# Studies on Domain Formation of the A–B-Type Block Copolymer from Its Solutions. Ternary Polymer Blend of the Styrene–Isoprene Block Copolymer with Polystyrene and Polyisoprene[1a]

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ABSTRACT: An approach to the problem of understanding the mechanism of domain formation in a ternary system, A–B-type block copolymer, A polymer, and B polymer, from its solution in a common solvent is discussed. Films were cast from toluene solutions for several compositions of the three components, A–B-type block copolymer of styrene and isoprene, homopolystyrene, and homopolyisoprene. The domain structures were investigated by ordinary light microscopy and by electron microscopy using the $OsO_4$ fixation technique. Results suggest a limitation of relative molecular weights of the homopolymers to those of corresponding blocks of the copolymer for the solubilization of homopolymers into the respective block domains. That is, if the fraction of the copolymer is kept relatively large, the inherent manner of domain formation of the block copolymer from its solution may be maintained even for the ternary or binary system. The mechanism of domain formation of the ternary system from its solution is discussed, qualitatively. The discussion is presented in terms of the relationship between the binodal surface of a phase diagram of four components (A–B-type block copolymer, A polymer, B polymer, and a common solvent) and a critical micelle concentration of the three polymer solutes.

Riess, *et al.*,[2] have carried out experimental studies on the emulsifying effects of block and graft copolymers, *i.e.*, their ability to restrain phase separation of mixed systems of the corresponding homopolymers into their macroscopic domains and to keep the system a microheterogeneous one. The transparency of the solvent-cast films was taken as a criterion for the emulsifying effect of the copolymers on the microphase separation of the ternary system. They speculated that the emulsifying efficiency of the block copolymer is usually superior to that of the graft copolymer, depending on the composition of the copolymers and molecular weights of the homopolymers relative to those of the corresponding blocks of the copolymers as well.

On the other hand, Molau, *et al.*,[3–5] demonstrated that the domain structure of rubber modified vinyl plastics, such as ABS resin and HIPS (high-impact polystyrene) in which spherical rubber domains are dispersed in the plastic matrix to form the microheterogeneous system,[6,7] is formed in a polymeric oil-in-oil emulsion (POO-emulsion) stabilized by the graft copolymer produced during the polymerization of a solution of the rubber in the vinyl monomers. This concept of treating the graft copolymer as a sort of stabilizer for the POO-emulsion has also been confirmed recently by Molau, *et al.*, for block copolymers.[8]

In this paper, the domain structures of solvent cast films of several compositions of three components, A–B-type block copolymer of styrene and isoprene, polystyrene, and polyisoprene, are investigated under ordinary light and electron microscopes by using the $OsO_4$ fixation technique. The results obtained are useful not only in justifying the speculation of Riess, *et al.*, for the emulsifying effect of the copolymers, but also in explaining the mechanism of domain formation of the ternary system from solution. The mechanism will be discussed in terms of thermodynamic parameters of phase equilibria in the four-component system including the solvent, taking account of the inherent nature of domain formation of the A–B-type block copolymer reported in the previous paper.[9]

## Procedures and Results

A–B-type block copolymers of styrene and isoprene, homopolystyrene, and homopolyisoprene were synthesized by the living polymerization technique initiated by *n*-BuLi in tetrahydrofuran at −78°. Characterization of the polymers was performed by ultracentrifugation, osmotic pressure, and ultraviolet and infrared spectra as in a previous paper.[9] The molecular weights of the polymers and the compositions of the block copolymers in weight fraction are indicated in the triangular diagrams in Figures 1–3.

The casting solvent, toluene, was dried over sodium and distilled. All films were cast from 5% solutions (total polymer concentration) of two or three components of the polymers in toluene by pouring onto glass plates and evaporating the solvent gradually at 30°. In Figures 1–3, the composition of the mixtures is shown by the equilateral triangular coordinates representing weight fractions. The transparency of the cast films is indicated in terms of the circular symbols

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[1] (a) Presented partly before the 18th Annual Meeting of the Society of Polymer Science, Japan, Kyoto Conference Hall, May 17, 1969; presented at the Division of Polymer Chemistry, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969. (b) Polymer Research Institute, University of Massachusetts, Amherst, Mass. 01002.

[2] (a) G. Riess, J. Kohler, C. Tournut, and A. Banderet, *Macromol. Chem.*, **101**, 58 (1967); (b) J. Kohler, G. Riess, and A. Banderet, *Eur. Polym. J.*, **4**, 173 (1968).

[3] G. E. Molau, *J. Polym. Sci., Part A-3*, 1267 (1965).

[4] G. E. Molau, *ibid., Part A-3*, 4235 (1965).

[5] G. E. Molau and H. Keskkula, *ibid., Part A-1*, **4**, 1595 (1966).

[6] K. Kato, *Polym. Eng. Sci.*, **7**, 38 (1967).

[7] C. B. Bucknall, *Brit. Plastics*, **40**, 118 (1967).

[8] G. E. Molau and W. M. Wittbrodt, *Macromolecules*, **1**, 260 (1968).

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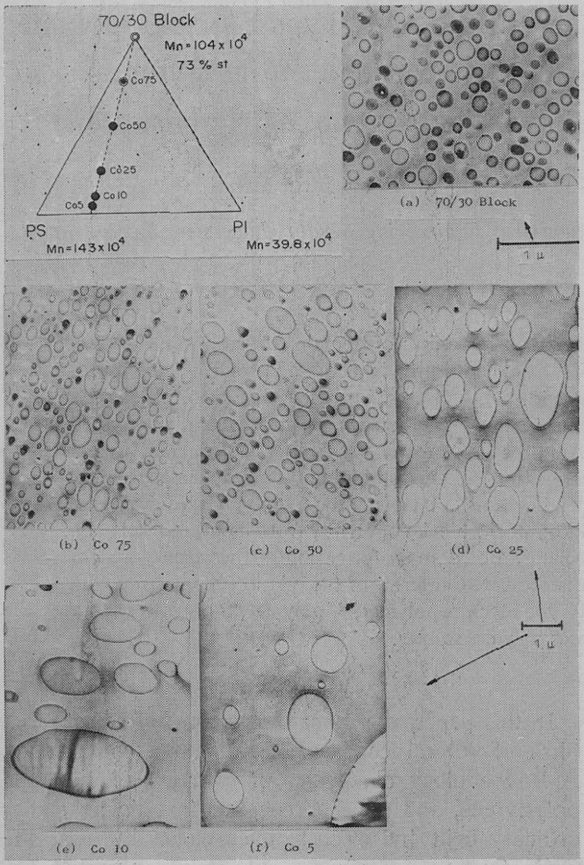

Figure 1. Triangular diagram representing the composition in weight fractions of ternary mixtures and electron micrographs of ultrathin sections of films cast from 5% toluene solutions and stained by $OsO_4$.

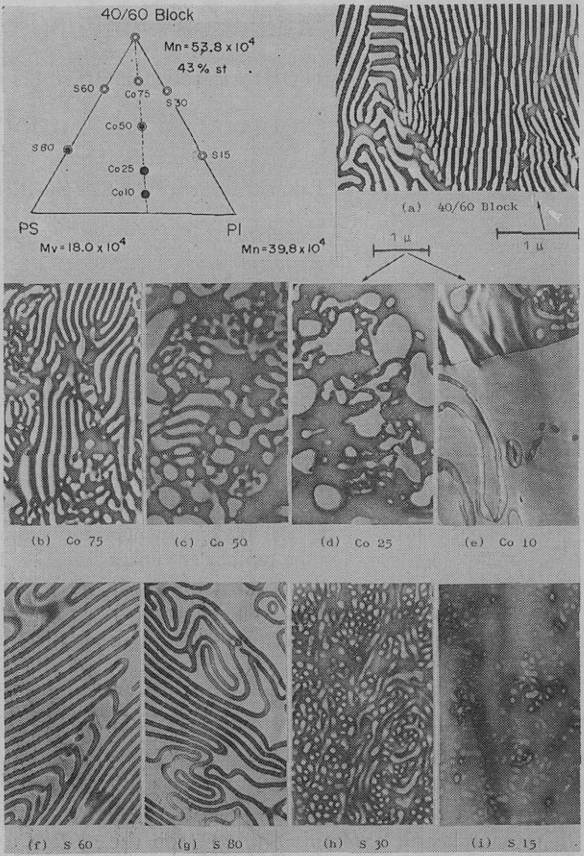

Figure 2. Triangular diagram representing the composition in weight fractions of ternary or binary mixtures and electron micrographs of ultrathin sections of films cast from 5% toluene solutions and stained by $OsO_4$.

in the triangular diagrams. An open circle designates transparent, a double open circle designates transparent but iridescent, a dot-open circle designates cloudy and iridescent, and a dot designates opaque.

The domain structure of the cast films was observed by light microscopy and by electron microscopy using the $OsO_4$ fixation technique.[6] Thin sections about 350 Å thick for electron microscopy and 5 $\mu$ thick for light microscopy were fixed with $OsO_4$ and then cut normal to the film surface and examined. The results obtained are illustrated in the photographs in Figures 1–3, together with the triangular diagrams indicating the composition of the binary or ternary components and the transparency of the cast films.

All specimens in Figure 1 are mixtures in which the ratio of styrene to isoprene is maintained at 73/27; this is similar to the styrene/isoprene ratio in 70/30 block copolymer. Thus the ratio is not changed on mixing the corresponding homopolymers. The molecular weights of the homopolymers are also similar to those of the corresponding copolymer blocks. The method for forming the domain structure of the 70/30 block copolymer from toluene solution, *i.e.*, to form spheres of isoprene component dispersed in a matrix of styrene component (Figure 1a), is still maintained for the ternary mixtures along the isopleth, as seen in Figures 1b–f. The size distribution of the domain structure is considerably broadened as the fraction of the copolymer decreases. It appears that each homopolymer added is solubilized into respective block domains composed of like components.[10]

For the ternary mixtures along the isopleth corresponding to the composition of 40/60 block copolymer, the original domain structure with an alternate lamellar arrangement, as seen in Figure 2a, is maintained only in the range corresponding to a large fraction of the copolymer and is gradually changed, as illustrated in Figures 2b–e with decreasing of the fraction of the copolymer, to a structure of very irregular fragments of styrene component dispersed in a matrix of isoprene component. For the binary mixtures of the 40/60 block copolymer with homopolystyrene or homopolyisoprene, where the total composition of styrene or isoprene sequences is not kept constant, the domain structure changes systematically with an increase in the fraction of styrene or isoprene sequences; *i.e.*, for the former case, the structure changes from the alternate lamellar arrangement, Figure 2a, to more separated lamellar arrangements, Figures 2f–g, due to thickening of styrene lamella; while for the latter case, the structure changes from the alternate lamellar arrangement to styrene rods, Figure 2h, to styrene

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(10) The matrix domain in Figures 1d–f is darker than the spherical domain. But, when one restains the ultrathin sections with $OsO_4$, the spherical domain becomes quite dark. This suggests that $OsO_4$ diffusing through the matrix domain deposits on the surface of the spherical domain of the isoprene component and reduces to matallic osmium preventing further diffusion into the spherical domain.

spheres, Figure 2i, both dispersed in a matrix of isoprene component. For every specimen in Figure 2, where the molecular weights of the homopolymers are again similar to those of the corresponding blocks of the copolymer, solubilization of the homopolymers into the respective block domains takes place. But the domain structure of alternate lamellar arrangement for the 40/60 block copolymer is not maintained if the copolymer fraction along the isopleth drops below 50%.

For the binary mixtures of hsM series in Figure 3, where the 20/80 block copolymer is mixed with homopolystyrene of relatively higher molecular weight than that of the corresponding block of the copolymer, it is noticeable that a phase separation into the homopolystyrene phase and the block copolymer phase occurs without any disturbance of the original domain structure of the block copolymer. This is obvious in a comparison of Figure 3b′, an electron micrograph of the block copolymer phase (matrix phase in Figure 3b) with Figure 3a, the original domain structure of the 20/80 block copolymer. Large ellipsoids of the homopolystyrene component are dispersed in a matrix of the block copolymer component which forms an inherent domain structure of spheres of styrene blocks in a matrix of isoprene blocks. The same phenomena are observed in a mixture of the block copolymer with a homopolystyrene of much higher molecular weight than the hsM series, as illustrated in Figure 3f. In this case, the interface between the homopolystyrene phase and the block copolymer phase is demonstrated clearly in Figure 3f′. On the other hand, when the block copolymer is mixed with a homopolystyrene of relatively low molecular weight, that is, lower than that of the corresponding block of the copolymer, the homopolystyrene is solubilized into the domain of styrene block of the copolymer, as seen in Figure 3g. This is in contrast to the above cases involving high molecular weight polystyrenes but is similar to the cases discussed in connection with Figures 1 and 2. For the binary mixtures of the 20/80 block copolymer with a homopolyisoprene, whose molecular weight is of the same order as that of the corresponding block of the copolymer, the homopolyisoprene added is solubilized into the matrix domain of isoprene block of the copolymer. This increases the separation of the spheres of styrene blocks, as seen in Figure 3h in comparison with those in Figure 3a.

The above results indicate that when the molecular weight of homopolymer added is of the same order or less than that of the corresponding block of the copolymer, the solubilization of the homopolymer into the domain of the corresponding block takes place. In this case, the two incompatible homopolymers can be blended well with each other by adding the corresponding block copolymer; that is, the block copolymer behaves just like an emulsifier in restraining phase separation of the homopolymers into their macroscopic domains. But when the molecular weight of the homopolymer added is much higher than that of the corresponding block, the copolymer can no longer act as the emulsifier; that is, the block copolymer behaves as if it were incompatible with the corresponding homopolymers and loses the tendency to incorporate the sequences of like homopolymers.

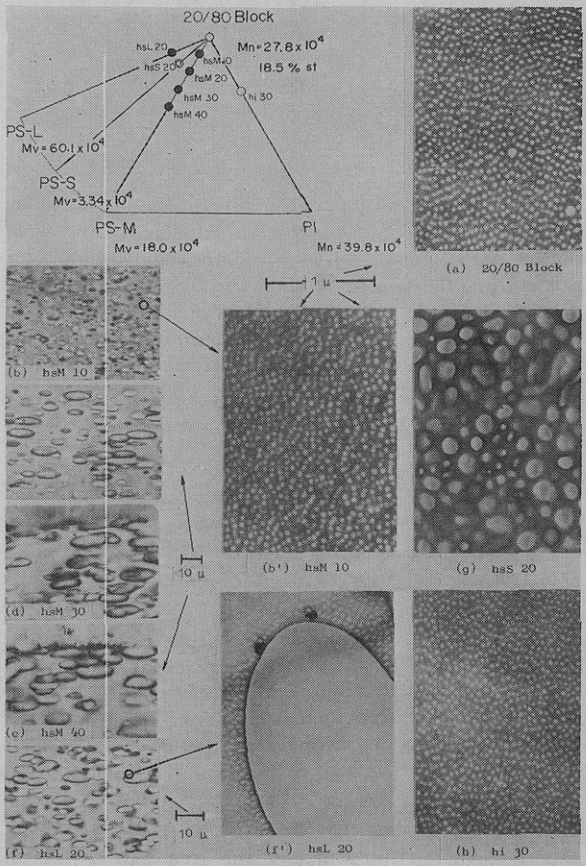

Figure 3. Triangular diagram representing the composition in weight fractions of binary mixtures and electron and ordinary micrographs of ultrathin and thin sections of films cast from 5% toluene solutions and stained by $OsO_4$.

The inherent manner of domain formation of the block copolymer from its solution[9a, 11] was discussed in a previous paper in terms of thermodynamic and molecular parameters.[9b] Results presented here suggest that when the above condition for solubilization of homopolymers into block domains of the copolymer is satisfied and the fraction of copolymer is kept relatively large,[12] the same manner of domain formation may be maintained even for the ternary and binary systems. Thus, the formation of five kinds of fundamental domain structures, A spheres in B matrix, A rods in B matrix, alternate lamellar arrangement, B rods in A matrix, and B spheres in A matrix, may be achieved, depending upon the total ratio of A sequences to B sequences in the system. This is demonstrated schematically in Figure 4, using the triangular diagram, in which the dash-dot line indicates the isopleth keeping the total sequence ratio identical with that of the A–B-type block copolymer. Thus, for the diagrams from Figures 4a–c the composition of the A–B-type block copolymer changes from A rich copolymer to rather B rich copolymer. In each diagram the

(11) M. Matsuo, S. Sagae, and H. Asai, *Polymer* (London), **10**, 79 (1969).

(12) The irregularity of domain shape, which is observed along the isopleth in Figure 2 in contrast to the broadening of domain size distribution along the isopleth in Figure 1, may be reflected, as discussed later in terms of the coalescence barrier in POO-emulsion, in a relatively larger interface area of the alternate lamellar arrangement than that in the spherical domain structure.

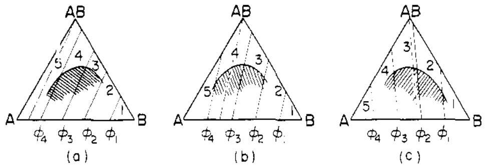

Figure 4. Triangular phase diagram representing the mode of domain structures formed from solutions of the three polymers in a common solvent, where the chain line indicates isopleth, and the area 1 corresponds to the domain structure of A spheres dispersed in B matrix, the area 2 to A rods in B matrix, the area 3 to the alternate lamellar arrangement, the area 4 to B rods in A matrix, and the area 5 to B spheres in A matrix.

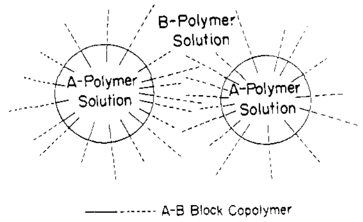

Figure 5. Polymeric oil-in-oil emulsion of A droplets in B solution type, stabilized by the A–B-type block copolymers accumulated at the interface between the spherical droplets and the matrix.

area 1 corresponds to the domain structure of A spheres dispersed in B matrix, the area 2 to A rods in B matrix, the area 3 to alternate lamellar arrangement, the area 4 to B rods in A matrix, and the area 5 to B spheres in A matrix. The above domain formation may be achieved stably only outside of the hatched area. The results of ternary systems in Figure 1 correspond to area 5 in Figure 4a when the component A is styrene. The results of binary systems in Figure 2 along the sides of 40/60 block-PS and 40/60 block-PI correspond to the side AB–A within the area 3 and the side AB–B in Figure 4c, respectively, when the component A is styrene. The results of the binary system in Figure 3, *i.e.*, Figures 3g and 3h, correspond to points on the side AB–B within the area 5 and the side A–AB both in Figures 4a when component A is isoprene.

Judging from the relationship between the transparency of the cast films represented by circular symbols and their domain structures, it may be said that the transparency depends on the size and distribution of the domain structure and that the iridescent phenomena are due to the periodic nature of the structure, both in relation to the wavelength of visible rays. This relationship confirms the criterion of the emulsifying effect of the copolymer, proposed by Riess, *et al.*, in terms of the transparency of cast films.[2]

## Discussion

**POO-Emulsion and Emulsifying Efficiency of Block Copolymer.** Molau, *et al.*,[3–5] demonstrated a mechanism for the formation of rubber particles during polymerization of solutions of rubber in vinyl monomers. They showed that a polymeric oil-in-oil emulsion, produced after a phase inversion at the beginning of the polymerization, is transformed into a solid structure as the polymerization proceeds. Assuming that the residual monomer at the stage of POO-emulsion can be considered as a casting solvent, and that the graft copolymer of the rubber and vinyl polymer produced during the polymerization is an A–B-type block copolymer, the polymerization process may be treated as similar to the solvent casting process in our experiments. Consider the process of casting from a dilute solution, the three polymer solutes, A–B-type block copolymer, A homopolymer, and B homopolymer, in a common solvent to form the ternary solid. Here a POO-emulsion, illustrated in Figure 5 as a microphase separation droplets of A solution dispersed in B solution, is produced and maintained as a whole at higher concentration until the solid structure is achieved. The block copolymer chains are squeezed out on the interface of the POO-emulsion (see Figure 5) as a result of the complete immiscibility[13] of the unlike sequences at sufficiently high polymer concentrations.

The formation of a microheterogeneous domain structure of two incompatible components by solvent casting of three polymer solutes, as demonstrated in Figures 1–3, suggests the emulsifying effect of the A-B-type block copolymer. This effect must now be discussed in terms of the POO-emulsion state. The uniformity of the domain size as well as the regularity of the domain shape in the cast films suggest that a high degree of stability of the POO-emulsion is achieved by the coalescence barrier which may prevent demixing of the system. This is indicated by the data in the figures, especially when the fraction of the block copolymer in the system is relatively large. In addition to Molau's discussion concerning sources of the coalescence barrier in POO-emulsions,[3–5] the concept of the entropic repulsion between approaching droplets, which are covered by block segments of opposite component, would have to be taken into account in the way proposed by Clayfield[14] and Meier.[15] These workers consider the repulsive force between particles, which adsorb polymer chains on each surface, in terms of a decrease in configurational entropy of the chains due to the loss of possible configurations as the space available to the chains is reduced between approaching particles.

A broad size distribution with decreasing fraction of the A–B-type block copolymer added is observed along the isopleth in Figure 1. Such behavior can be explained in terms of a random aggregation of the droplets of the POO-emulsions, which have low coalescence barriers due to the lack of copolymer chains on the surface of the droplets. The irregularity of domain shape, which is observed along the isopleth in Figure 2, may be also explained in terms of the lack of sufficient copolymer chains because of the relatively large surface area of the alternating lamellar rarangement compared to the spherical domain structure.

**Relationship between C* and the Binodal Surface of the Four-Component System; A–B-Type Block Copolymer, A Polymer, B Polymer, and Solvent.** The problem discussed next is the criterion for solubilization of the four component system. Since the A–B block

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(13) (a) A. Dobry and F. Boyer-Kawenoki, *J. Polym. Sci.*, **2**, 90 (1947); (b) R. S. Scott, *J. Chem. Phys.*, **17**, 279 (1949).

(14) E. J. Clayfield and E. C. Lumb, *J. Colloid Interfac. Sci.*, **22**, 269 (1966).

(15) D. J. Meier, *J. Phys. Chem.*, **71**, 1861 (1967).

copolymer has a molecular structure identical with that of the two incompatible homopolymer chains joined together, there may be a critical micelle concentration at which each block undergoes microphase separation and aggregates into characteristic molecular micelles in much the same way as soap molecules aggregate in aqueous solution at a critical micelle concentration.[16] For the four-component system, there may also be a critical concentration of total polymer, C*, at which the POO-emulsion is formed as a result of microphase separation.

When C* of the four component system is at $C_1^*$ in Figure 6, the solubilization has to occur in the following fashion. If C* is outside of the binodal surface of the four component phase diagram, the solution is homogeneous at C* and the three polymer solutes cooperate together for the micelle formation which results in the POO-emulsion stabilized by the copolymer. On the other hand, if the C* is at $C_2^*$ in the diagram of Figure 6, *i.e.*, inside of the binodal surface, the phase separation into the copolymer solution and the homopolymer solutions occurs before C* is reached during the casting process. Consequently, the block copolymer forms an inherent domain structure undisturbed by the homopolymers. Therefore, the problem is one of relating C* to the binodal surface.

A theoretical derivation of C* may be performed by developing Meier's formulation,[17] but this seems unlikely to give an analytic solution. Experimental values of C*, such as those obtained by Vanzo, *i.e.*, about 9% for a system of ethylbenzene and a block copolymer of styrene and butadiene,[16] may be utilized.

Derivation of the binodal surface of the four-component system may be very complicated. Even for the ternary system, it is still difficult to get an analytic representation of the binodal curve. However, in considering the three components without one of the homopolymers, generality is not lost, and a plait point of the system composed of A–B-type block copolymer, B polymer, and solvent will be derived in the following section.

**Phase Equilibria in the Ternary System; A–B-Type Block Copolymer, B Polymer, and Solvent.** First, let us consider a mixture of A–B-type block copolymer and B homopolymer in the absence of the solvent. The block copolymer has a molecular structure identical with that of the two homopolymer chains joined together, and the volume fraction of A block within the copolymer, $\psi_A$, can be given by

$$\psi_A = x_A/(x_A + x_B)$$

where $x_A$ and $x_B$ are degrees of polymerization of A and B block relating to the molar volume of chain segment, $x_c = (x_A + x_B)$ is the total degree of polymerization of the copolymer, and complete monodispersity of the degrees of polymerization is assumed.

According to the Flory–Huggins theory,[18] the entropy of mixing for the system composed of $n_c$ chains of the copolymer ($x_c$) and $n_h$ chains of B polymer ($x_{Bh}$), is given by

$$\Delta S_M = -k(n_c \ln v_c + n_h \ln v_h) \qquad (1)$$

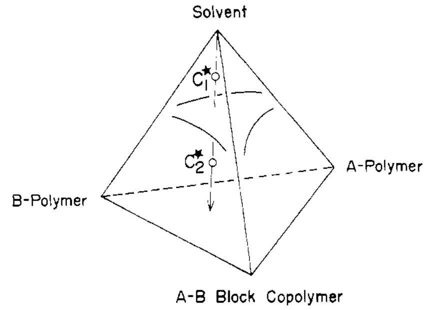

Figure 6. Schematic representation of the binodal surface in the phase diagram of a four-component system, where *C** is the critical micelle concentration of the system.

where $v_c$ and $v_h$ are the volume fractions defined by

$$v_c = x_c n_c/(x_c n_c + x_{Bh} n_h)$$

and

$$v_h = x_{Bh} n_h/(x_c n_c + x_{Bh} n_h)$$

respectively. On the other hand, the enthalpy of mixing may be obtained by means of van Laar's representation given by

$$\Delta H_M = kT\chi n_c(v_B - \psi_B) \qquad (2)$$

where $\psi_B$ is the volume fraction of B block within the copolymer, $v_B$ is the volume fraction of B segment within the system, which is defined by

$$v_B = (x_B n_c + (x_{Bh} n_h)/(x_c n_c + x_{Bh} n_h)$$

and $\chi$ is the copolymer–homopolymer interaction parameter defined by

$$\chi = z\Delta w_{AB} x_A/(kT)$$

where $z$ is the coordination number of lattice and $\Delta w_{AB}$ is the contact energy difference between the A and B segments.

So, the free energy of mixing can be given by

$$\Delta G_M = kT[n_c \ln v_c + n_h \ln v_h + \chi n_c(v_B - \psi_B)] \qquad (3)^{19, 20}$$

Differentiation of eq 3 gives the chemical potential of the homopolymer as

$$\mu_h - \mu_h^0 = RT\,[\ln v_h + v_c(1 - r) + \chi r \psi_A\, v_c^2] \qquad (4)$$

where $r = x_h/x_c$ and $R$ is a gas constant.

The critical condition for the phase separation between the copolymer and the homopolymer can be obtained by the familiar requirement that the first and second derivatives of eq 4 be zero. Solving such equations, the following relation may be obtained.

$$(\chi)_{crit} = (1 + 1/\sqrt{r})^2/(2\psi_A) \qquad (5)$$

Extending the above results to the ternary system composed of A–B-type block copolymer, B polymer, and solvent, by using the dilution approximation,[13b] the following relation may be obtained

$$(v_s)_{crit} = 1 - (1 + 1/\sqrt{r})^2/(2\chi\psi_A) \qquad (6)$$

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(16) E. Vanzo, *J. Polym. Sci., Part A-1*, 4, 1727 (1966).

(17) D. J. Meier, *ibid., Part C*, **26**, 81 (1969).

(18) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(19) The free energy of mixing given by eq 3 must be an approximation, when the intrachain interaction and the molecular shape of the block copolymer in a dilute solution, such as proposed by Inagaki and Miyamoto,[20] are taken into consideration.

(20) H. Inagaki and T. Miyamoto, *Macromol. Chem.*, **87**, 166 (1965).

where $v_s$ is the volume fraction of the solvent in the ternary system, given by

$$v_s = x_s n_s/(x_s n_s + x_c n_c + x_{Bh} n_h)$$

Then, total polymer concentration at the critical point, $C_c$, is given by

$$C_c = 1 - (v_s)_{crit} = (1 + 1/\sqrt{r})^2/(2\chi\psi_A) \qquad (7)$$

Equation 7 may predict the compatibility of the A–B-type block copolymer with the B polymer in a solution of common solvent as a function of the ratio of the degrees of polymerization, $r$, the composition of the block copolymer, $\psi_A$, and the copolymer–homopolymer interaction parameter, $\chi$.

Consequently, one may judge roughly whether the solubilization occurs or not, from the following condition.

$$2\chi\psi_A C^* \gtrless (1 + 1/\sqrt{r})^2 \qquad (8)$$

These results may be applicable for the system involving multiblock copolymers, such as ABA, BAB, ABAB or $(AB)_i$, as well as the graft copolymers, so far as the following condition is held.

$$\Delta H_M = z\Delta w_{AB} v_B \sum_i (x_A)_i \qquad (9)$$

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# Dynamic Properties of a Model Reinforced Elastomer. Styrene–Butadiene Reinforced with Polystyrene

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ABSTRACT: The dynamic storage and loss moduli of SBR 1503 reinforced with 400-Å polystyrene particles were measured at 110 cps over a 200° temperature range. The effect of the polystyrene filler on the rubber was to raise the storage modulus dramatically in the rubbery zone, but only slightly in the glassy region of viscoelastic response. As a result the transition zone appeared broadened and shifted toward higher temperature. Corresponding changes were observed in the loss maximum with a shift of 4° at the highest filler content (46%) investigated. The height of the loss maximum was nearly unaffected. The loss tangent of the filled and unfilled polymers showed no systematic shift with temperature and the dilatometric glass transition was raised only 2° at the highest filler content. All the essential features of the dynamic behavior could be described in terms of the properties of the component polymers by the phenomenological equivalent mechanical model treatment of Takayanagi. It is concluded that the effects of the polystyrene filler, which resemble those of other fillers as well, need not be caused by restriction of segmental motion in the rubber resulting from elastomer–filler interactions.

In an earlier paper it was shown that the free volume of a carbon black reinforced polymer in the rubbery region of viscoelastic response is only slightly affected by the presence of the filler.[1] It appears, therefore, that the adsorption of polymer segments on the filler surface cannot cause a major loss in segmental mobility in the bulk of the rubber. Nuclear magnetic resonance measurements have confirmed this conclusion.[2] On the other hand, dynamic mechanical measurements usually reveal much larger filler effects. These are a substantial broadening of the transition region, an increase in the loss tangent in the rubbery zone, and an apparent shift of the relaxation spectrum toward longer times or, in experiments at fixed frequency, toward higher temperatures.[3,4]

A filler-reinforced rubber may be regarded as a two-phase blend of materials of widely different viscoelastic properties. The physical properties of such a composite must depend on the properties of the components and on the morphology of the blend regardless of possible interactions between the phases. Various expressions have been developed for calculating properties of composites from those of the components and all predict the intuitively obvious fact that a high modulus material will stiffen a low modulus material proportionally more than it will stiffen a material of moderately high modulus. This is always observed when the properties of a filler-loaded rubber are studied over a temperature range which includes the glass transition and is illustrated schematically in Figure 1. Here the modulus might typically be the dynamic storage modulus (at fixed frequency) and the filler carbon black or an inorganic pigment, whose properties change little over the temperature range of the experiment. It is clear that, as the result of the larger relative contributions of the filler at higher temperatures, the entire modulus curve for the filled rubber appears shifted to the right. Obviously, any analysis which fails to take

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(4) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter XV.