Compatibilizing Effect of Random or Block Copolymer Added to Binary Mixture of Homopolymers

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ABSTRACT: When copolymer A–B is added to the mixture of homopolymer A and homopolymer B, the compatibility between the two homopolymers is enhanced under certain conditions. Analysis, based on the Flory–Huggins free energy of mixing, gives the specific conditions under which the critical, spinodal, or binodal temperature of the ternary mixture is expected to be lowered linearly with the amount of the added copolymer. Experimental measurements were performed on the changes in the cloud point of the mixtures of polystyrene and polybutadiene to which varying amounts of styrene–butadiene random or diblock copolymer were added. The results agree with the theoretical expectation. From quantitative analysis of the cloud point depression, the temperature coefficient of the interaction energy density between styrene and butadiene polymers is determined. The temperature coefficient is found to give an excellent agreement with the value previously determined by a curve-fitting procedure applied to the cloud point curves of binary mixtures.

Introduction

Incompatibility between two homopolymers A and B arises, as is well-known, from the fact that the very small gain in the entropy of mixing is usually not sufficient to overcome the unfavorable enthalpic interaction between the different types of segments. Enhancement in the degree of compatibility between the homopolymers can be sought by addition of a third component which reduces the number of unfavorable contacts between the segments of the two polymers. Addition of a mutual solvent usually results in such beneficial effect. It will be more useful if a similar enhancement of compatibility can be achieved by addition of a polymeric component. An A–B copolymer would be a natural candidate for such a purpose. In this work we investigate the effectiveness of a styrene–butadiene random copolymer or block copolymer as a compatibilizing agent when added to the mixture of polystyrene and polybutadiene.

First we examine some theoretical consequences that can be predicted on the basis of the Flory–Huggins free energy of mixing with regard to the compatibilizing effect of the copolymer. It is shown that under certain conditions the spinodal, the binodal, and the critical temperatures of the ternary mixture are expected to decrease linearly with the amount of the added copolymer. The specific conditions, constraining the relative amounts of the two homopolymers or the composition of the copolymer, differ depending on whether we want to achieve linear depression of the spinodal, the binodal, or the critical temperature. Next we report on the experimental measurement on the lowering of cloud points of a series of mixtures of polystyrene and polybutadiene, to which small amounts of styrene–butadiene random copolymers were added. The experimental data are in excellent agreement with theoretical expectation. Quantitative analysis of the data leads to the determination of the temperature coefficient of the polymer–polymer interaction energy density[1] Λ which agrees well with that previously determined.[1] Finally we compare the relative effectiveness of random and block copolymers as compatibilizing agents.

Theoretical Analysis

For mixtures containing only polymeric components, the mean field theory is expected[2] to provide an adequate framework for analysis of phase relations. In particular, we have earlier[1] shown that mixtures of homopolymers and copolymers containing styrene and butadiene monomers can be described satisfactorily in terms of the Flory–Huggins free energy of mixing.

For the ternary system being considered here, the free energy of mixing, ΔG_M, per unit volume of the mixture can be written as

$$\frac{\Delta G_M}{RT} = \sum_{i=1}^{3} \frac{\phi_i}{V_i} \ln \phi_i + \sum_{i>j} \frac{\Lambda_{ij}}{RT} \phi_i \phi_j \tag{1}$$

where Λ_{ij} is the polymer–polymer interaction energy density, V_i is the molar volume, and ϕ_i is the volume fraction. We identify the components 1 and 2 with the homopolymers A and B and component 3 with the copolymer A–B. If the volume fractions of monomers A and B in the copolymer are equal to f_1 and f_2, respectively, the Λ_{ij}'s can be written[1] as

$$\begin{aligned} \Lambda_{12} &= \Lambda \\ \Lambda_{13} &= \Lambda f_2^2 \\ \Lambda_{23} &= \Lambda f_1^2 \end{aligned} \tag{2}$$

and eq 1 is simplified to

$$\frac{\Delta G_M}{RT} = \sum \frac{\phi_i}{V_i} \ln \phi_i + \frac{\Lambda}{RT}(\phi_1\phi_2 + f_1^2\phi_2\phi_3 + f_2^2\phi_1\phi_3) \tag{3}$$

The interaction energy density Λ is related to the usual χ parameter by

$$\Lambda = RT\chi / V_{ref} \tag{4}$$

where V_{ref} is some reference volume, usually taken equal to the molar volume of a segment. The advantage of using Λ over χ has previously[1,3] been pointed out. In the following analysis we assume Λ to be independent of the composition of the mixture. This is a good approximation for the styrene–butadiene system[1] being considered here and is probably so also for many other polymer–polymer systems. Λ is moderately temperature-dependent as is shown by our previous results[1] and by the results to be given below.

Before considering the binodals obtainable from eq 3, we first consider the spinodals and the critical points which are more amenable to analysis. The spinodals are given by the condition[12,13]

$$U \equiv \begin{vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{vmatrix} = 0 \tag{5}$$

where

$$G_{ij} = \frac{\partial^2}{\partial\phi_i \partial\phi_j} \frac{\Delta G_M}{RT} \tag{6}$$

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The critical point is required to satisfy eq 5 as well as the condition[12,13]

$$U_{cr} \equiv \begin{vmatrix} \partial U/\partial \phi_1 & \partial U/\partial \phi_2 \\ G_{21} & G_{22} \end{vmatrix} = 0 \quad (7)$$

Substituting eq 3 into eq 5 and 7, we find

$$U = Q_1Q_2 + Q_1Q_3 + Q_2Q_3 - (2\Lambda/RT)(Q_1f_1^2 + Q_2f_2^2 + Q_3) \quad (8)$$

and

$$U_{cr} = -V_1Q_1^2(Q_2 + Q_3 - f_1^2(2\Lambda/RT))^2 + V_2Q_2^2(Q_3 + f_1f_2(2\Lambda/RT))(Q_1 + Q_3 - f_2^2(2\Lambda/RT)) + V_3Q_3^2(Q_1 + Q_2 - 2\Lambda/RT)(Q_2 - f_1(2\Lambda/RT)) \quad (9)$$

where

$$Q_i = 1/V_i\phi_i$$

(a) Spinodal. We are interested in knowing how the spinodal temperature changes as we add more of the copolymer to the mixture. Let ϕ_1^0 and ϕ_2^0 represent the volume fractions of the homopolymers before the addition of the copolymer. In any ternary mixture, then, ϕ_1 is equal to $\phi_1^0(1 - \phi_3)$.

When the composition of the initial binary mixture satisfies the special condition

$$\phi_1^0V_1/f_1 = \phi_2^0V_2/f_2 \quad (10)$$

the spinodal equation (8) gives a particularly simple solution

$$2\Lambda/RT = 1/f_1V_2\phi_2^0(1 - \phi_3) = 1/f_2V_1\phi_1^0(1 - \phi_3) \quad (11)$$

or

$$T/\Lambda = (T_0/\Lambda_0)(1 - \phi_3) \quad (12)$$

where T_0 is the spinodal temperature of the initial binary mixture of composition (ϕ_1^0, ϕ_2^0) and Λ_0 is the value of Λ at T_0. Equation 12 means that, if one initially chooses the composition of the homopolymer mixture to satisfy eq 10, then, as more copolymer is added the spinodal temperature decreases linearly with ϕ_3 (provided, of course, that Λ varies only moderately with temperature, as is probably true with most polymer pairs).

When the relative amounts (ϕ_1^0 and ϕ_2^0) of the homopolymers differ greatly from those required by eq 10, the spinodal temperature decreases less rapidly with added copolymer, or may even increase initially, and then goes through a maximum. To illustrate this, the solution of $U = 0$, with U given by eq 8, is plotted numerically in Figure 1 for the case of $V_1 = V_2 = V$, $V_3 = 10V$, $f_1 = f_2$, and various values of ϕ_1^0. In Figure 2 the isothermal spinodal curves in the ternary phase diagram are plotted for several values of $V\Lambda/RT$. Here, point A denotes the composition (ϕ_1^0, ϕ_2^0), which satisfies the condition (10), and point B denotes the composition beyond which the added copolymer leads to initial increase in the spinodal temperature. Point B is give in general by

$$\frac{1}{V_3} = \frac{f_1^2}{\phi_1^0V_1} + \frac{f_2^2}{\phi_2^0V_2} - \frac{1}{\phi_1^0V_1 + \phi_2^0V_2} \quad (13)$$

In Figure 2, the straight line joining a point on the 1–2 axis with the apex 3 is the composition line which is traversed as we add copolymers. It is when this line cuts an isothermal spinodal curve twice that the spinodal temperature initially increases and then goes through a maximum as more copolymer is added. Equation 13 shows that, as the volume V_3 of the copolymer is increased, the point B is pushed away from the pure homopolymer. In other words,

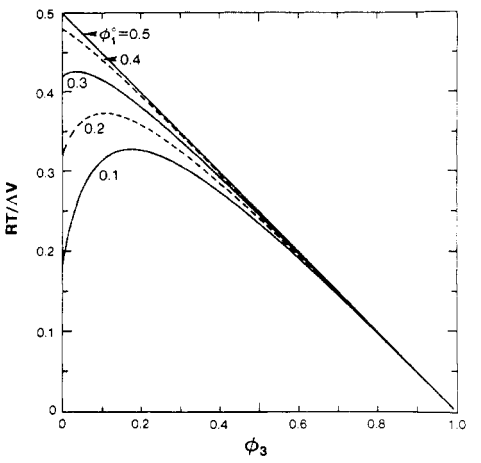

Figure 1. Spinodal temperature T against volume fraction ϕ_3 of added copolymer, calculated for the system homopolymer A–homopolymer B–random copolymer A–B with $V_1 = V_2$, $V_3 = 10V_1$, $f_1 = f_2$, and the initial volume fraction ϕ_1^0 of homopolymer A as indicated.

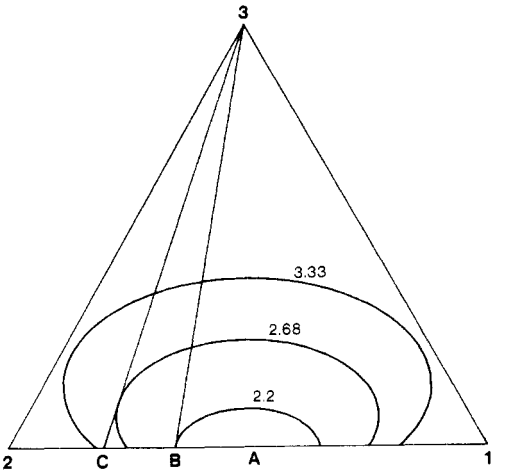

Figure 2. Spinodal isotherms calculated for the ternary mixture with $V_1 = V_2$, $V_3 = 10V_1$, and $f_1 = f_2$. Indicated with the curves are the values of $\Lambda V/RT$. The straight line connecting a point on the 1–2 axis with the apex 3 is the composition line which is traversed as we add the copolymer. When the initial composition of the homopolymers is to the right of point B, the addition of the copolymer lowers the spinodal temperature, whereas when it is to the left of B, the spinodal temperature goes through a maximum before decreasing.

when the size of the copolymer is made larger, the range of composition (ϕ_1^0, ϕ_2^0) in which the added copolymer leads to monotonic decrease in the spinodal temperature becomes smaller.

(b) Critical Point. For a critical point, eq 8 and 9 have to be satisfied simultaneously. As shown above, for the homopolymer composition satisfying eq 10, eq 8 for the spinodal leads to a very simple solution (11). When eq 11 is substituted into eq 9, it is seen that eq 9 is satisfied only if

$$\phi_1^0V_1^{1/2} = \phi_2^0V_2^{1/2} \quad (14)$$

which, in view of eq 10, implies also that

$$V_1^{1/2}/f_1 = V_2^{1/2}/f_2 \quad (15)$$

The conditions specified by eq 14 and 15 suggest the following interesting consequence. Suppose one starts with a binary homopolymer mixture at the critical composition, which is given by eq 14. One then chooses a copolymer in which the composition of monomers is related to the homopolymer sizes according to eq 15. Then the ternary

mixture formed by addition of this copolymer, irrespective of the amount of the copolymer added, undergoes a phase separation at some temperature which is at once the spinodal, binodal, and critical point. As more of the copolymer is added, the critical temperature decreases linearly with the volume fraction of the copolymer in accordance with eq 12.

(c) Binodal. The free energy expression is much more difficult to solve for binodals analytically. Solutions were obtained by Scott[4] and Leibler[5] for the very special case of

$$V_1 = V_2; \qquad f_1 = f_2 \tag{16}$$

Because of the symmetry, it is at once expected that when the ternary mixture separates into two phases, the compositions of the coexisting phases formed are given by

$$\phi_1' = \phi_2''; \qquad \phi_2' = \phi_1''; \qquad \phi_3' = \phi_3'' \tag{17}$$

Using the condition that the chemical potentials of the coexisting phases should be equal and substituting eq 17 into the resulting expression, one can show that the binodal temperature is given by

$$T = (\Lambda V/R)(\phi_1 - \phi_2)/\ln(\phi_1/\phi_2) \tag{18}$$

Since both ϕ_1 and ϕ_2 decrease with increasing ϕ_3 as $\phi_i = \phi_i^0(1 - \phi_3)$, it is clear that the binodal temperature also follows eq 12 and decreases linearly with increasing ϕ_3. It should be noted that the condition (16) for the linear decrease in binodal temperature is, in a sense, more general than the corresponding condition (10) for the spinodal and is realized irrespective of the composition (ϕ_1^0, ϕ_2^0) of the initial homopolymer binary mixture.

Leibler[5] has demonstrated that when the amount of the copolymer exceeds a certain limit, the ternary mixture, on lowering the temperature, may separate into three, rather than two, coexisting phases. When this happens, eq 18 is not valid and the binodal temperature no longer decreases linearly according to eq 12. According to Leibler, the ternary phase diagram, for a system satisfying the condition (16), contains a three-phase region when

$$T < \Lambda V/2R(2V_1/V_3 + 1) \tag{19}$$

Thus, as more of the copolymer is added to the mixture of homopolymers, the binodal temperature will decrease linearly with ϕ_3, until the temperature indicated by eq 19 is reached; thereafter the decrease in the binodal temperature is much less than indicated by the linear law, eq 12. From eq 19 it is seen that this threshold temperature of three-phase formation rises as the molar volume V_3 of the copolymer molecule increases. In other words, copolymer molecules of larger chain lengths are less effective as compatibilizing agent, in agreement with what one might have expected intuitively.

The fact that three-phase formation eventually intervenes with sufficient amounts of added copolymer can readily be understood if we look at the plots in Figure 1 once again. There it is seen that the spinodal temperature, in general, decreases with ϕ_3 but, depending on the value of ϕ_1^0 and ϕ_2^0, it decreases initially rather slowly or it goes through a maximum before it starts its descent. The binodal temperature is always higher than the spinodal initially when ϕ_3 is equal to zero (except, of course, for $\phi_1^0 = 0.5$, satisfying the critical condition) but decreases linearly with ϕ_3. With increasing ϕ_3, the descent in the spinodal is thus slower than the descent in the binodal and eventually a point is reached where the spinodal temperature becomes higher than the binodal. The contradiction of spinodal being higher than binodal is eliminated by the intervention of three coexisting phases.

Table I
Characterization Data of Polymer Samples

sample	remarks	styrene content, %	M_w	M_w/M_n
PS	polystyrene	100	1900	1.06
PBD	polybutadiene	0	2650	1.13
R50/50	random copolymer	52.5	25000	1.04
B50/50	diblock copolymer	52.2	26000	1.04
RF50/50	random copolymer	46.7	16300	1.55
SPP45	random copolymer	45	[a]	

[a] $[\eta] = 2.51$ dL/g at 30 °C in toluene. The M_w calculated from $[\eta]$ range from 2.3×10^5 to 3.2×10^5, depending on the several Mark–Houwink constants[11] reported for SBR rubber.

Experimental Section

Molecular weight data for the polymers used are given in Table I. The polystyrene homopolymer was an anionically polymerized sample obtained from Pressure Chemical Co. The polybutadiene was sample CDS-B-3 obtained from Goodyear Chemical Co. According to the manufacturer, the latter contains 53% trans, 41% cis, and 6% vinyl unsaturation.

The characterization data of the copolymer samples, comprising three random copolymers and one diblock copolymer, are also listed in Table I. The random copolymer designated R50/50 and the block copolymer designated B50/50 were anionically polymerized and were kindly prepared for our use by Dr. H. L. Hsieh of Philips Petroleum Co. Random copolymer SPP45 was obtained from Scientific Polymer Products Ltd. and is believed to have been prepared by radical polymerization. Finally, random copolymer RF50/50 was prepared in this laboratory by free-radical polymerization using a mixture of benzene and ethylbenzene as solvent.

The method used to determine the cloud points of the mixtures has been described in detail elsewhere.[1] Briefly, the various components are thoroughly mixed under vacuum in glass tubes, which are then sealed. The sample is then mounted within a furnace whose temperature can be accurately controlled, and light from a He/Ne laser is passed through the sample. The cloud temperature is first determined approximately and then the temperature of the furnace is cycled between limits a few degrees above and below this temperature. In order to avoid spurious undercooling effects we have defined the cloud temperature as the temperature at which the mixture just becomes clear on heating.

The method normally employed for mixing the samples involved weighing the individual components into the sample tubes, giving a total of ca 0.3 g of polymer, and then mixing mechanically under vacuum using a magnetically activated stirrer placed within the sample tube, while heating to ca 200 °C in a silicone oil bath. However, in the case of sample SPP45, in view of its high molecular weight, the individual components were first dissolved and mixed in toluene, which was then evaporated before completing the mixing process under vacuum in the usual manner.

Results and Discussion

Cloud temperatures were determined for the mixtures containing equal weights of polystyrene and polybutadiene ($\phi_{PS}/\phi_{PBD} = 0.84$) and varying amounts of one of the four copolymers. The cloud point data obtained are plotted in Figure 3 against volume fraction ϕ_3 of added copolymer. The solid points in this figure were obtained with the random copolymers and the open points with the block copolymer.

Although all the random copolymers produce an almost linear decrease in cloud point, it is apparent that addition of the very high molecular weight sample SPP45 results in only a very slight lowering of cloud point. In contrast, the two other random copolymer samples produce a much more pronounced lowering of cloud point, and in this respect the two samples behave almost identically, despite differences of ~40% in M_w and a factor of more than 2 in M_n and despite the difference in the monomer compo-

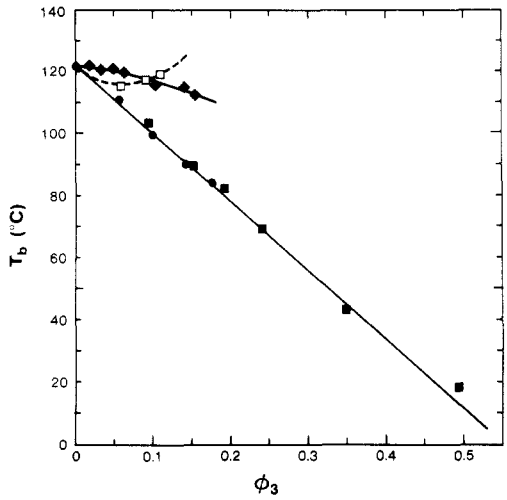

Figure 3. Cloud temperatures obtained with mixtures containing equal weights of polystyrene (M_w = 1900) and polybutadiene (M_w = 2650) and varying amounts of copolymers. Filled circles, random copolymer R50/50 (M_w = 25 000); filled squares, random copolymer RF50/50 (M_w = 16 300); filled diamonds, random copolymer SPP45 ($M_w \geq 2.3 \times 10^5$); open squares, diblock copolymer B50/50 (M_w = 26 000).

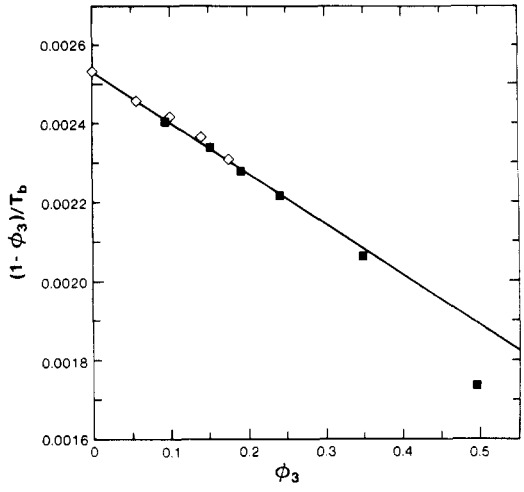

Figure 4. The cloud temperature data, obtained with the two lower molecular weight copolymers R50/50 and RF50/50 and shown in Figure 3, are replotted here in the form of $(1 - \phi_3)/T_b$ against ϕ_3. The slope gives the temperature coefficient of the interaction energy density Λ.

sition: f_S/f_{BD} = 0.92 (by volume at 120 °C) for sample R50/50 and 0.72 for sample RF50/50.

Equation 12 predicts that, if Λ were independent of temperature, T_b would decrease linearly with ϕ_3 and extrapolate to 0 K for $\phi_3 \to 1$. Although in Figure 3 the data obtained with the two lower molecular weight copolymers exhibit good linearity, the rate of decrease with ϕ_3 is less than expected. This discrepancy can be ascribed to the temperature dependence of Λ. Our previous study[1] has shown that Λ for polystyrene–polybutadiene system has a moderate dependency on temperature, and one can, in the first approximation, write

$$\Lambda = \lambda_0 + \lambda_T T \tag{20}$$

Substitution of eq 20 into eq 12 then gives

$$(1 - \phi_3)/T_b = 1/T_{b,0} + (\lambda_T/\lambda_0)\phi_3 \tag{21}$$

Figure 4 gives the plot of $(1 - \phi_3)/T_b$ against ϕ_3, as suggested by eq 21, for the data obtained with sample R50/50 and RF50/50. A good straight line can be drawn through the data points with the exception of the point at ϕ_3 = 0.49 (and perhaps at ϕ_3 = 0.35).

From the slope in Figure 4 we determine λ_T/λ_0 to be -1.28×10^{-3} K^{-1}. The Λ values were previously determined by applying a curve-fitting procedure to the cloud point curves of binary mixtures, and the average of nine separate determinations gave

$$\Lambda = 0.718 \pm 0.051 - (0.0021 \pm 0.00045)(T\ (°C) - 150\ °C) \tag{22}$$

where Λ is in cal/cm^3 and the error limits are standard deviations. From eq 22, λ_T/λ_0 (λ_0 being the value of Λ at T = 0 K) is calculated to be $(-1.31 \pm 0.32) \times 10^{-3}$ K^{-1}. Thus the values of λ_T/λ_0 determined by the two methods show an excellent agreement, which testifies to the validity of the present procedure.

As a method of determining the temperature coefficient of the interaction parameter, the present approach is potentially simpler than the one relying on the analysis of the shape of cloud point curves. In the systems we studied, the homopolymer molar volumes V_{PS} and V_{PBD} are not exactly equal to each other and the composition of the copolymers also deviates appreciably from 50/50 (in volume). The seemingly satisfactory value of λ_T value obtained in this work despite these deviations from the ideal symmetry requirements suggests the robustness and practicality of the present procedure. The shape of cloud point curves is affected by the polydispersity of the polymers involved. Our numerical study on the effect of polydispersity[6] shows that the cloud point curves will become flatter as the polydispersity increases, and the temperature coefficient of Λ determined from the analysis of the curve shape will be in error unless the polymers involved are of narrow molecular weight distribution. The present method, in contrast, is expected to give good values of the temperature coefficient of Λ even when the polymers involved are polydisperse.

The point corresponding to ϕ_3 = 0.49, which lies somewhat below the straight line in Figure 4, has a value of $T_b/T_{b,0}$ equal to 0.739, while that at ϕ_3 = 0.35, which lies only slightly below the line, has $T_b/T_{b,0}$ = 0.801. If one calculates the value of $T_b/T_{b,0}$ at which a three-phase region is expected to appear, using V_3 = 15 000 and $V_1 = V_2$ = 2290 cm^3/mol in eq 19, then one obtains T/T_0 = 0.77. Thus the phase diagram at the cloud temperature for ϕ_3 = 0.49 is predicted to contain a three-phase region, while that at ϕ_3 = 0.35 lies somewhere near the border line, and, as such, the rather high value of T_b at ϕ_3 = 0.49 may reflect experimentally the presence of a three-phase region.

The fact that the highest molecular weight copolymer, sample SPP45, fails to function as a compatibilizer can also be explained on the same basis. Equation 19 predicts that for a copolymer having a molecular weight in the range 2.3×10^5 to 3.2×10^5 will cause a separation into three coexisting phases when $T_b/T_{b,0}$ is 0.98 or lower. According to eq 12, this condition is expected to be reached when ϕ_3 is equal to 0.02. In Figure 3, the first point obtained with SPP45 is at ϕ_3 = 0.019, where the observed T_b is already much higher than predicted, suggesting that the three-phase separation may have already intervened at this point. Despite such minor discrepancy, it seems reasonable to ascribe the failure of sample SPP45 to function as a compatibilizer to its high molecular weight and the consequent inducement of three-phase separation.

For the polystyrene–polybutadiene blends considered here, the interaction energy density Λ remains positive at all temperatures, and the compatibility is achieved only by virtue of low molecular weight even in the presence of the copolymer. The theoretical analysis given in this work

should, however, be useful also in dealing with the blends of high molecular weight polymers that are normally compatible but develop incompatibility at high temperatures. The changeover from a compatibility to an incompatibility in such blends arises from the change in Λ from a negative to a positive value as a result of increased disparity in the free volumes of the pure polymers accompanying the temperature rise. The detrimental effect of the positive interaction parameter, irrespective of its origin, however, can be mitigated by the presence of a copolymer of intermediate composition. Our theoretical analysis should apply to such cases also, as long as the composition dependence of the value of Λ is so small as to be neglected. In particular, eq 12 remains valid, and as the volume fraction ϕ_3 of the copolymer is increased, the ratio T/Λ decreases. Because of the rapid rise in Λ with increasing temperature (usually much faster than T) around the temperature range where Λ changes its sign, the decrease in the ratio T/Λ actually demands that the temperature be increased. In other words, the binodal temperature (or the spinodal or critical temperature, as the case may be) is raised and the temperature range of compatibility is enlarged by the addition of copolymer.

Finally, we consider the results obtained on adding block copolymer to the polystyrene–polybutadiene mixture, depicted by the dotted line in Figure 3. Although the compositions and molecular weights of samples B50/50 and R50/50 closely resemble each other (see Table I), one observes markedly different behavior in the case of the block copolymer, as T_b at first decreases slightly before passing through a shallow minimum at about 6% copolymer and then rising again. At larger copolymer contents (>21%) the mixture becomes optically clear at all temperatures above room temperature.

The behavior of the mixtures containing a relatively large amount of block copolymer can be explained readily by recalling the results we obtained previously[7,8] for the phase diagram of mixtures of a block copolymer with a homopolymer. The block copolymer, having a regular structure consisting of segregated microdomains of styrene and butadiene segments, is capable of dissolving appreciable amounts of low molecular weight polystyrene and polybutadiene in their respective domains. The mixture then remains optically clear as long as the size of the microdomains remain much smaller than the wavelength of light. With increasing amount of the added homopolymers, however, the solubility limit of the latter is eventually reached and a macroscopic phase separation ensues, leading to a turbid mixture. This point was probably reached in our system when the volume fraction of the combined homopolymers was about 80%. The situation prevailing at even lower concentration of the block copolymer is much less clear at this moment and requires further study for full explanation. We may, however, add the following speculative comments. The solubility of the block copolymer either in the mixed polystyrene–polybutadiene phase or in the demixed phases consisting predominantly of polystyrene or polybutadiene is probably very small. Thus the block copolymer possesses very little capability of lowering the binodal or spinodal temperatures. The block copolymer molecules locate themselves predominantly at the boundary between phases, thus lowering the surface free energy and reducing the phase-separated domain sizes. The presence of block copolymer can thus promote the reduction in the turbidity of the mixture, without in fact enhancing the compatibility between the two homopolymers. The efficacy of block copolymers in promoting the compatibility of homopolymer mixture was reported in the past,[9] but such results have to be interpreted to mean an enhancement of "apparent" or "optical" compatibility, in contrast to the thermodynamic compatibility with which we are concerned here. In this regard it should also be mentioned that, when the molecular weight of the block copolymer is sufficiently small so as to make it remain disordered (i.e., without microdomain segregation), then it behaves essentially the same as the corresponding random copolymer and exhibits a compatibilizing effect, as the results obtained by Gallot et al.[10] indicate.

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Registry No. Polystyrene (homopolymer), 9003-53-6; polybutadiene (homopolymer), 9003-17-2; (styrene)-(butadiene) (copolymer), 9003-55-8.

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