the same for the first two (with polystyrene), and in making this plot we have in effect neglected the influence of the variable M_B/M_A in eq 1. The ratio M_B/M_A affects the solubility mostly through its role as a factor in determining the geometry (spherical, cylindrical, or lamellar) of the microdomains attained. Although there is a good reason to believe that the solubility in spherical microdomains will be somewhat less than in lamellae under otherwise identical conditions, the difference is probably small and can be neglected in this semiquantitative discussion. (According to Leibler's theory,[6] all block copolymers, irrespective of the ratio M_B/M_A, attain a lamellar structure at sufficiently low temperatures, and if that is the case, the variable M_B/M_A in eq 1 can legitimately be neglected.) The solid line drawn through the points flattens out at low values of M_H/M_A and suggests that the homopolymer will be soluble in the block copolymer at all concentrations when M_H/M_A is below about 0.3.

When a mixture consists mostly of a homopolymer and contains only a small concentration of a block copolymer, the latter is likely to aggregate into micelles and become suspended in the continuous matrix of the homopolymer. With increasing concentration, the block copolymer micelles may eventually aggregate further into ordered arrays of microdomains swollen withthe homopolymer. The broken line on the right in Figure 6 has been drawn from a qualitative consideration to represent the limit of stability of micellar suspension. A mixiture with a composition within the range bounded by the solid curve on the left and the broken curve on the right then should separate spontaneously into two phases, each having the composition represented by these two curves. Figure 6 in fact resembles the phase diagram of a binary liquid mixture if the M_H/M_A axis is replaced by the temperature axis. In Figure 6 there then should exist a critical point C at which the distinction between the microdomain structure and the micellar solution disappears and, in addition, the mixture exhibits a large fluctuation in the density of micelles (or microdomains). Our data suggests that such a critical point is attained when M_H/M_A is approximately equal to 0.3 and p is between 0.8 and 0.9.

On the basis of the observed cloud points and the small-angle X-ray measurements,[1] we now construct the phase diagram with the temperature and the composition as the independent variables. The phase diagrams of course have to satisfy the basic thermodynamic principles,[7,8] embodies for example in the Gibbs phase rule. For any complex phase relations such as exhibited by our systems a direct applicaton[7] of the thermodynamic principles in terms of the free energy curves is difficult. A set of convenient rules guiding the construction of phase diagrams has, however, been formulated and has found utility in the study of complex phase diagrams arising with metallic and ceramic alloy systems. Two of these rules state[8] as folows. (1) The boundary rule: On the phase diagram, any region containing p phases can be bounded only by regions containing $p \pm 1$ phases. (2) The boundary-curvature rule: Boundaries of one-phase regions must meet with curvatures such that the boundaries extrapolate into the adjacent two-phase regions. The phase diagrams constructed according to these rules are shown in Figure 7 for the mixtures containing the polystyrene ($M_w = 2400$) and in Figure 8 for those containing the polybutadiene. Some of the observed cloud points are indicated in these figures with circles, and the temperatures of transition from an ordered morphology to a disordered structure, determined[1] by small-angle X-ray scattering, are also indicated by squares. In the two liquid phases, designated L_1 and L_2, the block copolymer is molecularly dispersed and no aggregated structure of the latter, in the form of either micelles or microdomains, remain. In the meso phase M_1, the microdomains, swollen with dissolved homopolymer, are organized into an ordered structure. The micellar phase M_2, in which micellar aggregates of block copolymers are suspended with no ordering among them, is considered to constitute a separate phase.

Point A in Figure 7 represents the disordering temperature of the pure block copolymers. At small polystyrene concentrations, the boundary between M_1 and L_1 is indicated by two lines AB and AC enclosing a small region in which the two phases coexist. These two lines are drawn here mainly to make it conform to the boundary rule mentioned above. The rule applies strictly only when the

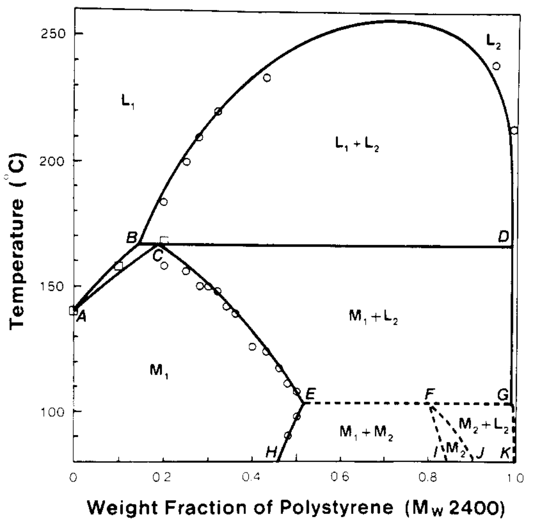

Figure 7. Phase diagram of the mixture containing polystyrene (M_w = 2400), drawn to agree with the observed cloud points (circles) and the block copolymer transition temperatures (squares, determined by small-angle X-ray scattering[1]). The liquid phases L_1 and L_2 consist of the disordered block copolymer and the polystyrene. Mesophase M_1 consists of ordered microdomains of the block copolymer swollen with polystyrene. Mesophase M_2 contains micellar aggregates of the block copolymer suspended in the medium of the polystyrene. The two lines AB and AC are considered to coalesce into a single line representing the transition temperature between the ordered and disordered structure. The features on the lower right, drawn in broken lines, are more speculative than the rest.

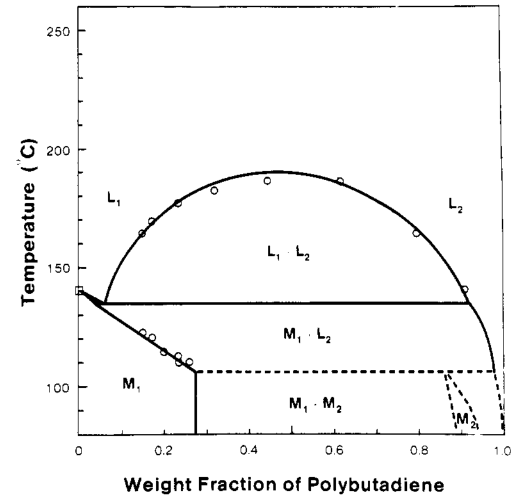

Figure 8. Phase diagram of the mixture containing polybutadiene (M_w = 26 000). Note that, in order to be consistent with the observed cloud points, the order–disorder transition temperature of the block copolymer has to decrease with increasing amount of the homopolymer, in contrast to the case shown in Figure 7.

underlying phase transition is of a first order. In block copolymer systems, the transition from an ordered to a disordered state is very diffuse. Our previous study,[3] by small-angle X-ray scattering, of the same diblock copolymer as used here shows that the intensity of X-ray scattering due to the ordered structure diminishes continuously, without any sudden change, as the temperature is raised. This indicates that the order in the organization of the block copolymer molecules undergoes no discontinuous transition but rather gradual and continuous modifications. When the block copolymer is mixed with small concentrations of homopolymer, the transition is again gradual, as ascertained from our small-angle X-ray study.[1] It in a way resembles the phenomenon of the so-called "order–disorder" transition in binary alloys. In such cases, it is known[8] that the transition from an ordered to a disordered phase can occur without an intervening region of two-phase stability. The transition points in Figure 7, indicated by squares, were obtained from X-ray measurements while no increase in the optical turbidity was noted in the corresponding temperature range. This shows that in this system the two lines AB and AC in fact coalesce into one.

The line BCD is horizontal, signifying that there exists a temperature at which three phases L_1, M_1, and L_2 coexist. According to the phase rule, a two-component system at a fixed pressure can have three coexisting phases only at a fixed temperature, often called the eutectic point or invariant region.

The line CE in Figure 7 shows that the solubility of homopolymer in the ordered block copolymer phase decreases rather rapidly with increasing T in this moderately high temperature range. According to Le Chatelier's principle, the equilibrium point of a system shifts with increasing T toward a higher energy state. In our system an increase in the energy can arise only from an increased number of unfavorable contacts between different types of monomers, if we neglect the minor effect due to the change in the polymer conformation with temperature. Since the solubility of homopolymer in the block copolymer is observed to decrease at higher T, the only way of increasing the energy of the system is through increased mixing of the A and B blocks in the copolymer. In our previous study,[3] in order to explain the gradual, continuous decrease in the X-ray intensity scattered from the pure block copolymer, we proposed that the transition of an ordered to a disordered structure proceeds through gradual intermixing of the component blocks in the microdomains. The negative temperature dependence of the homopolymer solubility, shown by curve CE, supports this view. In fact, the increase in the degree of intermixing of blocks with T is so steep that the dissolved homopolymer is driven out of the block copolymer microdomains and forced to form a separate phase.

In Figure 7, curves FI and FJ, denoting the limits of stability of the micellar solution phase, are based on a conjecture. In drawing these curves, the following observations are taken into consideration. (i) The two curves, CE and EH, denoting the homopolymer solubility limits in the ordered block copolymer, meet at an angle at E instead of forming a continuous single curve. (ii) The turbidity in region IV having coexisting M_1 and L_2 phases is much higher than in region III below the line EG. The discontinuity at E suggests the presence of a eutectic point, which can be accounted for by the formation of the micellar solution phase M_2. The lower turbidity below the eutectic point suggests that the two phases which coexist have a much smaller difference in composition between them (curves EH and FI) in comparison to the two phases which coexist above the eutectic point (curves CE and DG). The region corresponding to the area GFIK has not been studied carefully in this work and remains the subject of future study. The location of F has yet to be determined. Since regions III and IV in Figure 2 both contain two phases (as evidenced by the turbidity) the boundary rule mentioned above dictates that these two regions can only be separated from each other by an invariant three-phase region, or in other words, by a eutectic point, as denoted by the horizontal line EFG. The observed boundary between the regions III and IV, as determined from the change in turbidity, does not, however, lie on a constant temperature, and it is not clear whether this discrepancy arises solely from the difficulty of determining the cloud

Table II
Polymer–Polymer Interaction Energy Density Λ[a]

	f_A[b]	λ_0	λ_1	λ_T	$\lambda_T/(1-f_A)^2$	$\Lambda_{12}/(1-f_A)^2$[c]
mixture with PS (M_w = 2400)	0.27	3.1	−0.3	−0.0063	−0.012	3.2
mixture with PBD (M_w = 26000)	0.73	0.50	0	−0.0014	−0.019	3.0
av of previous results[d]					−0.009 ± 0.003[e]	2.8 ± 0.4[e]

[a] Given in units of J/cm³. [b] Weight fraction of the block in the block copolymer having the same monomer as the homopolymer. [c] Evaluated for 200 °C and ϕ_1 = 0.5. [d] Reference 2. [e] Standard deviation.

point between two regions which are both turbid. Another interesting question which has to be settled in the future is whether the micellar solution phase M_2 exists as a phase distinct from the true solution phase L_2 and separated by an intervening two-phase region GFJK.

The phase diagram for the mixtures containing polybutadiene, shown in Figure 8, is qualitatively similar to Figure 7, except in one aspect. At low concentration of polybutadiene, the curve giving the temperature of transition from an ordered to a disordered structure has a negative slope here, whereas in the case of the mixtures containing polystyrene it has a positive slope. This probably arises from the asymmetry of the block copolymer sample used here—27% styrene against 73% butadiene. Thus, when polystyrene is added, the mixiture becomes a little more symmetrical, approaching toward an equal proportion of the two types of monomers, whereas when polybutadiene is added the mixture becomes even more asymmetric. In the theory of block copolymers by Leibler,[6] the transition temperature is predicted to decrease as the relative size of the blocks becomes more disparate (while the total chain legnth of the copolymer remains the same). A qualitative similar trend evidently results even when the relative amount of the monomers is altered by addition of homopolymers as in our systems.

The phase equilibria at temperatures above the "pseudoeutectic point" BCD can be interpreted in terms of the free energy of mixing of two polymer liquids, if the disordered block copolymer is assumed to behave essentially as the corresponding random copolymer does. The observed cloud points dividing regions II and IV in Figures 2 and 4 are therefore analyzed by means of the Flory–Huggins expression:

$$\Delta G_M = RT[(1/V_1)\phi_1 \ln \phi_1 + (1/V_2)\phi_2 \ln \phi_2] + \Lambda_{12}\phi_1\phi_2 \qquad (2)$$

where ΔG_M is the free energy change, per unit volume, of mixing component 1 of molar volume V_1 and component 2 of molar volume V_2, and ϕ_1 and ϕ_2 are the volume fractions. Λ_{12} is the polymer–polymer interaction energy density and is treated here as a parameter to be determined by comparison with the experimental data. Λ_{12} is related to the more usual χ parameter through

$$\chi = \Lambda V_{\text{ref}}/RT \qquad (3)$$

where the reference volume V_{ref} is often taken equal to the monomer volume. Our reason for preferring Λ to χ was given previously.[2] When one (or both) of the components is a random copolymer, the experimentally determined Λ_{12} can be related[2] to the interaction energy density Λ_{AB} between the homopolymers A and B by

$$\Lambda_{AB} = \Lambda_{12}/(f_{A1} - f_{A2})^2 \qquad (4)$$

where f_{A1} and f_{A2} are the fractions of the comonomer A in components 1 and 2, respectively.

Since Λ_{12} usually depends on the temperature and the composition of the mixture moderately, we write

$$\Lambda_{12} = \lambda_0 + \lambda_T T + \lambda_1\phi_1 \qquad (5)$$

and seek the values of the adjustable parameters λ_0, λ_T, and λ_1 which give a best fit to the observed cloud points. The results are summarized in Table II. The last column in the table gives the value of Λ_{AB} calculated according to eq 4 at 200 °C and ϕ_1 = 0.5. The values obtained in the current work from the mixtures of a block copolymer and a homopolymer agree well with the average of the previous values obtained from the study[2] of homopolymer mixtures and mixtures of a homopolymer with a random copolymer. The temperature coefficients of Λ_{AB} given in the sixth column in the table, however, are larger than the average of the previous results. This suggests the possibility that a block copolymer, even when disordered, exhibits properties which deviate more from those of the corresponding random copolymer as the temperature is lowered.

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Registry No. Butadiene–styrene copolymer, 9003-55-8; polystyrene (homopolymer), 9003-53-6; polybutadiene (homopolymer), 9003-17-2.

References and Notes

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