# Theory of supermolecular structures in polydisperse block copolymers: 4. Cylindrical domains in binary mixtures of diblock copolymers and cylinder–lamellae transition

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*(Received 12 October 1990; accepted 17 December 1990)*

The theory of well defined superstructures formed in binary mixtures of diblock copolymers with different molecular weights and composition in a strong segregation limit has been developed. Three types of binary mixtures were considered: a mixture of two cylinder-forming block copolymers; a mixture of cylinder- and lamellae-forming block copolymers; and a mixture of two lamellae-forming block copolymers. The formation (conditions and the thermodynamic characteristics) of mixed lamellar and cylindrical superstructures and their thermodynamic stability were investigated. It was shown that in the case of non-isomorphous block copolymers the change in mixture composition leads to a first-order phase transition from one morphology of the superstructure to another, i.e. to real phase segregation (each phase remains microphase segregated). The theory was compared with experimental data. The possibility of the formation of cylindrical domains in the mixture of two lamellae-forming block copolymers was predicted.

**(Keywords: mean field theory; grafted chain layers; polymer mixtures; block copolymers)**

## INTRODUCTION

It has been shown in earlier papers[1,2] in this series that the thermodynamic advantage of a mixture of molecules of different length grafted onto a planar surface (under conditions of mutual overlapping) ensures the thermodynamic stability of a single lamellar structure formed by a binary mixture of lamellae-forming diblock copolymers with different block lengths. This structure, referred to as a mixed superstructure, is thermodynamically more advantageous than the two lamellar structures formed by the individual components (at least in a certain range of mixture composition). The effect of mixing in a planar layer of grafted chains and in the lamellar superstructure of the block copolymers is related to a decrease in the degree of stretching of long chains (blocks) on mixing with short chains grafted onto the same surface (in the case of a block copolymer onto a narrow interface).

In order to investigate block copolymer superstructures with other morphologies, we considered[3] the thermodynamics of a mixture in the layers of chains grafted onto internal and external cylinder surfaces. It was shown that the thermodynamic advantage of mixing chains of two lengths is obtained when the chains are grafted onto the external and internal cylinder surfaces (convex and concave cylindrical layers). However, for a convex layer this effect is relatively weak, and the gain in free energy upon mixing is much lower than in the case of a planar layer. In contrast, for the internal cylindrical layer this effect is much more pronounced than for a planar layer. Moreover, in contrast to the monotonic gain in free energy for a planar layer with increasing long-chain fraction, for the dry cylindrical layer densely filling the internal part of the cylinder, the composition dependence of the free energy of the layer is non-monotonic and passes through a minimum for a low fraction of long chains. Just as in the case of a planar layer, the thermodynamic advantage of mixing is determined by a decrease in the degree of stretching of long chains, whereas the additional effect in a concave cylindrical layer is due to a decrease in area per chain with increasing distance from the grafting surface.

The aim of this paper is to further develop the theory of well organized superstructures formed in binary mixtures of type $A_{N_A^i}B_{N_B^i}$ ($i = 1$ and $2$) diblock copolymers with different molecular weights, $N_A^i + N_B^i$, and composition far from the transition point of the system into the disordered state. Here a case will be considered in which, at least in a certain range of mixture composition, superstructures with cylindrical domains containing the minor component of block copolymers are formed. We will restrict ourselves to the case when only a lamellar superstructure can be a second mixed superstructure. Furthermore, since it follows from the theory of grafted cylindrical layers[3] that the strongest and the most interesting effects of mixing are observed for concave layers, only the case in which components are bidisperse with respect to one of the blocks, the block forming a cylindrical domain, will be considered.

Three types of binary mixtures will be considered: A—a mixture of two cylinder-forming block copolymers forming a single cylindrical domain; B—a mixture of cylinder- and lamellae-forming block copolymers. In this case the morphology of the superstructure depends on

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0032-3861/92/020343-09

mixture composition, and when it changes, a transition between morphologies occurs; and C—a mixture of two lamellae-forming block copolymers. As will be shown below, in this case the non-monotonic dependence of free energy on the composition of the binary chain mixture in a concave cylindrical layer may lead to the stability of the cylindrical morphology in the mixture (certain requirements should be met with respect to the composition of the entire mixture and of individual block copolymers).

## CHARACTERISTICS OF BLOCK COPOLYMER MIXTURES

A binary mixture of diblock copolymers $A_{N_A}B_{N_B^1}$ and $A_{N_A}B_{N_B^2}$ will be considered (bidisperse only with respect to block B forming cylindrical domains). Just as before, a symmetrical chain element is a unit of length $a$ (equal to chain thickness). Polymer stiffness which is assumed to be equal to both blocks is characterized by the parameter $p = A/a$ where $A$ is the Kuhn segment. The values of $N_A \gg 1$ and $N_B^2 > N_B^1 \gg 1$ are the number of units in the corresponding blocks and

$$\alpha = \frac{N_B^2 - N_B^1}{N_B^1} \geqslant 0 \qquad (1)$$

is the relative difference between the lengths of B blocks in the mixture components. The composition of these components is characterized by the values

$$f_1 = N_A/N_B^1 \qquad f_2 = N_A/N_B^2 = f_1/(1+\alpha) < f_1 \qquad (2)$$

Numerous experimental data[4] show that the composition of an individual diblock copolymer determines the morphology of the superstructure formed by this copolymer in a strong segregation limit. The values of $f$ relatively close to unity correspond to lamellar (L) morphology and the range of higher $f$ values corresponds to cylindrical (C) morphology with domains of the minor B component on a hexagonal lattice. Upon further increase in $f$, spherical (S) domains of the minor component on a cubic lattice are formed. (At $f < 1$ the A component becomes minor and, correspondingly, domain-forming.) Theoretical investigations have established[5–7] the boundaries of the transition between different morphologies: $f_C(L/C) = 2.54$, $f_S(C/S) = 7$. For superstructures with A domains, $f_C^{-1}$ and $f_S^{-1}$ correspond to the boundaries of L/C′ and C′/S′ transitions. Hence, for the three types of binary mixtures of block copolymers mentioned earlier, we have

$$\begin{array}{lll} \mathrm{A} & f_C < f_1, f_2 < f_S & \\ \mathrm{B} & f_C < f_1 < f_S, & f_C^{-1} < f_2 < f_C \qquad (3) \\ \mathrm{C} & f_C^{-1} < f_1, f_2 < f_C, & f_C - f_1 \ll 1 \end{array}$$

(for the inequality C, see below).

The mixture composition will be characterized by the numerical fraction $q$ of the molecules of component 2 in the system

$$q = \frac{n_2}{n_1 + n_2} \qquad (4)$$

where $n_i$ are the number of molecules in each component.

## FREE ENERGY OF THE MIXED SUPERSTRUCTURE

In order to solve the problem of the stability of a mixed superstructure, its free energy per molecule is written as

$$\Delta\Phi = \Delta F + q \ln q + (1-q)\ln(1-q) \qquad (5)$$

where the last two terms are the contributions of the entropy of mixing of the components, and $\Delta F$ is the free energy of the chain in the system without taking into account the entropy of mixing. All the energetic values are expressed in kT units.

In the case of a well defined superstructure (far from the point of microphase separation) it is possible, as before[2,7], to use the approximation of a narrow interphase layer. Then we have

$$\Delta F = \Delta F_S + \Delta F_A + \Delta F_B \qquad (6)$$

where $\Delta F_S$ is the surface free energy on the interface and $\Delta F_A$ and $\Delta F_B$ are the conformational free energies of A and B blocks treated as chains grafted onto an interface of a given geometry. For the case of a cylindrical interface between A and B microphases (*Figure 1*) we have

$$\Delta F_S = \frac{\Phi\sigma}{a^2} = \frac{\Phi 2\bar{N}_B a}{R} \qquad (7)$$

where $\Phi/a^2$ is the surface tension coefficient of the interface, $\sigma$ is the interface (grafting) area per block copolymer molecule and $\bar{N}_B$ is the averaged length of B blocks in the mixture.

$$\bar{N}_B = (1-q)N_B^1 + qN_B^2 = N_B^1(1+\alpha q) \qquad (8)$$

The last equality in equation (7) takes into account the fact that B blocks densely fill the interior of the cylindrical domain, so that its radius $R$ is related to $\sigma$ and $\bar{N}_B$ by the equation $R\sigma = 2\bar{N}_B a^3$.

The expressions for the conformational free energies of A blocks in the matrix and B blocks in the domains of the cylindrical mesophase may be taken from the theory of grafted polymer layers. For monodisperse A blocks which are equivalent to the layer of chains grafted onto the external surface of the cylinder of radius $R$ with grafting density $1/\sigma$, we have[3,4]

$$\Delta F_A = \frac{3}{8p}\frac{R^2}{a^2\bar{N}_B}\ln(1 + N_A/\bar{N}_B) \qquad (9)$$

As for the free energy of bidisperse domain-forming B blocks densely filling the interior of the cylindrical domain, this value has been considered in an earlier paper

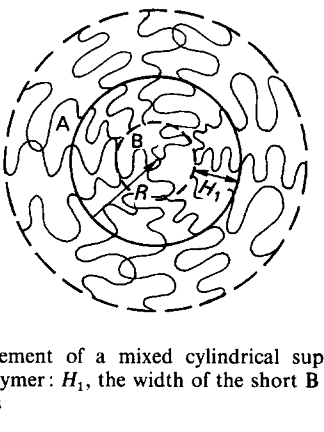

**Figure 1** The element of a mixed cylindrical superstructure of a diblock AB copolymer: $H_1$, the width of the short B chains sublayer; $R$, cylinder radius

in this series[3] and it has been shown [see equations (38) and (39) and Figure 8 in ref. 3] that

$$\Delta F_{\mathrm{B}} = \frac{\pi^2}{16p} \frac{R^2}{a^2 N_{\mathrm{B}}^1} G(\alpha, q) \tag{10}$$

where

$$\begin{aligned} G(\alpha, q) = {} & (1 + \alpha q)\{\sqrt{u^2 - l_1^2}[6(1 + \alpha)u^2 \\ & + 0.5 l_1^2 u(1 - 5\alpha - 10\alpha^2) - l_1^2(1 + \alpha)/2 \\ & - u^3(6 - \alpha - 5\alpha^2)] + [-0.5 l_1^4(1 + 5\alpha) \\ & + 0.5 l_1^2 u^2(-10 + 3\alpha + 15\alpha^2) \\ & - 5(1 + \alpha)u^2(u^2 - l_1^2) \\ & + u^4(6 - \alpha - 5\alpha^2)]\} - 3 l_1^2 \alpha q \end{aligned} \tag{11}$$

and $l_1 = H_1/R$ is the relative thickness of the short-block layer in the cylindrical domain related to $\alpha$ and $q$ [see equation (34) and Figure 5 in ref. 3] by the equation

$$\begin{aligned} \frac{q}{1 + \alpha q} = {} & \frac{\sqrt{1 - l_1^2(1 - \alpha^2)} - \alpha}{1 - \alpha^2} \\ & - l_1^2 \ln \frac{l_1(1 - \alpha)}{1 - \sqrt{1 - l_1^2(1 - \alpha^2)}} \end{aligned} \tag{12}$$

and

$$u = \frac{2(1 + \alpha q)}{1 - \alpha^2}[1 - \alpha\sqrt{1 - l_1^2(1 - \alpha^2)}] \tag{13}$$

[see equations (31) and (32) in ref. 3].

Using equations (7), (9) and (10) the summation of the three contributions to equation (6) for the cylindrical superstructure yields:

$$\begin{aligned} \Delta F = {} & \frac{2 N_{\mathrm{B}}^1 (1 + \alpha q) a \Phi}{R} + \frac{R^2}{a^2 N_{\mathrm{B}}^1 p (1 + \alpha q)} \\ & \times \left\{ \frac{3}{8} \ln[1 + N_{\mathrm{A}}/N_{\mathrm{B}}^1(1 + \alpha q)] \right. \\ & \left. + \frac{\pi^2}{16}(1 + \alpha q) G(\alpha, q) \right\} \end{aligned} \tag{14}$$

## EQUILIBRIUM PARAMETERS OF THE MIXED SUPERSTRUCTURE

It can be seen from equations (5) and (14) that $\Delta F$ is a function of the only one independent parameter of the superstructures: the radius of the cylindrical domain $R$. The entropy of mixing does not depend on structural parameters. Hence, for the determination of the equilibrium characteristics of the superstructure of cylindrical morphology, which is formed by a mixture of block copolymers with a fixed composition, it is sufficient to minimize $\Delta F$ with respect to $R$. [The problem of the equilibrium of the mixed superstructure with a given morphology requires special consideration (see below).] As a result of minimization, one obtains the values of the equilibrium radius $R_{\mathrm{C}}$ of the cylindrical domain consisting of B blocks and, hence, the areas $\sigma_{\mathrm{C}}$ of the interface per chain as well as free energy per chain $\Delta F_{\mathrm{C}}$. In reference 2 similar expressions have been obtained for the equilibrium parameters of the mixed lamellar superstructures [see equations (9) and (12) in ref. 2]. The results for superstructures with both morphologies may be written in the form of general expressions

$$R_x = i_x(3a/2)(1 + \alpha q)(N_{\mathrm{B}}^1)^{2/3}(A Q_x)^{-1} \tag{15}$$

$$\sigma_x = i_x \bar{N}_{\mathrm{B}} a^3/R_x = (2/3)a^2(N_{\mathrm{B}}^1)^{1/3} A Q_x \tag{16}$$

$$\Delta F_x = \Phi(N_{\mathrm{B}}^1)^{1/3} A Q_x \tag{17}$$

where $x = \mathrm{C}, \mathrm{L}$, $i_{\mathrm{L}} = 1$, $i_{\mathrm{C}} = 2$

$$A = (\pi^2/4\Phi p)^{1/3} \tag{18}$$

$$\begin{aligned} Q_{\mathrm{C}}(q) = 3\Bigg[ & \frac{1}{4}(1 + \alpha q)^2 G(\alpha, q) \\ & + \frac{3}{2\pi^2}(1 + \alpha q) \ln\left(1 + \frac{f_1}{1 + \alpha q}\right)\Bigg]^{1/3} \end{aligned} \tag{19}$$

$$Q_{\mathrm{L}}(q) = (3/2)(1 + f_1 + \alpha q^3)^{1/3} \tag{20}$$

Equations (19) and (20) for $Q_{\mathrm{L}}$ and $Q_{\mathrm{C}}$ are given for identical systems: a binary mixture of AB copolymers bidisperse only for block B.

The values of $R_x$ in equation (15) determine the layer width of bidisperse B blocks ($R_{\mathrm{C}}$ is the radius of the B cylinder and $R_{\mathrm{L}}$ is the half-width of the B lamellae). The transition to the case of monodisperse B blocks[5,7] is carried out at $q = 0$ or $q = 1$ or $\alpha = 0$.

The structure of cylindrical B domains or B lamellae is determined by that of the layers of grafted bidisperse chains (concave cylindrical or planar layers). It has been shown in references 1–3 that the ends of short and long chains in these layers are segregated. The ends of shorter $\mathrm{B}_{N^1}$ blocks are concentrated in a sublayer of thickness $H_1$ adjoining the interface [*Figure 1* and equation (11)]. The ends of longer blocks are located in the central part of a cylindrical B domain of radius $R_{\mathrm{C}} - H_1$ or a planar B domain with a half-width $R_{\mathrm{L}} - H_1$. It should be recollected that the planar B domain consists of two counter layers with no mutual penetrability. The free ends in the planar and concave cylindrical layers are distributed throughout the thickness of the corresponding sublayer, the distribution being more uniform in the case of the concave cylindrical layer[3].

Blocks A forming a solid matrix are monodisperse, so that their conformations are the same as in the case of a cylindrical superstructure formed by a monodisperse block copolymer. According to the results of references 3, 5 and 8, their ends are concentrated near the external boundary of the convex cylindrical layer of thickness $H - R_{\mathrm{C}}$ where

$$\frac{H}{R_{\mathrm{C}}} = \sqrt{1 + N_{\mathrm{A}}/\bar{N}_{\mathrm{B}}} = \sqrt{1 + f_1/(1 + \alpha q)} \tag{21}$$

It should be emphasized that equations (9) and (11) for the free energy of the blocks are written with the assumption that they are extended with respect to the Gaussian size. Correspondingly, equations (15)–(20) describe the equilibrium characteristics of single cylindrical or lamellar structures under the condition of stretching of all blocks with respect to the Gaussian size. It has been shown in reference 2 that for the case of lamellar structures this stretching induces certain restrictions in the range of mixture compositions in which equations (15)–(20) are applicable. For cylindrical structures, this problem will be discussed later.

## STABILITY OF MIXED SUPERSTRUCTURES

So far we have considered only the characteristics of mixed superstructures without investigating their thermodynamic stability. In order to determine the stability of a mixed structure, its free energy should be compared to that of an alternative state. It should be borne in mind that we are interested in the behaviour of block copolymers under the conditions of strong segregation, so it is necessary to investigate the thermodynamic stability only of the microsegregated states. Let us consider the various binary mixtures described by equation (3).

### *A: Mixture of cylinder-forming block copolymers*

If each component of a block copolymer mixture formed its own cylindrical structure, the dependence of the relative free energy $Q_0$ (per molecule) on the mixture composition would be described by a straight line:

$$\begin{aligned} Q_0 &= \frac{\Delta F_{\text{average}}}{\Phi(N_B^1)^{1/3}A} \\ &= \frac{1}{\Phi(N_B^1)^{1/3}A}[(1-q)\Delta F_C(q=0) + q\Delta F_C(q=1)] \\ &= [(1-q)Q_C(q=0) + qQ_C(q=1)] \qquad (22) \end{aligned}$$

It can be easily seen that in the case of a mixed cylindrical structure formed by both mixture components the value of $Q_C(q)$, with equations (17) and (19) determining the dependence of the conformational contribution of the free energy on mixture composition, is a concave function of $q$ (*Figure 2*). The contribution of the entropy of mixing to the total free energy $\Delta\Phi(q)$, equation (4), can only additionally increase the concavity of this dependence. Hence, a mixed cylindrical structure formed by cylinder-forming diblock copolymers is stable against phase separation of individual mixture components into cylindrical structures. Moreover, since the curve of the dependence $\Delta F = \Delta F(q)$ is concave over the entire range $0 \leqslant q \leqslant 1$, i.e. $d^2\Delta F/dq^2 > 0$, a mixed cylindrical structure with any composition is also stable with respect to phase separation into any two cylindrical structures with different compositions.

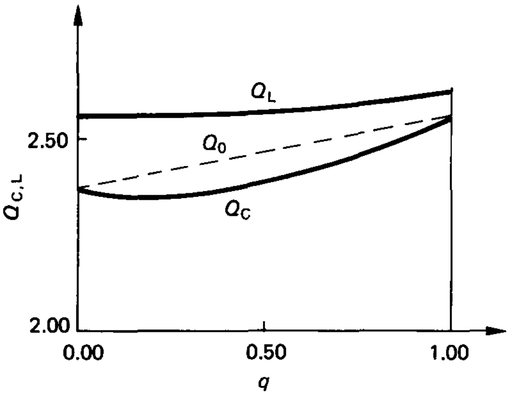

**Figure 2** Conformational contribution to a free energy of mixed cylindrical ($Q_C$) and lamellar ($Q_L$) superstructures *versus* composition $q$ of a mixture of two cylinder-forming block copolymers: $f_1 = 4$ and $f_2 = 3$

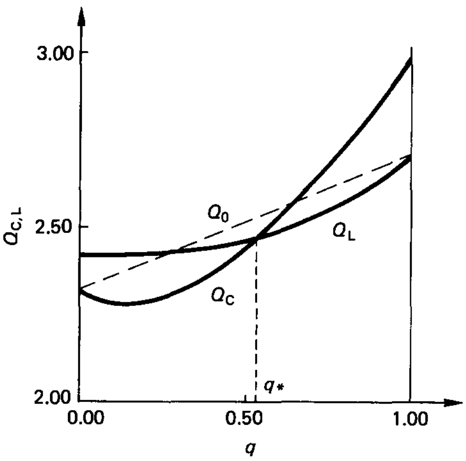

**Figure 3** Conformational contribution to a free energy of mixed cylindrical ($Q_C$) and lamellar ($Q_L$) superstructures *versus* composition $q$ of a mixture of cylinder- and lamellae-forming block copolymers: $f_1 = 3.2$ and $f_2 = 1.2$. The broken line represents the free energy $Q_0$ of the system separated into two individual structures

### *B: Mixture of cylinder and lamellae-forming block copolymers*

In this case the limiting structures at $q = 0$ and $q = 1$ are different. It is evident that the structures formed at a low content of one of the components, $q \ll 1$ or $1 - q \ll 1$, are also different and are determined by the predominant mixture component. Hence, as the mixture composition $q$ changes, a transition from one morphology of the structure to another morphology should occur in the system.

*Figure 3* shows the dependences of relative free energies of mixed superstructures $Q_C(q)$ and $Q_L(q)$ formed by both mixture components [without taking into account the contribution of the mixing entropy, see equations (5), (17), (19) and (20)] on the fraction $q$ of the lamellae-forming component. The broken straight line corresponds to the free energy of the system separated into two structures (lamellae and cylinders) formed by the individual components.

$$Q_0 = (1-q)Q_C(q=0) + qQ_L(q=1) \qquad (23)$$

It can be seen from *Figure 3* that the conformational free energy of the mixed superstructure is always lower than the average free energy of the individual superstructures. At low $q$ the lowest conformational free energy is exhibited for a mixed cylindrical superstructure containing not only a host (cylinder-forming component) but also a guest (lamellae-forming component) [curve $Q_C(q)$ lies lower than curve $Q_L(q)$ and broken line $Q_0$]. In contrast, at high $q$ the lowest conformational free energy corresponds to a mixed lamellar structure including a guest, a cylinder-forming component [curve $Q_L(q)$ lies lower than curve $Q_C(q)$ and broken line $Q_0$].

Consequently, *Figure 3* shows that in this system mixed superstructures should be formed containing both components: a host determining the morphologies of the superstructure and a guest inserted into the superstructure of the host. When the mixture composition changes, the transition from one morphology to the other takes place, i.e. the host and guest exchange roles. The semiquantitative evaluation of the position of the middle of the transition (mixture composition $q_*$) may be obtained from the condition $Q_{\mathrm{L}} = Q_{\mathrm{C}}$, which gives the equation for the determination of $q_*$ as a function of $f_1$ and $f_2 = f_1/(1 + \alpha)$.

$$1 + \alpha q_*^3 + f_1 = 2(1 + \alpha q_*)\left[(1 + \alpha q_*)G(\alpha, q_*) + \frac{6}{\pi^2}\ln\left(1 + \frac{f_1}{1 + \alpha q_*}\right)\right] \tag{24}$$

The value of $q_*$ is a function of the composition of the individual block copolymers $f_1$ and $f_2 = f_1/(1 + \alpha)$. The dependence $q_* = q_*(f_2)$ at a fixed $f_1 > f_{\mathrm{C}}$ value is shown in *Figure 4* (curves A and B). At $f_2 = f_1/(1 + \alpha) > f_{\mathrm{C}}$ when both components are cylinder-forming, equation (24) has no solutions. A single cylindrical structure is formed in the system at all $q$ values (case A). With increasing $\alpha$ and the transition into the range $f_2 < f_{\mathrm{C}}$, a solution $q_*$ of equation (24) appears and is the increasing function of $f_1$ and $f_2$. [Curves C–E in *Figure 4* at $f_1 < f_{\mathrm{C}}$ will be considered below (case C).]

*Transition between morphologies.* So far we have considered only conformational contributions to the free energy of a mixed superstructure without taking into account mixing entropy, equation (5). This did not affect the conclusions of the stability of the mixed structure because mixing entropy can only increase the advantages of this structure. However, it is necessary to take into account the entropy contribution to obtain a complete picture of the intermorphology transition. This transition is a first-order phase transition (the dependence of the conformational contribution to free energy has a break at point $q_*$, *Figure 3*), and it is possible to expect phase coexistence in the region of this transition.

In order to determine the region of the coexistence of cylindrical and lamellar phases, the conditions of the equality of chemical potentials $\mu_i$ $(i = 1, 2)$ of each component of both phases are written as

$$\begin{aligned} \mu_1^{\mathrm{C}}(q_{\mathrm{C}}) &= \mu_1^{\mathrm{L}}(q_{\mathrm{L}}) \\ \mu_2^{\mathrm{C}}(q_{\mathrm{C}}) &= \mu_2^{\mathrm{L}}(q_{\mathrm{L}}) \end{aligned} \tag{25}$$

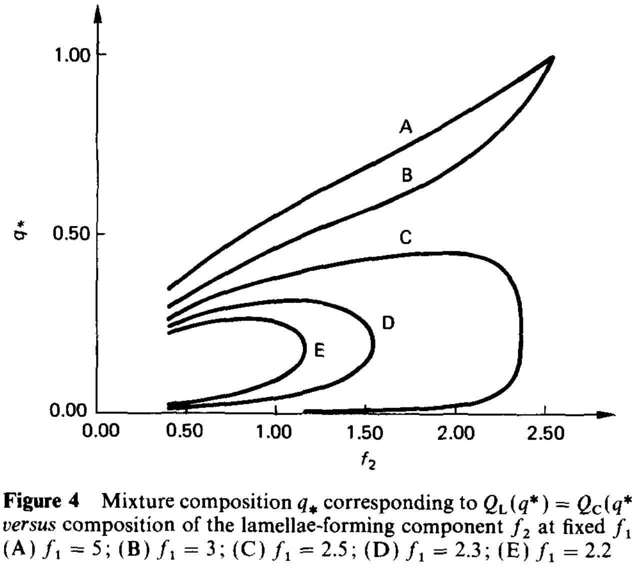

**Figure 4** Mixture composition $q_*$ corresponding to $Q_{\mathrm{L}}(q^*) = Q_{\mathrm{C}}(q^*)$ *versus* composition of the lamellae-forming component $f_2$ at fixed $f_1$: (A) $f_1 = 5$; (B) $f_1 = 3$; (C) $f_1 = 2.5$; (D) $f_1 = 2.3$; (E) $f_1 = 2.2$

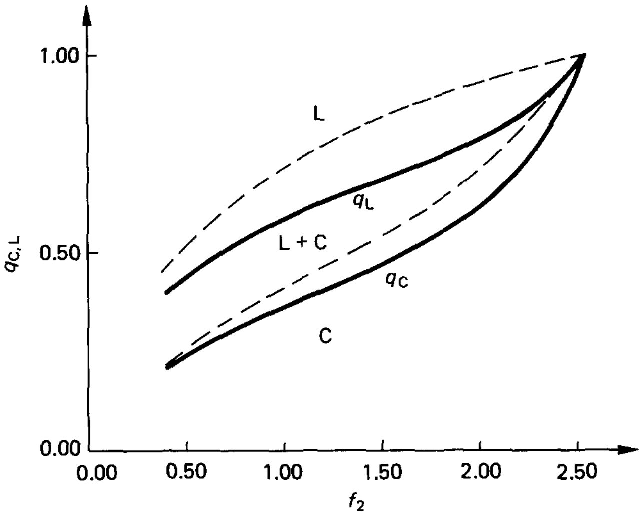

**Figure 5** Boundaries $q_{\mathrm{C}}$ and $q_{\mathrm{L}}$ of the two-phase region *versus* composition of the lamellae-forming component $f_2$ at fixed $f_1$ and $N_{\mathrm{B}}^1 = 100$: (———) $f_1 = 3$; (– – –) $f_1 = 5$

Here, as follow from equations (4) and (5), we have

$$\begin{aligned} \mu_1^x &= \left(\frac{\delta\Delta\Phi_x}{\delta n_1}\right)_{n_2=\mathrm{const}} = \Delta F_x - q\frac{\delta\Delta F_x}{\delta q} + \ln(1 - q) \\ \mu_2^x &= \left(\frac{\delta\Delta\Phi_x}{\delta n_2}\right)_{n_1=\mathrm{const}} = \Delta F_x + (1 - q)\frac{\delta\Delta F_x}{\delta q} + \ln q \end{aligned} \tag{26}$$

where $\Delta F_x$ at $x = \mathrm{C}$, L is determined by equations (17)–(20).

The solution of equation (25) makes it possible to obtain the values of mixture content $q_{\mathrm{C}}$ and $q_{\mathrm{L}} > q_{\mathrm{C}}$ corresponding to a binodal (boundaries of the two-phase region, *Figure 5*). At $q < q_{\mathrm{C}}$ a single cylindrical mesophase is formed. Its domains are formed by the blocks of both components mixed on the molecular level, equations (15)–(19). In this composition range, the increase in $q$ does not change the type of the superlattice and leads only to a change in the size of its elements, as in case A when the content $q$ of the more symmetric of the cylinder-forming components increases. At $q_{\mathrm{C}} \leqslant q \leqslant q_{\mathrm{L}}$ the system forms two phases: a cylindrical phase containing the fraction $q_{\mathrm{C}}$ of the lamellae-forming component (a guest) and a lamellar phase containing the fraction $q_{\mathrm{L}}$ of this component (which is a host in this case). The change in mixture composition $q$ in this range leads only to a change in the content of cylindrical and lamellar superstructures, their compositions remaining invariable. With increasing $q$ the fraction of the lamellar superstructure increases and that of the cylindrical superstructure decreases until it completely disappears at $q = q_{\mathrm{L}}$. At $q > q_{\mathrm{L}}$ the system again consists of one phase and a single lamellar structure is formed, equations (15)–(19). The increase in $q$ in this composition range leads to an increase in the thickness of B lamellae and specific surface $\sigma$ and a decrease in the thickness of A lamellae with retention of the morphology of the superlattice. The characteristics of mixed lamellar superstructures have been described previously[2].

The position of the binodals $q_{\mathrm{C}}$ and $q_{\mathrm{L}}$ which was determined by the numerical solution of equation (26) depends on a number of parameters: not only on the parameters of the individual block copolymers $f_1$ and

$f_2 = f_1/(1+\alpha)$ on which $q_*$ depended (*Figure 4*) but also on the molecular weight $N_B^1$ [used as the basis, see equations (1) and (2)], the surface tension coefficient $\Phi$ on the interface and the stiffness parameter $p$ [equations (5), (17)–(20)]. It is clear from these equations that the last three parameters appear in the form of a single combination $\Phi^{2/3}(N_B^1/p)^{1/3}$. With the increase in this combination the relative contribution of conformational free energy to the total free energy increases and that of mixing entropy decreases.

The positions of the boundaries, $q_C$ and $q_L$, of the two-phase region (*Figure 5*) were calculated for the values $\Phi \cong 0.53$ and $p \cong 1$ for the polystyrene–polyisoprene (PS–PI) block copolymer[7,10] and $N_B^1 = 100$ (where $N_A$ and $N_B$ are the numbers of the chain segments). With increasing $N_B^1$ (and a proportional increase in the molecular weights of other elements) and with increasing $(\Phi^2/p)$, the boundaries of the two-phase region become wider but this effect is slight (*Figure 6*).

As for the dependence of the boundaries $q_C$ and $q_L$ on the compositions $f_1$ and $f_2$ of individual block copolymers, it can be seen from *Figure 5* that at a fixed composition ($f_2$ = constant) of the lamellae-forming component the increase in the asymmetry $f_1$ of the cylinder-forming component leads to a displacement of the two-phase region towards larger $q$ and to its slight broadening. The increase in $f_2$ at a fixed $f_1$ leads to a decrease in the width of the two-phase region and to its displacement to larger $q$. At $f_2 \geqslant f_C$ when both components become cylinder-forming, the system exhibits a cylindrical superstructure over the entire composition range (case A).

### *C: Mixture of lamellae-forming components with the composition of one of the components being* $f_1 \cong f_C$

It can be seen from *Figure 4* (curves C–E) that at certain values of $f_1$ and $f_2$ equation (24) has two roots, i.e. there are two points of intersection of curves $Q_C(q)$ and $Q_L(q)$; these will be called $q^*$ and $q'^*$ ($q'^* < q^*$). An example of this behaviour is shown in *Figure 7*. Since $Q_L(q)$ is a monotonically increasing function of $q$ and $Q_C(q)$ passes through a minimum at low $q$, it can be easily seen that the situation can occur when both components are lamellae-forming. Moreover, the composition $f_1$ of a symmetric component is close to the boundary $f_C = 2.54$ of the transition to the cylindrical morphology [the difference between $Q_L(q=0)$ and $Q_C(q=0)$ is not great].

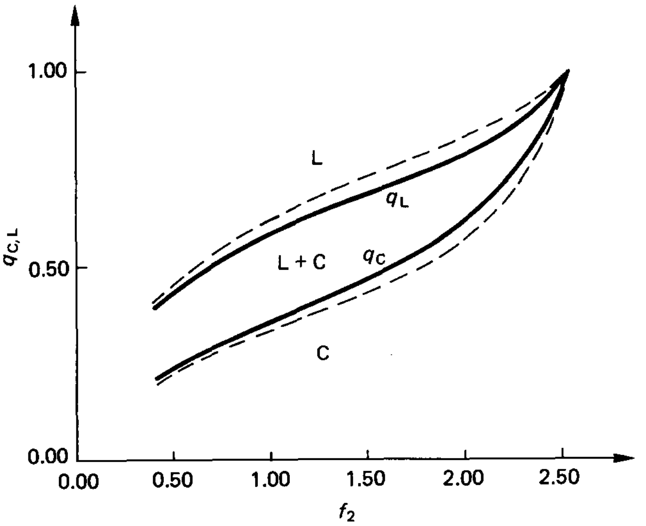

**Figure 6** Boundaries $q_C$ and $q_L$ of the two-phase region *versus* composition of the lamellae-forming component $f_2$ at fixed $f_1 = 3$: (———) $N_B^1 = 100$; (– – –) $N_B^1 = 1000$

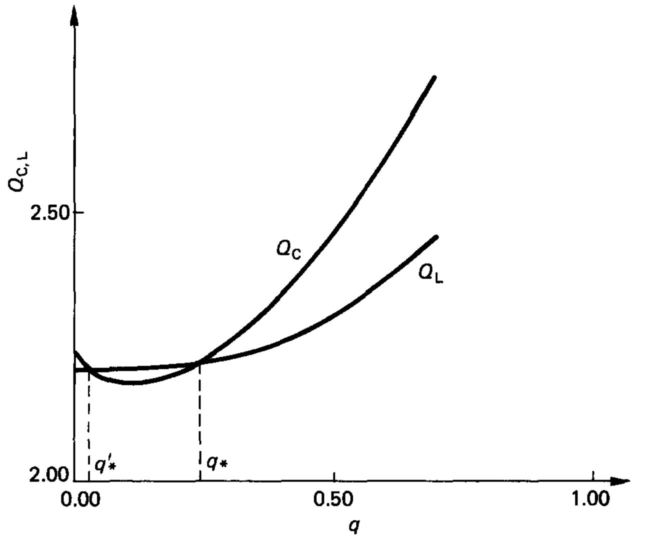

**Figure 7** Conformational contribution to a free energy of mixed cylindrical ($Q_C$) and lamellar ($Q_L$) superstructures *versus* composition of a mixture of two lamellae-forming block copolymers: $f_1 = 2.2$ and $f_2 = 0.5$

The intersections of $Q_L(q)$ and $Q_C(q)$ indicate that their sequence changes with $q$ and, hence, the morphology of the system also changes. Consequently, the change in mixture composition $q$ of two lamellae-forming block copolymers should lead to two consecutive phase transitions. At low $q$ the system forms a lamellar superstructure. Near $q'^*$ the transition to a cylindrical structure (which is in equilibrium in a certain composition range) takes place. On a further increase in $q$ near $q^*$ phase transition occurs again but this time from the cylindrical to the lamellar structure. It should be noted that in our consideration $f_2 < f_1$, i.e. component 2 is more symmetric. Hence, the transition C–L near $q^*$ caused by an increase in the content of the more symmetric component (and, hence, exhibiting a higher lamellae-forming capacity) may be called 'normal'. The transition near $q'^* < q^*$, when an increase in the content of the more symmetric component leads to the rearrangement of the morphology L–C, will be called 'anomalous'.

Both transitions with a change in morphology are first-order phase transitions. Their complete description provides the solution of equation (25). The results shown in *Figure 8* represent the binodal limiting of the two-phase regions. It is clear that with a decrease in $f_C - f_1$ the range of compositions corresponding to the lamellar phase with low $q$ (existing up to the anomalous L–C transition) becomes more narrow. For the lower boundary $q'_L$ of the two-phase region of this transition we have $q'_L \to 0$. At $f_1 > f_C$ this region is absent and the anomalous transition disappears. At the same time a decrease in $f_C - f_1$ leads to an increase in the width of the range of compositions corresponding to the existence of the cylindrical phase (*Figure 8*). At $f_1 > f_C$ it is stable in the entire range up to the normal transition C–L (case B).

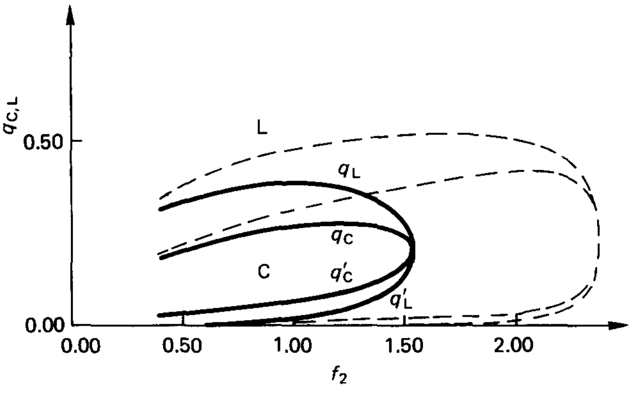

**Figure 8** Boundaries $q'_L$ and $q'_C$; $q_C$ and $q_L$ of the two-phase regions *versus* composition of the lamellae-forming component $f_2$ at fixed $f_1$ and $N_B^1 = 100$: (——) $f_1 = 2.3$; (– – –) $f_1 = 2.5$

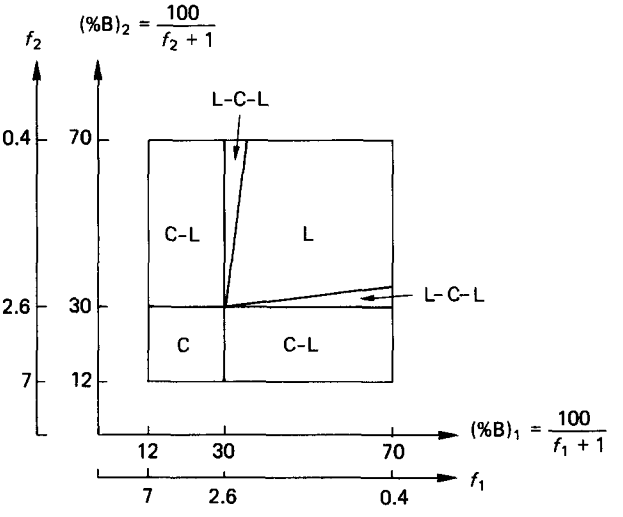

**Figure 9** Diagram of the morphology of block copolymers of compositions $f_1$ and $f_2$

## MORPHOLOGY AND CHARACTERISTICS OF A BLOCK COPOLYMER MIXTURE

*Figure 9* shows a diagram of the morphology of block copolymers bidisperse for the B block and being lamellae- and cylinder-forming $f_C^{-1} < f_2$, $f_1 < f_S$ (with block B inside the cylindrical domain). The diagram shows four types of region corresponding to different behaviour in the system. Regions L and C correspond to mixtures of isomorphous block copolymers (both of them are either lamellae- or cylinder-forming). They form a single structure with the same morphology as the components over the entire range of mixture compositions. At the values of $f_1$ and $f_2$ corresponding to these regions equation (24) has no solution [dependences $Q_L(q)$ and $Q_C(q)$ do not intersect]. These systems have been considered elsewhere[2] and in this paper (case A).

Region C–L in *Figure 9* corresponds to a mixture of lamellae- and cylinder-forming block copolymers (case B). In this region equation (24) has one root $q^*$ (*Figure 4*). An increase in the fraction $q$ of the lamellae-forming (more symmetric) component leads to the transition C–L (*Figure 5*).

A narrow region L–C–L between regions L and C–L in *Figure 9* corresponds to the existence of two roots in equation (24) (*Figure 4*). In this region a mixture of two isomorphous lamellae-forming components undergoes two consecutive phase transitions: anomalous L–C and normal C–L, when the fraction $q$ of the more symmetric component changes (*Figure 8*, case C).

The behaviour of the characteristics of the superstructure upon the change in mixture composition will now be considered, equations (15)–(19). When the content $q$ of the more symmetric (and longer) component increases up to the phase transition range, a single superstructure containing a mixture of both components is formed. With increasing $q$ in this superstructure, the value of $R_x$ (half-width of the B lamellae in the lamellar superstructure or the radius of the B domain in the cylindrical structure) increases, mainly because of an increase in the mean size $\bar{N}_B$ of the B blocks, equation (8). In the case of a mixture of block copolymers, this effect is stronger than for individual block copolymers[7]. The value of $R_x$ for the mixture always exceeds that of an individual block copolymer for which $N_B = \bar{N}_B$. Moreover, this difference is greater for the cylindrical morphology than for the lamellar morphology.

The behaviour of the system changes when it approaches the phase transition range. Let us consider the normal C–L transition with the boundaries of the two-phase region $q_L$ and $q_C > q_L$. Two superstructures with a constant composition coexist over the entire range $q_L \leqslant q \leqslant q_C$: a lamellar superstructure with composition $q_L$ and a cylindrical superstructure with composition $q_C$. The increase in $q$ in this range leads only to the redistribution of the content of these structures. Equation (15) makes it possible to evaluate the ratio between the characteristic dimensions of the B elements of structures $R_L$ and $R_C$. It can be seen from this equation that at the point $q^*$ where $Q_L(q^*) = Q_C(q^*)$ we have

$$R_L(q^*) = 1/2R_C(q^*) \qquad (27)$$

However, the compositions of the coexisting phases do not coincide $q_C < q^* < q_L$. Hence, the difference between the sizes should be smaller

$$R_C(q_C)/R_L(q_L) < 2 \qquad (28a)$$

For an anomalous L–C transition condition (27) should also be met. However, in this case the lower boundary $q'_L$ of the two-phase region limits the lamellar structure, and the upper boundary limits the cylindrical structure: $q'_L < q'^* < q'_C$. Hence, in this case the absence of coincidence between the compositions of the coexisting phases leads to an increase in the difference between the sizes

$$R_C(q'_C)/R_L(q'_L) > 2 \qquad (28b)$$

Schematic dependences $R_x(q)$ are shown in *Figure 10*.

Equations (15)–(20) also make it possible to analyse the behaviour of other characteristics. The area $\sigma_x$ per chain increases monotonically with increasing $q$ in the range of a one-phase region of the lamellar structure. In this case the size $H$ of the A sublamellae decreases. For a cylindrical structure the dependence $\sigma_C(q)$ coinciding with $\Delta F_C(q)$ is non-monotonic and passes through a minimum. As for the behaviour of $\sigma_x$ upon transition, at point $q^*$ (and also $q'^*$) we have $\sigma_L(q^*) = \sigma_C(q^*)$. Since phase compositions do not coincide, the values of $\sigma_x$ in the coexisting structures also do not coincide. In this case both for the normal C–L transition and for the anomalous L–C transition we have $\sigma_C(q_C) < \sigma_L(q_L)$.

*Figure 11* shows the average mixture composition

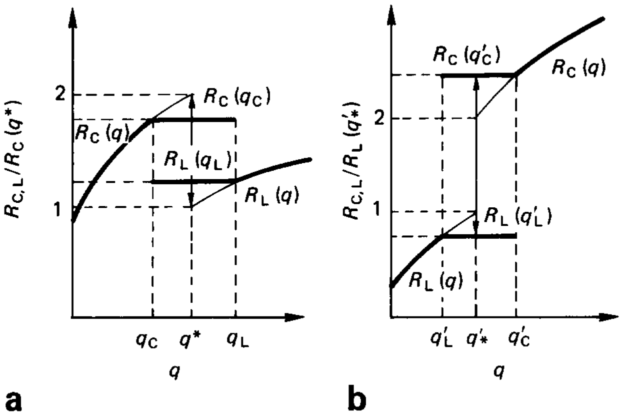

**Figure 10** Schematic dependence of the size of the superstructure elements $R_C$ and $R_L$ on composition of the block copolymer mixture for the transitions C–L (a) and L–C (b)

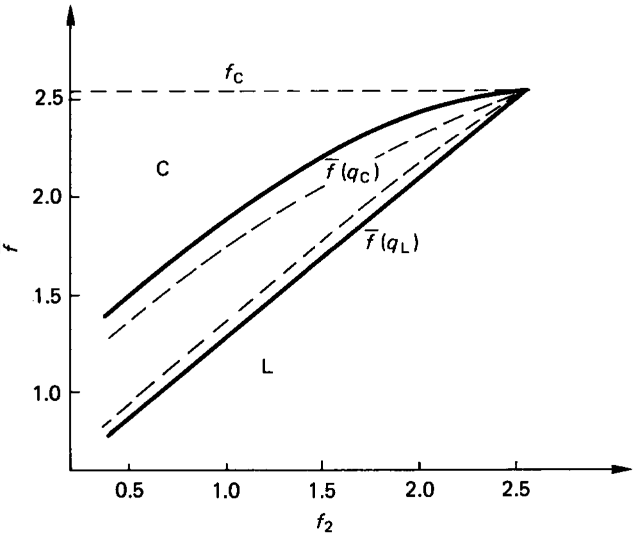

**Figure 11** Average mixture composition $\bar{f}(q_C)$, $\bar{f}(q_L)$ on the binodals *versus* composition of the lamellae-forming block copolymer $f_2$ at fixed $f_1$: (——) $f_1 = 5$; (---) $f_1 = 3$; straight line corresponds to $f_C = 2.54$

$\bar{f} = (1 - q)f_1 + qf_2$ corresponding to the boundaries of the two-phase region as a function of the composition of the lamellae-forming block copolymer $f_2$ at fixed $f_1$. It is clear that the values $\bar{f}(q_L)$, $\bar{f}(q_C)$ greatly differ from the value of $f_C = 2.54$ corresponding to the transition L–C in the individual block copolymers. The two-phase region lies in the range of the lamellar structure, $\bar{f}(q_L)$, $\bar{f}(q_C) < f_C$. It follows from *Figure 11* that the approximation of the monodisperse chain layer with an average composition $\bar{f}$ does not correspond to the real state of the system.

It should be noted that, generally speaking, *Figure 9* may be incomplete even for the range of values of $f_1$ and $f_2$ considered here. By analogy with the behaviour of the system in the region L–C–L, it may be expected that in a mixture of two cylinder-forming block copolymers in which the composition of one of the block copolymers is close to $f_S$, i.e. to that of the transition to spherical morphology, the region C–S–C can exist. We hope to further discuss this problem in future work.

## CHAIN STRETCHING IN SUPERSTRUCTURES

As has already been emphasized, the theory of cylindrical and lamellar mesophases formed by a binary mixture of diblock copolymers developed here and previously[2] assumes the stretching of blocks of both components with respect to the Gaussian size. This requirement imposes certain restrictions on both the molecular weight of the blocks and on the mixture composition $q$. This problem has been discussed in detail in reference 2 taking as an example a lamellar mesophase formed by a binary mixture of block copolymers with the same compositions but different molecular weights. In particular, it was shown that the main restricting factor is the condition of stretching of longer blocks. When this condition is not met, the problem of the stability of a single structure remains unsolved. If the condition of stretching of shorter blocks is not fulfilled, this is not so important and leads only to an error in the evaluation of the geometric parameters of the structure being formed without affecting the conclusion of thermodynamic preference of the resulting supermolecular structure.

In the case considered here, a cylindrical structure formed by block copolymers bidisperse for the domain-forming block B and monodisperse for the matrix block A, the requirement of block stretching in the elements of the mesophase reduces to three inequalities:

$$\begin{aligned} H_1 &> a\sqrt{pN_B^1} \\ R &> a\sqrt{pN_B^2} \qquad (29) \\ H - R_C &> a\sqrt{pN_A} \end{aligned}$$

The first two inequalities ensure the stretching of short and long blocks in the cylindrical domain, and the third ensures the stretching of matrix blocks with respect to the Gaussian size. Just as in the case of the lamellae-forming mesophase, when the conditions of short-block stretching are not met, equations (15)–(19) give slightly excessive values for the specific surface $\sigma/a^2$, whereas the values of $R_C$ and $H$ are underestimated. In this case the conclusion of the thermodynamic preference of the formation of a single mixed structure is retained.

## COMPARISON WITH EXPERIMENTAL DATA

The experimental investigations of the supermolecular structure in a binary mixture of narrow-disperse cylinder- and lamellae-forming block copolymers with different molecular weights and composition have been carried out[9] by small-angle X-ray scattering. A change in the content $q$ of one of the components of the mixture always led to a change in the morphology of the supermolecular structure. This was indicated by a change of the positions of the Bragg reflections characterizing the type of structure. In the range of mixture composition close to the transition value, a two-phase region was observed in some systems with the coexistence of two structures with different morphologies: a cylindrical and a lamellar superstructure. Experimentally two sets of Bragg reflections corresponding to two different types of structures were fixed in this range of mixture compositions.

In all the systems investigated in reference 9, one of the components was a cylinder-forming three-block

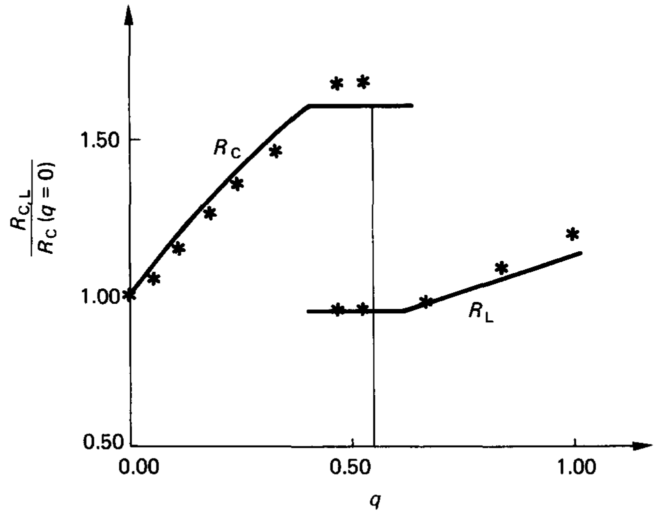

**Figure 12** Experimental data[9] for the dependence of relative domain width $R/R_C$ ($q = 0$) on the composition of the block copolymer mixture and theoretical curves for $f_1 = 3.18$ and $\alpha = 1.6$. The experimental points are calculated from equation (30)

symmetric PS–PI–PS copolymer with a molecular weight of $10.5 \times 10^4$ and the weight fraction of the domain-forming block PS $\cong 26\%$. The second component was a two- or three-block lamellae-forming PS and PI copolymer. Let us compare the experimental results in reference 9 with the theoretical predictions of the present work by choosing for comparison a mixture of SIS–2C–SI–5 copolymers[9] the parameters of which correspond to the conditions of the present work: the monodispersity of both components for block A (PI block). If a molecule of a three-block PS–PI–PS copolymer with molecular weight $M = (2M_B + M_A)$ is regarded as two molecules of a two-block copolymer with a molecular weight of $M/2$, we obtain for the equivalent two-block copolymer $M_{PS} = 13\,600$, $M_{PI} = 38\,900$, $f_1 = (M_{PS}/M_{PI})(v_S/v_I) \cong 3.18$. According to reference 9, the molecular weights of the blocks of the second component SI–5 are $M_{PS} = 35\,300$ and $M_{PI} = 36\,700$, so that the matrix blocks of PI are approximately identical for both components and $\alpha = (35\,300 - 13\,600)/13\,600 \cong 1.60$.

The values of the Bragg spacings $d$ reported in reference 9 are used for the calculation of the radius $R_C$ of the cylindrical domain and the half-width $R_L$ of lamellar layers formed by PS blocks:

$$R_L = \frac{d}{2}\frac{1}{1 + f_1/(1 + \alpha q)}$$
$$R_C = d\sqrt{\frac{2}{\pi\sqrt{3}(1 + f_1)/(1 + \alpha q)}} \qquad (30)$$

where $q$ is the numerical fraction of the lamellae-forming component. *Figure 12* shows the theoretical dependence of relative dimensions on $qR_C(q)/R_C(q = 0)$ and $R_L(q)/R_C(q = 0)$ calculated from equations (15) and (19) for $f_1 = 3.18$ and $\alpha = 1.6$. The boundaries of the two-phase region $q_C \cong 0.433$ and $q_L \cong 0.642$ were calculated from equation (25) at $N_B^1 = 40$ and $\Phi = 0.53$. It should be noted that because the dependence of $q_C$ and $q_L$ on $N_B^1$ is slight, the arbitrary character of the calculation of the number of units $N_B^1$ in the domain-forming block (due to the simplified model for a block copolymer chain as a chain with a constant thickness $a$) hardly affects the position of the boundaries $q_L$ and $q_C$. Thus, at $N_B^1 = 50$ we have $q_L \cong 0.646$ and $q_C \cong 0.429$. It can be seen from *Figure 12* that the theory developed in this paper describes with good precision the behaviour of a real system[9]: the position and the width of the region of the two-phase transition and the dependence of the domain size on mixture composition in the range of each one-phase region.

Unfortunately, there are no systematic investigations of binary mixtures of block copolymers under conditions of microphase separation. Consequently, it is not possible to compare the experimental data with some other predictions from the results of the present work: in particular, the possibility of the coexistence of a cylindrical structure in a mixture of lamellae-forming block copolymers in a narrow composition range. It is desirable to search for these non-trivial states of the mixture by using high molecular weight samples because an increase in molecular weight leads to a broadening in the stability range of the mixed states of the system (lamellae).

## ACKNOWLEDGEMENT

EBZ would like to acknowledge the financial support of the A.v.H. Foundation and the hospitality of the Max Plank Institüt für Polymerforschung in Mainz, Germany.

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