Theory of supermolecular structures in polydisperse block copolymers: 5. New double cylindrical structure in binary mixture of cylinder-forming diblock copolymers

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Analytical self-consistent field theory of superstructure formation in a binary mixture of cylinder-forming diblock copolymers in the strong segregation limit is developed. It is shown that for the case when both components of the mixture are 'quasi-isomorphous', i.e. when the domain-forming blocks of the components are different, several types of supermolecular structure are possible depending on the composition of the mixture. The possible types of structure are: mixed cylindrical structure (C), mixed lamellar structure (L), two cylindrical structures (C + C′) formed by individual components of the mixture, and, finally, a new double cylinder structure (CC′), formed by cylindrical domains of one component coated by cylindrical layers of another component. Stability ranges of these structures are investigated for different compositions of block copolymers and mixture content.

(Keywords: supermolecular structures; strong segregation limit; binary mixture; block copolymers; mixed superstructures; double cylinder structure; cylinder-forming block copolymers)

INTRODUCTION

It is well known that under the conditions of the strong segregation limit three conventional types of supercrystalline structures are formed in diblock copolymer systems. They are: planar lamellar structure (L) and cylindrical (C) or spherical (S) domains of the minor component regularly arranged in a matrix of the major component. Recently a new non-conventional (bitetrahedral) superstructure was observed experimentally, initially in melts of block copolymer stars and later in melts of linear block copolymers[1–3]. Theoretical interpretation of this new structure[4,5] followed the experimental observations.

The transition from narrow-dispersed block copolymers to mixtures of block copolymers with the same chemical structure but different molecular weights and compositions enlarges the variety of possibilities of superstructure formation in such systems. In previous papers of this series[6–9] we considered binary mixtures of lamellar (L)- and cylinder (C)-forming block copolymers and showed the possibility of formation of the so-called mixed superstructures comprising molecules of both components of the mixture. Such structures were also experimentally observed[10,11]. The morphologies of these mixed structures, however, were of conventional types (L or C).

In the present paper we make an attempt to predict theoretically the possibility of the formation of a new non-canonical superstructure named by us a 'double cylinder' structure. It will be shown that the formation of such a structure can be thermodynamically more advantageous than that of conventional superstructures when the binary mixture contains two C-forming block copolymers but their domain-forming blocks are different. Note that in our previous paper[9] we considered the mixture of C-forming components with similar domain-forming blocks. Thus, the results of this paper supplement the theoretical results of previous papers of this series and extend the theory of superstructure formation for the new range of compositions of mixture components.

CHARACTERISTICS OF A BLOCK COPOLYMER MIXTURE

Let us, as before[9], consider a binary mixture of block copolymers differing from each other only by the length of block B, i.e. $A_{N_A}B_{N_{B^1}} + A_{N_A}B_{N_{B^2}}$ (*Figure 1*). Here N_A, N_{B^1}, $N_{B^2} \gg 1$ are the numbers of units in the blocks. As before, a chain of length a is chosen as a unit and both blocks are assumed to be of the same thickness and thermodynamic stiffness. Let the compositions of both components be characterized by

$$f_1 = N_A/N_{B^1}; \qquad f_2 = N_A/N_{B^2} \qquad (1)$$

The value of f determines the morphology of the superstructure formed by the individual components of

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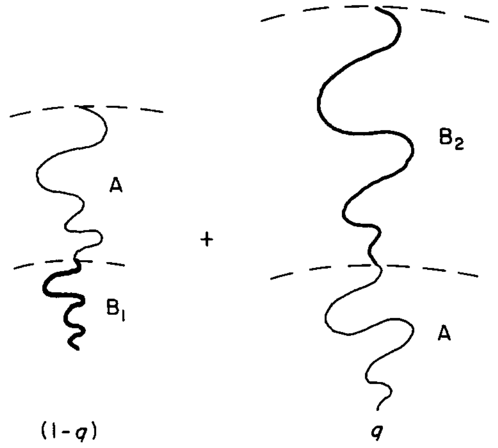

Figure 1 Mixture of C-forming diblock copolymers AB_1 and AB_2 (q is the fraction of diblock copolymer AB_2)

the mixture under the conditions of the strong segregation limit. For L, C and C′ superstructures one has

$$\text{L} \quad f \in [f_{C'}, f_C] \tag{2a}$$

$$\text{C} \quad f \in [f_C, f_S] \tag{2b}$$

$$\text{C}' \quad f \in [f_{S'}, f_{C'}] \tag{2c}$$

where C and C′ denote cylindrical superstructures with domain-forming block B and A, respectively, and f_C, $f_{C'} = f_C^{-1}$, f_S, $f_{S'} = f_S^{-1}$ are the boundaries between the L/C, L/C′, C/S and C′/S′ morphology ranges, respectively. According to references 12 and 13, $f_C \sim 2.6$, and $f_S \sim 7.0$. It should be noted that according to experimental observations[1–3] there is also a narrow interval of f values between the L and C stability ranges for which the bitetrahedral superstructure is the most stable morphology. Unfortunately, there are no theoretical estimations for its stability range for the case of linear block copolymers which is why we did not include it in equation (2).

Figure 2 shows the morphology diagram of block copolymer mixtures obtained in previous papers of this series (shaded regions). It was assumed[9] that both components had B domain-forming blocks and compositions f_1 and f_2 of the components obeyed the condition $f_1, f_2 \in [f_{C'}, f_S]$. The regions of formation of mixed lamellar structures, cylindrical structures (and combinations thereof) over a wide range of mixture composition, are denoted by letters L, C and CL, respectively. In the first case both components of the mixture are L-forming while in the second case both components are C-forming. In the regions CL that correspond to L- and C-forming block copolymer mixtures, the morphology of the system depends on the mixture composition (fraction q of the L-forming component),

$$q = \frac{n_2}{n_1 + n_2} \tag{3}$$

where n_1 and n_2 are the number of molecules of each component. At low q values a mixed cylindrical structure is formed, while at large q values a mixed lamellar structure is formed. The transition between the two morphologies, caused by increasing q, is characterized by the appearance of the two-phase coexistence region. Finally, narrow regions LCL correspond to the mixtures of L-forming block copolymers capable of mixed cylindrical structure formation in a certain range of mixture compositions (see ref. 9 for details).

The aim of this paper is the extension of the investigated interval of f_1 and f_2 values and the analysis of superstructure formation (also in the strong segregation limit) in a binary mixture of two C-forming components with different domain-forming blocks (i.e. B and A blocks as the first and second components, respectively). For this case

$$f_C < f_1 < f_S; \qquad f_S^{-1} < f_2 < f_C^{-1} \tag{4}$$

In the morphology diagram in *Figure 2* this and symmetrical regions are denoted by the letters CC′.

HYPOTHETICAL SUPERSTRUCTURES OF THE MIXTURE AND THEIR FREE ENERGIES

The theory does not allow us to minimize the free energy of the system in the general case with respect to morphology. We can use only a trial and error method in which one must choose possible structures and then minimize their free energies with respect to parameters of these structures. Taking into account condition (4) we have a wide range of possibilities (*Figure 3*):

1. Two individual cylindrical structures (C + C′)
2. A mixed cylindrical structure with blocks B_1 and B_2 inside the domain (C)
3. A mixed cylindrical structure with blocks A inside the domain (C′)
4. A mixed lamellar structure (L)
5. A structure with a cylinder in a cylinder or a double cylinder (CC′)

The need to consider the three first structures is quite evident. The structure L may be realized in a mixture since one component has block B as a minor block, and the other block A, so that in general the ratio of A to B in the mixture can be close to 50:50. Finally, structure

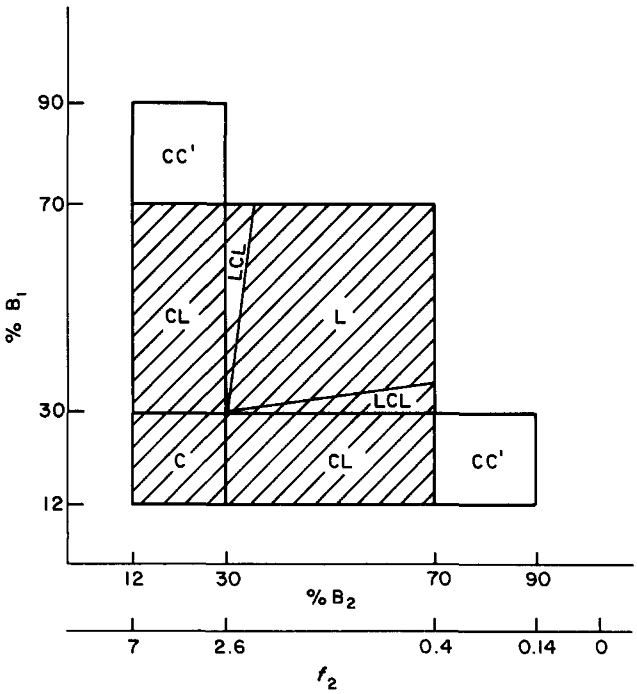

Figure 2 Morphology diagram of diblock copolymer mixture

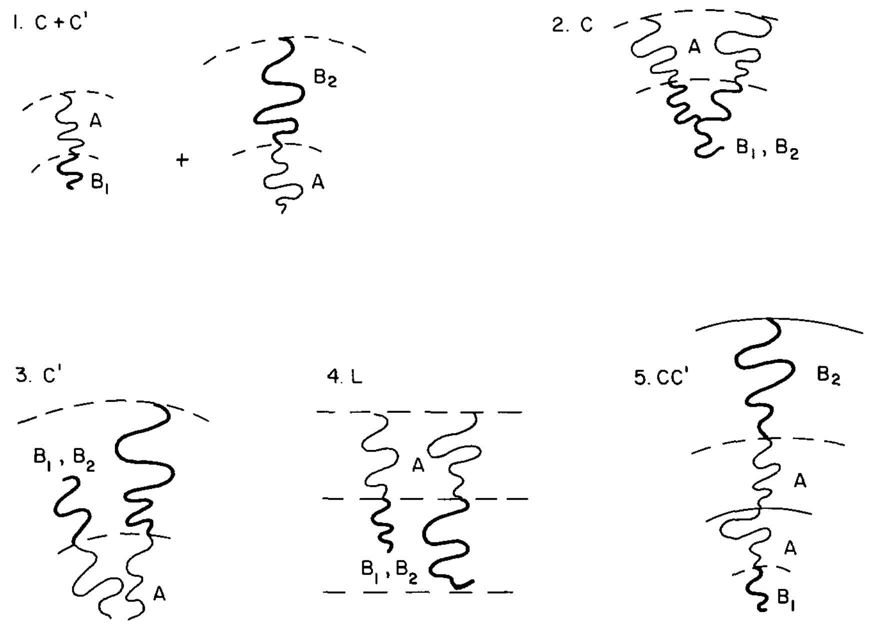

Figure 3 Possible structures in a mixture of block copolymers AB$_1$ ($f_C < f_1 < f_S$) and AB$_2$ ($f_S^{-1} < f_2 < f_C^{-1}$)

CC′ is a new structure and will be considered in detail in the next section.

According to references 8 and 9, free energy ΔF_x in the superstructure with morphology $x = \mathrm{L, C}$ can be presented in the following form:

$$\Delta F_x = \phi (N_{\mathrm{B}^1})^{1/3} A Q_x \qquad (5)$$

where ϕ/a^2 is the surface tension coefficient of the A/B interface, $A = (\pi^2/4\phi p)^{1/3}$ (where p is the parameter of chain stiffness, i.e. the number of units in the Kuhn segment) and Q_x is the relative free energy dependent on the morphology and composition of the mixture and obtained by minimization with respect to the parameters of a structure with a given morphology. (All energetic values are expressed, as before, in kT units.) For possibilities 1–4 (*Figure 3*), expressions for Q_x were obtained earlier. We have:

1. C + C′.

$$Q_{\mathrm{C+C'}} = (1 - q) Q_{\mathrm{C}} + q Q_{\mathrm{C'}} \qquad (6)$$

where according to reference 6

$$Q_{\mathrm{C}} = 3\left[\frac{1}{4} + \frac{3}{2\pi^2}\ln(1 + f_1)\right]^{1/3} \qquad (7)$$

$$Q_{\mathrm{C'}} = 3\left[\frac{1}{4} + \frac{3}{2\pi^2}\ln(1 + f_2^{-1})\right]^{1/3} f_1^{1/3} \qquad (8)$$

Here and below q is the mole fraction of the second component with domain-forming block A, equation (3) (*Figures 1* and *3*).

2. C. The free energy of a mixed cylindrical structure with bidisperse domain-forming blocks B was obtained by us in references 8 and 9:

$$Q_{\mathrm{C}} = 3\left[\frac{1}{4}(1 + \alpha q)^2 G(\alpha, q) + \frac{3}{2\pi^2}(1 + \alpha q)\ln\left(1 + \frac{f_1}{1 + \alpha q}\right)\right]^{1/3} \qquad (9)$$

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

where l_1 is the relative thickness of the short block layer given by[8,9]:

$$\frac{q}{1 + \alpha q} = \frac{[1 - l_1^2(1 - \alpha^2)]^{1/2} - \alpha}{1 - \alpha^2} - l_1^2 \ln\frac{l_1(1 - \alpha)}{1 - [1 - l_1^2(1 - \alpha^2)]^{1/2}} \qquad (11)$$

and

$$u = \frac{2(1 + \alpha q)}{1 - \alpha^2}[1 - \alpha[1 - l_1^2(1 - \alpha^2)]^{1/2}] \qquad (12)$$

Here

$$\alpha = (N_{\mathrm{B}^2} - N_{\mathrm{B}^1})/N_{\mathrm{B}^1} \geqslant 0 \qquad (13)$$

is the relative difference in lengths of B blocks.

3. C′. The free energy of a mixed cylindrical structure with bidisperse blocks B in the matrix outside the cylindrical domains can be obtained on the basis of the results in reference 8, where convex cylindrical layers formed by grafted molecules of various lengths were considered. We have:

$$Q_{\mathrm{C'}} = 3 f_1^{1/3}\left[\frac{1}{4} + \frac{3}{2\pi^2}\ln(1 + f_1^{-1}) + q\frac{3}{2\pi^2}\ln\left(1 + q\frac{(f_1 - f_2)}{f_2(1 + f_1)}\right)\right]^{1/3} \qquad (14)$$

4. L. For the free energy of a mixed lamellar structure we have, according to reference 4,

$$Q_{\mathrm{L}} = 3[1 + f_1 + \alpha q^3]^{1/3} \qquad (15)$$

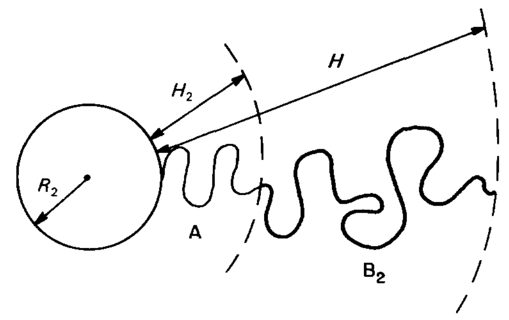

Figure 4 Scheme of a cylindrical structure with a fixed inner cavity

Double cylinder structure CC′

As can be seen from *Figure 3*, the double cylinder structure CC′ comprises a cylindrical structure formed by the first mixture component, bordered by an annular layer formed by the second component. Blocks A of both components thus form a double cylindrical layer and due to their considerable stretching with respect to Gaussian dimensions are practically impermeable[14,15]. Hence, in order to consider the free energy of such a structure one has first to calculate the free energy of a cylindrical layer of diblock copolymer with an internal cavity.

Cylinder with cavity. Under the Narrow Interface Approximation (NIA) valid in the strong segregation limit the free energy of a cylindrical diblock copolymer layer can be presented as:

$$\Delta F = \Delta F_{\mathrm{A}} + \Delta F_{\mathrm{B}^2} + \Delta F_{\mathrm{S}} \qquad (16)$$

where ΔF_{A} and ΔF_{B^2} are the conformational free energies of A and B blocks 'grafted' onto an A/B interface and ΔF_{S} is the interfacial free energy of area σ_2 (the area of interface per molecule of block copolymer). According to reference 8:

$$\Delta F_{\mathrm{A}} = \frac{\pi^2}{4\sigma_2^2} N_{\mathrm{A}} \frac{(R_2 + H_2)^2 (4R_2 + H_2)}{(2R_2 + H_2)^3} \qquad (17)$$

$$\Delta F_{\mathrm{B}^2} = \frac{3}{4\pi} f_2 \ln\left(\frac{R_2 + H}{R_2 + H_2}\right) \qquad (18)$$

$$\Delta F_{\mathrm{S}} = \phi\sigma_2/a^2 \qquad (19)$$

where R_2 is the radius of the cavity, H_2 is the thickness of the inner A layer and H is the total thickness of the cylindrical layer (*Figure 4*). Equation (18) for ΔF_{B^2} is written in the Free Ends Fixation (FEF) approximation (see ref. 8 for details). Note, that equation (16) does not comprise free energy contributions from both the inner and outer surfaces of the double cylindrical layer since in the CC′ superstructure corresponding blocks contact similar ones.

For a dry block copolymer (in the absence of solvent) one has:

$$\pi(2R_2 + H_2)H_2 = N_{\mathrm{A}}a^2/\sigma_2 \qquad (20)$$

$$\pi(2R_2 + H)H = (N_{\mathrm{A}} + N_{\mathrm{B}^2})a^2/\sigma_2 \qquad (21)$$

So, at a fixed value of R_2 only one of the three parameters H_2, H and σ_2 is independent. Let us choose H_2 as an independent parameter and minimize ΔF in equations (16)–(18) with respect to H_2. Then, introducing relative coordinates

$$h = \frac{H_2}{a\phi^{1/3} N_{\mathrm{A}}^{2/3}} \qquad (22)$$

and

$$r_2 = \frac{R_2}{a\phi^{1/3} N_{\mathrm{A}}^{2/3}} \qquad (23)$$

we obtain the equation for h,

$$\frac{\pi^2}{8}\frac{(8r_2^2 + 5r_2h + h^2)h}{(2r_2 + h)^2} - \frac{2(2r_2^2 + 2r_2h + h^2)}{h^2(2r_2 + h)^2} + \tfrac{3}{4}(r_2 + h)\ln\left[1 + f_2^{-1} - \frac{r_2^2}{f_2(r_2 + h)^2}\right] + \frac{3}{4}\frac{(2r_2 + h)hf_2^{-1}r_2^2}{\left[1 + f_2^{-1} - \dfrac{r_2^2}{f_2(r_2 + h)^2}\right](r_2 + h)^3} = 0 \qquad (24)$$

The equilibrium free energy (16) of the double cylindrical layer with a cavity of radius r_2 is then given by

$$\Delta F = N_{\mathrm{A}}^{1/3}\phi^{2/3}\left\{\frac{\pi^2}{16}\frac{h^2(4r_2 + h)}{(2r_2 + h)} + \tfrac{3}{8}h(2r_2 + h)\ln\left[1 + f_2^{-1} - \frac{r_2^2}{f_2(r_2 + h)^2}\right] + 2\frac{(r_2 + h)}{h(2r_2 + h)}\right\} \qquad (25)$$

where h is determined by equation (24).

Figures 5 and *6* show the dependence of the relative free energy of the block copolymer on its composition for cylindrical layers with various dimensions of internal cavity and on the radius of the internal cavity for block copolymers with various compositions. It can be seen from *Figures 5* and *6* that at any composition of a C-forming block copolymer the formation of the cylindrical layer with an internal cavity with a radius that does not exceed some certain value $r_{2\max}$, turns out to be thermodynamically more advantageous than that of a completely filled cylindrical domain. As shown in *Figures 6* and *7*, $r_{2\max}$ increases with decreasing block copolymer asymmetry: $1/f_2 = N_{\mathrm{B}^2}/N_{\mathrm{A}} > 1$.

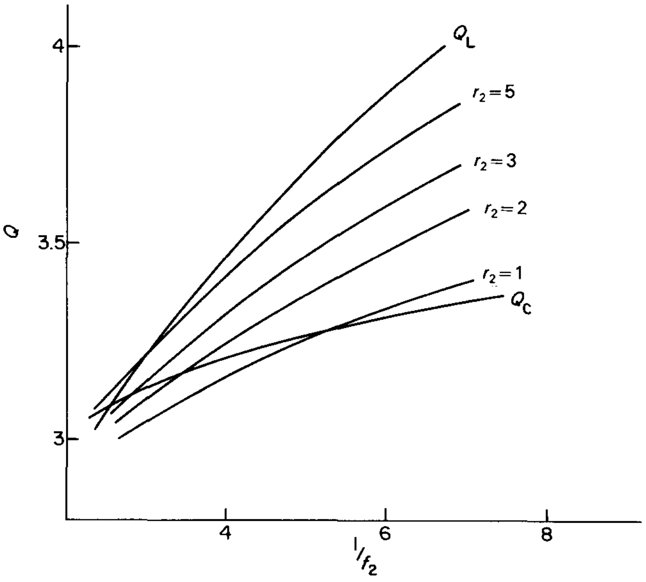

Figure 5 Dependence of the relative free energy Q of the block copolymer on its composition $1/f_2$ for various values of the radius r_2 of the inner cavity

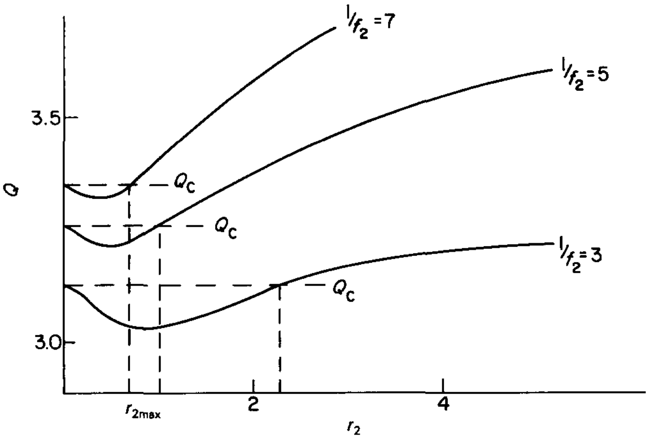

Figure 6 Dependence of the relative free energy Q of the block copolymer on the radius r_2 of the inner cavity for various values of the composition $1/f_2$

It is evident that in a real superstructure the cavity cannot be hollow. This means that such a superstructure with a cavity cannot be realized in a monodisperse diblock copolymer system. It can, however, be realized as the element of a CC′ superstructure in a binary mixture of diblock copolymers. Leaving the more detailed investigation to the next section, we restrict ourselves here to simple estimations.

Let more low molecular weight block copolymer (component 1) (*Figure 1*) form stable cylindrical domains. According to reference 9, we have for the radius of the domain

$$R = a\phi^{1/3}(N_{B^1})^{2/3}\left[\frac{\pi^2}{16} + \tfrac{3}{8}\ln(1+f_1)\right]^{-1/3} \qquad (26)$$

the radius of the cylinder comprising the whole block copolymer 1:

$$R_1 = R(1+f_1)^{1/2} \qquad (27)$$

and its relative value

$$r_1 = \frac{(1+f_1)^{1/2}}{f_1^{2/3}}\left[\frac{\pi^2}{16} + \tfrac{3}{8}\ln(1+f_1)\right]^{-1/3} \qquad (28)$$

It should be noted that since we consider the binary mixture of block copolymers with equal blocks A (*Figure 1*) the relative coordinates coincide with those given by equations (22) and (23).

Curve B in *Figure 7* shows the dependence of r_1 on f_1. It can be seen that the radius of the inner cylinder turns out to be lower than $r_{2\max}$ for a wide range of compositions f_1 of the first component, especially if the second (high molecular weight) component is of not too high asymmetry $1/f_2$. In this case the contribution to the total free energy of the first component remains the same as in the case of individual cylindrical structure and that of the second component is lower than that of the individual cylindrical structure formed by the second component. This means that the formation of a double cylinder structure must be thermodynamically more advantageous than separation into two individual cylindrical phases C and C′.

Free energy of the double cylinder

In order to calculate correctly the total free energy of the double cylindrical structure consider it as a sum of the free energies of the inner C cylinder formed by the first component AB_1 and the hollow C′ cylinder formed by the second component AB_2

$$Q_{CC'} = (1-q)Q_C + qQ_{C'} \qquad (29)$$

Two additional conditions must be taken into account. The first is the equality of the total radius r_1 of the inner cylinder to the radius r_2 of the cavity ($r_1 = r_2 = r$). The second condition is connected with the content of the binary mixture, forming the double cylinder structure. This determines the ratio of the linear densities m_1 and m_2 of the first and second components in a double cylinder

$$m_1/m_2 = (1-q)/q \qquad (30)$$

The analysis shows that under the conditions of complete filling of the double cylinder the variable r is the single free geometrical parameter of the system and the problem is reduced to the minimization of the free energy (29) with respect to r.

From the results of references 8 and 9 we have for the inner completely filled cylinder of total radius r:

$$Q_C = Q_{C_0}\frac{1}{3}\left[\frac{r^2}{r_{10}^2} + 2\frac{r_{10}}{r}\right] \qquad (31)$$

where Q_{C_0} is the minimal value of relative free energy of the C structure [equation (7)] corresponding to $r = r_{10}$ given by equation (28). It follows from equations (7) and (28) that Q_{C_0} and r_{10} are functions of the parameter f_1 only.

The free energy of the cylindrical layer with a cavity of radius r is determined by relationships (5) and (16)–(19). Taking into account the relationships (20), (21) and (30) one has

$$Q_{C'} = Q_{C'_0}\frac{1}{3}\left[\frac{r^2}{r_{20}^2} + 2\frac{r_{20}}{r}\right] \qquad (32)$$

where $r_{20} = r_{20}(f_1, q)$ is the cavity radius which provides at given values of q and f_1 the minimal relative free energy $Q_{C'_0}(q, f_1)$ of the molecules of a second component in an external C′ structure (see *Figure 6*).

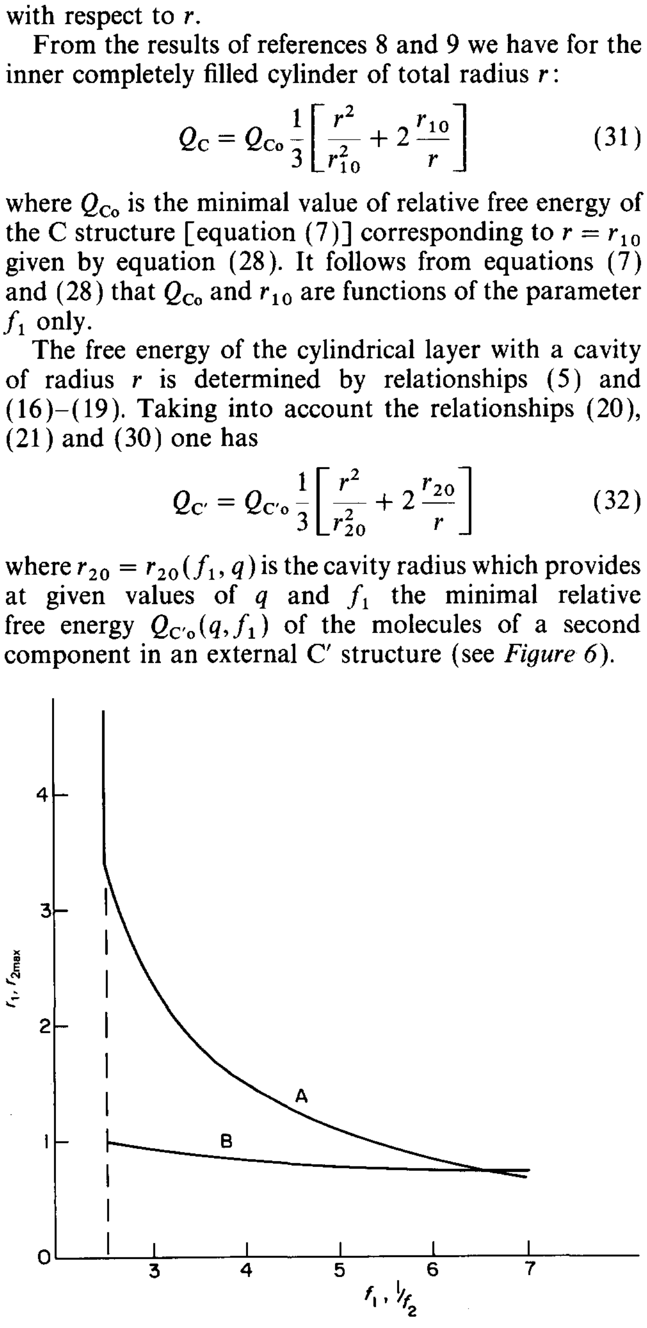

Figure 7 Dependence of the radius $r_{2\max}$ on the block copolymer composition $1/f_2$ (A) and total radius r_1 of the inner cylinder on f_1 (B)

Minimization of the total free energy (29) gives us the final expression for the equilibrium free energy in a double cylindrical CC′ structure

$$Q_{\mathrm{CC'}} = \left[(1-q)Q_{\mathrm{Co}} + qQ_{\mathrm{C'o}} \frac{r_{10}^2}{r_{20}^2} \right]^{1/3} \times \left[(1-q)Q_{\mathrm{Co}} + qQ_{\mathrm{C'o}} \frac{r_{20}}{r_{10}} \right]^{2/3} \qquad (33)$$

The radius of the total A domain formed by A blocks of both components and containing the internal domain B (*Figure 3₅*) is given by

$$r_{\mathrm{A}} = r + h = r_{10}\left[1 + \frac{(1-q)f_1}{q(1+f_1)} \right]^{1/2} \times \frac{\left[(1-q) + q\dfrac{r_{20}Q_{\mathrm{C'o}}}{r_{10}Q_{\mathrm{Co}}} \right]^{1/3}}{\left[(1-q) + q\dfrac{r_{10}^2 Q_{\mathrm{C'o}}}{r_{20}^2 Q_{\mathrm{Co}}} \right]^{1/3}} \qquad (34)$$

where, as before, the relative coordinates are introduced [see equations (22) and (23)].

RESULTS AND DISCUSSION

We performed numerical calculations for the free energies for all the structures considered, equations (6)–(15) and (33), for a wide range of compositions f_1 and f_2 of mixture components [equations (2b) and (2c), respectively] and mixture content q [equation (3)].

Typical dependences of the free energies on mixture composition q at fixed values f_1 and f_2 are shown in *Figure 8* for all five variants of structures. It can be seen that there are four types of structures that are of minimal free energy in some certain interval of q values. They are:

1. Mixed C structure with blocks B_1 and B_2 inside cylindrical domains. This appears to be thermodynamically most advantageous with a high predominance of B domain-forming component 1 (small q values);
2. In the region of intermediate values of q the minimum free energy corresponds to a lamellar structure;
3. In the region of predominance of A domain-forming component 2 (high q values) segregation into two macrophases C + C′ appears to be most favourable;
4. Between C + C′ and L stability ranges there is more or less a narrow interval of q values where the double cylinder CC′ structure appears to be thermodynamically most advantageous.

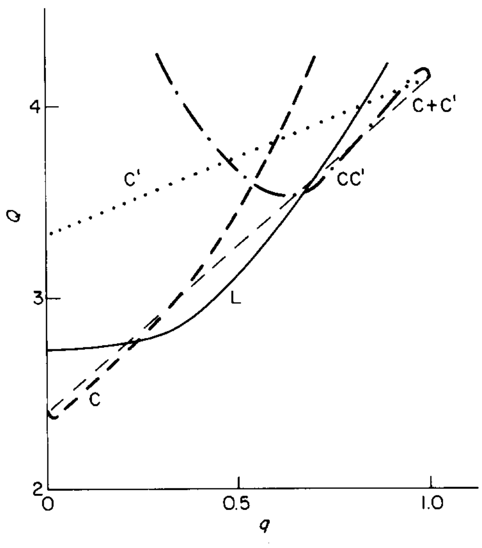

Figure 8 Relative free energies of five possible structures *versus* mixture content $q, f_1 = 1/f_2 = 5$

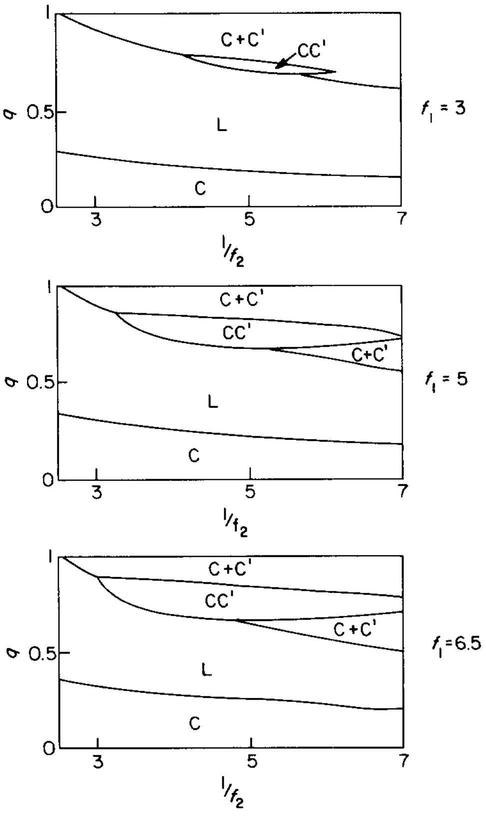

Figure 9 Morphology diagram of mixture with $(q, 1/f_2)$ coordinates

Typical dependences on $1/f_2$ of q values corresponding to the intersections of free energy curves and, hence, the transitions between various morphologies, are presented in *Figure 9*. Data were calculated for the fixed values of $f_1 = 3$,5 and 6.5. It can be seen that an increase in f_1 leads to a broadening of the region CC′ in the main at the expense of region C + C′ which is divided into two subregions.

It should be noted that *Figure 9* is not a full phase diagram. Since intermorphology transitions are first-order phase transitions, the boundary curves in *Figure 9* are to be bordered with two-phase corridors (for details see ref. 9). We shall not consider this problem in detail here, because from our point of view, the most interesting result illustrated by *Figures 8* and *9* is the prediction of the possibility of double cylinder structure formation (*Figure 3₅*) in a binary mixture of 'quasi-isomorphous' diblock copolymers with different blocks B (domain-forming in component 1 and matrix-forming in component 2) and identical blocks A.

Figure 10 shows the dependences of *Figure 9* recalculated with respect to average mixture composition

$$\bar{f} = f_1 f_2 / [(1-q)f_2 + qf_1] \qquad (35)$$

As is seen from *Figure 10*, CC′ and C + C′ structures are found in the region of the diagram where according to symmetry considerations a C′ structure with bidisperse blocks B_1 and B_2 as matrix blocks could be located.

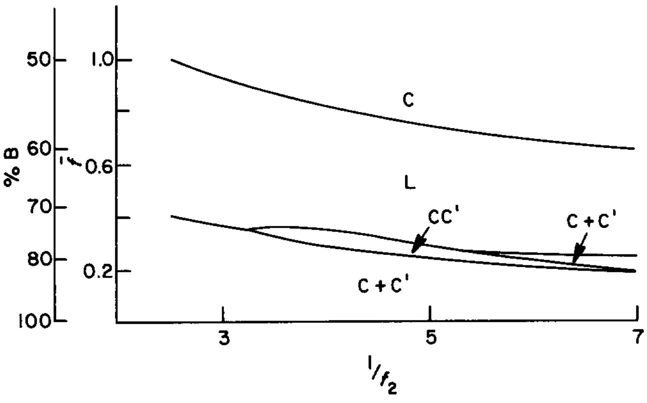

Figure 10 Morphology diagram of *Figure 9* with ($\bar{f}$, $1/f_2$) coordinates, $f_1 = 5$

However, as already mentioned in reference 8, in the case of convex layers the difference in lengths of grafted chains does not lead to a marked gain in free energy of the system. As a result, the C′ structure does not correspond to the minimum of the system free energy at all values of f_1, f_2 and q under consideration, and this structure gives up its place in *Figure 10* to CC′ and C + C′ structures. In general, for all possible f_1 and f_2 values at mean mixture composition $\lesssim 50\%$ B mixed cylindrical structure C is realized, in the interval ~55–75% B lamellar structure L is formed, at $\gtrsim 80\%$ B segregation into two macrophases C + C′ is favourable and in the narrow window near 75–80% B the double cylinder CC′ structure is the most stable.

We hope that the prediction of the existence of a double cylindrical structure will stimulate experimental investigation. It should be noted in conclusion that in this structure three microphases appear to be formed instead of two as in the usual case. They are: microphase B of the inner cylinder, microphase A of the external cylinder and microphase B of the matrix. Such a structure may be stable in the mixture of quasi-isomorphous C-forming block copolymers not only of AB_{N_1}/AB_{N_2} type but also in an AB_{N_1}/AC_{N_2} mixture, i.e. when the components of the mixture are chemically different.

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