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Triblock copolymers: the role of interfacial tension coefficients at two interfaces

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The mean-field theory of formation of triblock copolymer superstructure is developed in the strong segregation limit, taking into account the difference in local characteristics of the blocks (widths, persistence lengths). Special attention was paid to the role of the interfacial tension coefficients at the two interfaces during formation of the triblock copolymer superstructure. It is shown that there are different mechanisms of morphology variation, guided both by the difference in local parameters of the blocks and the difference in the interfacial tension coefficient. It is also shown that a great difference in the interfacial tension coefficients at the two interfaces can lead to the formation of (1) an asymmetrical cylindrical superstructure in the case of symmetry in the local characteristics and volume fractions of the triblock copolymers and (2) a symmetrical lamellar superstructure in the case of triblock copolymers with asymmetry in the local characteristics of the blocks.

(Keywords: triblock copolymers; morphology variation; interfacial tension)

INTRODUCTION

The superstructures of block copolymers formed in the strong segregation limit have been intensively studied, both experimentally and theoretically[1]. During the past decades insight has been gained into the inner organization of block copolymer superstructures and the dependences of the main characteristics of the superstructure (such as free energy, domain width, interdomain distances, surface area per chain at the interface) on the molecular features (molecular weight of the chain, stiffness, etc.) have been determined[2–8]. The current problem is the more delicate question of the morphology variation. In the case of a binary mixture of diblock copolymers it was shown that the morphology of the mixed superstructure can be guided by the composition of the mixture[9,10]. In more recent investigations[11] the influence of the local parameters of the blocks (width, stiffness) on the morphology of the superstructure was also shown. Triblock copolymers obey additional possibilities of morphology variation[12], one of them being the difference in the interfacial tension coefficients at the two interfaces. Two situations can be realized: one with two chemically identical outer blocks divided by the third block, and the second with all three blocks being chemically different. We consider only the last case because the first one can be easily reduced to the case of diblock copolymers[7].

The aim of this paper is to analyse the role of the interfacial tension coefficients in superstructure formation. This problem is of special interest in view of the fact that two different experimental studies indicated lamellar[13] and coaxial cylindrical[14] morphologies in samples of ABC triblock copolymers, of volume fraction 33/33/33%, with a single difference in the sequence of the blocks: in the first case it was P2VP–PS–PI (poly(2-vinylpyridine)–polystyrene–polyisoprene)[13]; in the second case, P2VP–PI–PS[14]. Moreover, in the last case the external blocks A and C, equal in volume, form greatly different structural elements. Although some new non-canonical structures have previously been observed in triblock copolymers[12,15], we consider here only the four morphologies experimentally observed in refs 13 and 14 to analyse the role of the interfacial tension coefficients in the superstructure formation.

MODEL AND GENERAL FORMALISM

We consider a triblock copolymer ABC with chemically different and strongly segregated blocks A, B and C. The lengths of the blocks that are the numbers of spherically symmetric elements of the chains are $N_i \gg 1$ (i = A, B, C) and the volume fractions of the components are $f_i = N_i a_i^3 / \Sigma_i N_i a_i^3$ (i = A, B, C). The lengths of spherically symmetric monomer units a_i and persistence lengths l_i (i = A, B, C) of the blocks are considered to be different. Two coefficients of the interfacial tension at the interfaces A/B and B/C, $\phi_{A/B}$ and $\phi_{B/C}$, are put into consideration.

To solve the problem about the stability of a superstructure of a certain morphology (in the strong segregation limit), a trial-and-error method is used[9,10]; i.e. the free energy of this morphology should be compared with that of another one. The superstructure with minimal free energy is the stable one. We consider here only four superstructures, *Figure 1*:

- lamellar, L (*Figure 1a*);

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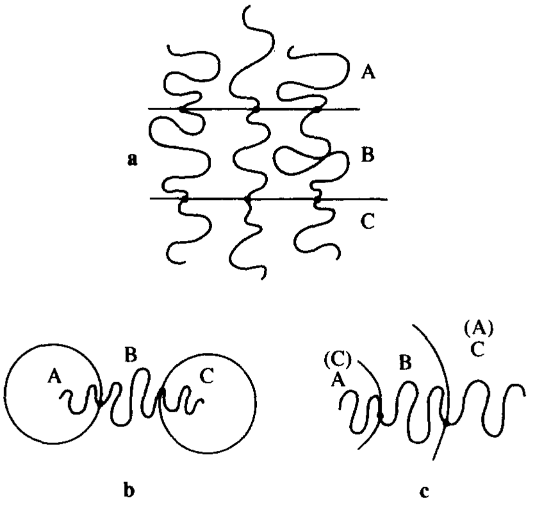

Figure 1 Superstructures of different morphologies: (a) lamellar L; (b) cylindrical with blocks A and C inside cylindrical domains, C(A,C); (c) coaxial cylinders CC(A) and CC(C)

- cylindrical with blocks A and C inside cylindrical domains and block B in between, C(A,C) (*Figure 1b*);
- two coaxial cylindrical superstructures, CC(A) and CC(C), with block A (or C) inside the inner cylindrical domain, block B in the outer coaxial cylinder and external block C (or A) in the surrounding medium (*Figure 1c*).

Both interfaces in the triblock copolymer have the same symmetry in these superstructures (that is not the case in general consideration[12,14,15]).

We did not consider here analogous superstructures with spherical A and C domains or coaxial spherical morphology or the OBTD superstructure observed experimentally[13], in order to make the consideration clearer. All qualitative conclusions of this work are the same for all morphologies, although the regions of spherical superstructure stability are shifted to smaller values of the volume fraction of domain-forming block. Thus, we shall discuss below the boundaries between lamellar and cylindrical superstructures only.

We consider the external blocks A and C as chains grafted onto an interface, and the inner block B as chains stretched between two interfaces. As in the case of diblock copolymers, the theory of grafted polymer layers[16–21] forms the basis of the theory of triblock copolymer superstructures. Using the results of this theory[18,19] and equilibrating the geometry of superstructures, we obtain a general expression for the free energy of the block copolymer chain in the superstructure of given morphology X:

$$\frac{F_X}{kT}=\frac{3}{2}\left(\frac{\pi^2}{4}l_A^{-1}a_A^5\right)^{1/3}\phi_{A/B}^{2/3}N_A^{1/3}Q_X \qquad X=\mathrm{L},\mathrm{CC(A)},\mathrm{C(A,C)} \tag{1}$$

where Q_X depends on the morphology of the triblock copolymer superstructure. Thus, we have for

1) the lamellar superstructure, L:

$$Q_L=\left[\left(1+\frac{12}{\pi^2}Y_B\frac{f_B}{f_A}+Y_C\frac{f_C}{f_A}\right)(1+k)^2\right]^{1/3} \tag{2}$$

2) the superstructure of coaxial cylinders (with inner block A), CC(A):

$$Q_{CC(A)}=2\left\{\left[\frac{1}{4}+\frac{3}{2\pi^2}\left(Y_B\ln\left(1+\frac{f_B}{f_A}\right)-Y_C\ln(f_A+f_B)\right)\right]\right.$$
$$\left.\times\left[1+k\left(1+\frac{f_B}{f_A}\right)^{1/2}\right]^2\right\}^{1/3} \tag{3}$$

3) the cylindrical superstructure with two domains composed from blocks A and C, C(A,C):

$$Q_{C(A,C)}=2\left\{\left[\frac{1}{4}+\frac{3}{2\pi^2}Y_B\ln\left(1+\frac{f_B}{2f_A}\right)\right]^{1/3}\right.$$
$$\left.+Y_C^{1/3}\left(\frac{f_C}{f_A}\right)^{1/3}k^{2/3}\left[\frac{1}{4}+\frac{3}{2\pi^2}\frac{Y_B}{Y_C}\ln\left(1+\frac{f_B}{2f_C}\right)\right]^{1/3}\right\} \tag{4}$$

The parameter Y_i in equations (2)–(4)

$$Y_i=\frac{a_i^2}{a_A^2}\frac{l_A}{l_i} \qquad i=\mathrm{B},\mathrm{C} \tag{5}$$

describes the difference in the local characteristics of block $i=\mathrm{B}$, C and block A. As shown in ref. 11 for diblock copolymers, this parameter greatly influences the position of the boundaries between different morphologies.

The parameter

$$k=\phi_{B/C}/\phi_{A/B} \tag{6}$$

is the ratio of the coefficients of the interfacial tension at two interfaces. This parameter did not appear in the theory of diblock copolymers[11,18,19] and is introduced into the theory for triblock copolymers due to existence in the system of three components and, hence, two interfaces.

Equations (2)–(4) were obtained under the assumption that all blocks are stretched. Analysis shows that this condition can be violated only in the case of a relatively short external block (C) grafted to a coaxial cylinder. In this case, equation (3) for $Q_{CC(A)}$ must be changed to:

$$Q_{CC(A)}=2\left\{\left[\frac{1}{4}+\frac{3}{2\pi^2}Y_B\ln\left(1+\frac{f_B}{f_A}\right)\right]\left[1+k\left(1+\frac{f_B}{f_A}\right)^{1/2}\right]^2\right\}^{1/3} \tag{7}$$

Notice also that equation (4) is obtained as a sum of the free energies of diblock copolymers AB and CB, i.e. we assume the location of the middle point of segment B on the cylindrical surface that is not the case for this superstructure. We also used the approximation that the outer ends of the external block are fixed[19] when obtaining equation (3) (outer block is C) and equation (4) (outer block is B). The assumptions used do not influence the main conclusions concerning the boundaries between morphologies, although they can give some error in the position of these boundaries.

Comparison of the energies in equations (2)–(4) gives the regions of stability of (1) the lamellar superstructure, $Q_L<Q_C$, Q_{CC}; (2) the coaxial cylindrical superstructure, $Q_{CC}<Q_L$, Q_C; and (3) the cylindrical superstructure with A and C domains, $Q_C<Q_L$, Q_{CC}.

RESULTS

Consider first the case of equal local characteristics (width and stiffness) of the three blocks, $Y_B=1$, $Y_C=1$. The

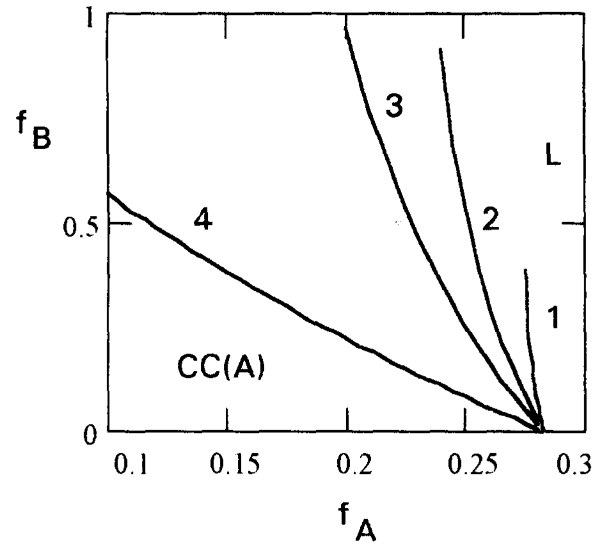

Figure 2 Phase diagram in coordinates f_A,f_B for the regions of stability of L and CC morphologies. $k=0.1$ (1), 0.15 (2), 0.2 (3), 0.5 (4)

regions of stability for the different morphologies were obtained by numerical comparison of the free energies of these morphologies, equations (2)–(4), at different values of k, and the results for L/CC transition were introduced in the form of a phase diagram in coordinates f_A and f_B, *Figure 2*. It is seen that a decrease in the volume fraction f_A of the external block A (at a fixed volume fraction f_B of the intermediate component B) leads to the transition from lamellar superstructure L to coaxial cylindrical superstructure CC(A). In the limit $k=0$ ($\phi_{B/C}=0$, identical B and C blocks), we reverted to the case of a diblock copolymer A(B + C) with the boundary between regions C (cylindrical morphology) and L (lamellar morphology) at $f_A \approx 0.28$. Notice that the value $f_A \approx 0.28$ is slightly different from that of $f_A=0.3$ obtained previously for diblock copolymers[6,9], due to the approximation that the B ends are fixed at the B/C interface.

As seen from *Figure 2*, an increase in k results in broadening of the L region and also in a shift of the boundary $f_A^{L/CC}$ in the direction of the smaller values. This result is not surprising because non-planar morphologies are always characterized by greater values of surface area per chain at the outer interface compared with that at the inner interface, which shifts the equilibrium state to the region of more planar geometry. The result obtained shows that triblock copolymers obey a new (as compared with diblock copolymers) mechanism of morphology variation that is governed by the ratio of the interfacial tension coefficients at the boundaries of microphases: $k=\phi_{B/C}/\phi_{A/B} \sim \sqrt{\chi_{B/C}/\chi_{A/B}}$, where χ_{AB} and χ_{BC} are the Flory–Huggins parameters.

The role of k can be better understood from the example where the volume fractions of the blocks in the ABC triblock copolymer are symmetrical: $f_A=f_C$, $f_B=1-2f_A$. In this case an assumption of equal interfacial tensions at both interfaces A/B and B/C ($k=1$) evidently leads to the formation of symmetric superstructures. At $f_B \leqslant f_A$ lamellar (L) superstructure is formed, and a decrease in f_A results in sequential formation of (1) cylindrical (C(A,C)) superstructure with blocks A and C in cylindrical domains and block B in the matrix and then (2) spherical (S(A, C)) superstructure with blocks A and C in spherical domains and block B in the matrix. This sequence of superstructures was observed experimentally[13], but here we shall discuss only the L/C(A,C) transition. The free energies of the superstructures considered in equations (2)–(4) are shown in *Figure 3*. It is shown that the superstructure of coaxial cylinders can never be formed in the case when $f_A=f_C$ and the transition from the cylindrical morphology to the lamellar one is realized at $f_A=0.18$, in good agreement with the experimental data[13].

Asymmetry in triblock copolymers leads to asymmetry in the observed superstructures that is realized first as a difference in the dimensions of A and C lamellar sublayers (or cylindrical domains) and then in a change of the morphology of the superstructure. In the last case one can expect the formation of a new superstructure of coaxial cylinders CC(A) or CC(C), equation (7), *Figure 1*, not observed in the case of symmetric triblock copolymers.

The asymmetry of block copolymers is usually associated only with volume fractions of blocks A and C. Nevertheless, as will be shown below, there are also other parameters governing the asymmetry of triblock copolymers. We consider now in detail the influence of two of them: Y_C, describing the difference in local characteristics of blocks C and A, and k, describing the difference in interfacial tension coefficients at the two interfaces. Only the case when $f_A=f_C$ is considered here.

If $k<1$, corresponding to a lower interfacial tension at interface B/C than at interface A/B, then the planar structure tends to increase in curvature. The lamellar structure can become the coaxial cylindrical one CC(A) with inner block A, or can form two cylindrical domains A and C with a great difference in their size. This arises because the difference in interfacial tension energies $\phi_{A/B}\sigma$ in curved and planar morphologies is greater than difference in the energies of chain stretching for large values of $\phi_{A/B}$. *Figure 4a* shows the dependences of the free energies (2), (4) and (7) on the parameter k for a triblock copolymer with $f_A=f_B=f_C$. It is seen that decrease in k leads to the transition from L superstructure to CC(A) superstructure even in the case of the symmetric triblock copolymer considered. Notice that we used

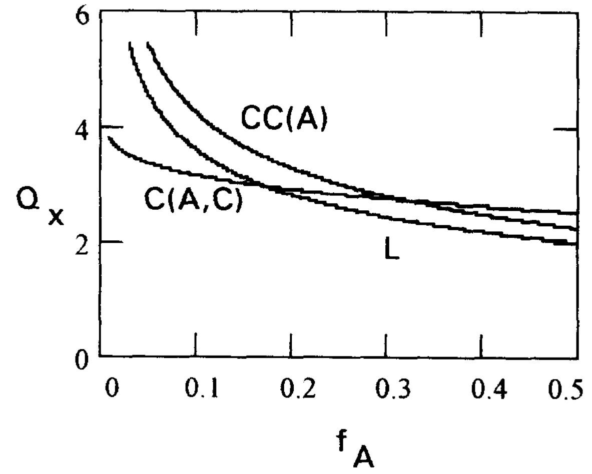

Figure 3 Free energies Q_X of the superstructure morphologies L, C(A,C) and CC(A) *versus* volume fraction of component A in the triblock copolymer. $f_A=f_C$, $k=1$, $Y_B=Y_C=1$

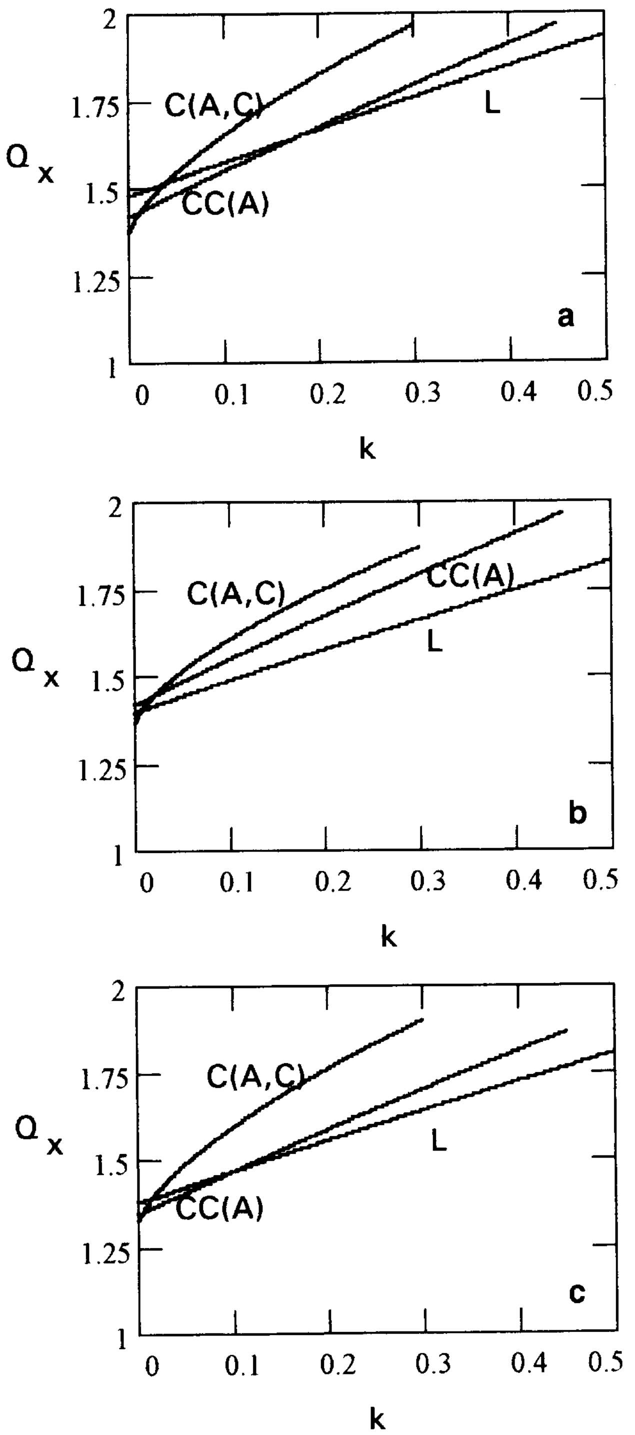

Figure 4 Free energies Q_X of the superstructure morphologies L, C(A,C) and CC(A) *versus* k in the triblock copolymer with $f_A=f_B=f_C$: (a) $Y_B=Y_C=1$; (b) $Y_B=1$, $Y_C=0.5$; (c) $Y_B=0.5$, $Y_C=1$

equation (7) for CC structure because the estimation shows that for $f_A=f_B=f_C$, the external block C in the CC(A) superstructure is not stretched and does not contribute to the free energy (3). If $k>1$, meaning that the interfacial tension at surface B/C is stronger than that at surface A/B, the coaxial cylindrical superstructure with inner block C, CC(C), is stable.

This effect can be both strengthened and weakened by the difference between the local characteristics of the blocks. As shown in our previous paper[11], the difference in the widths and persistence lengths of the components of a diblock copolymer with $Y\neq 1$ results in a shift of the L/C boundary in such a way that a thinner and stiffer block tends to expand the region of its existence inside (and to narrow the region of its existence outside) the cylindrical domain. This makes, for example, the lamellar morphology advantageous compared with the coaxial cylindrical CC(A) morphology with outer block C if $Y_C<1$. It is seen from *Figure 4b* that at $Y_C<0.5$ the CC(A) structure does not form in contrast to the case of triblock copolymer with $Y_C=1$, and the stability region of the lamellar morphology is wider at $Y_C<0.5$ than at $Y_C=1$.

Thus we have different mechanisms of superstructure morphology variation in triblock copolymers. Both increase in k (at $k<1$) and decrease in Y_C and Y_B (*Figure 4c*) make the lamellar superstructure more stable. On the contrary, decrease in k (at $k<1$) and increase in Y_C and Y_B can lead to the transition from lamellar to curved geometries. *Figure 5* shows the dependence of the boundary between morphologies $f_A^{CC/L}$ on the parameters k, Y_C and Y_B. It is seen that $f_A^{CC/L}$ decreases with increase in k (at $k<1$) and decrease in Y_C and Y_B. At $k>1$ the effect changes its sign. Meanwhile, all observations remain valid when changing A by C.

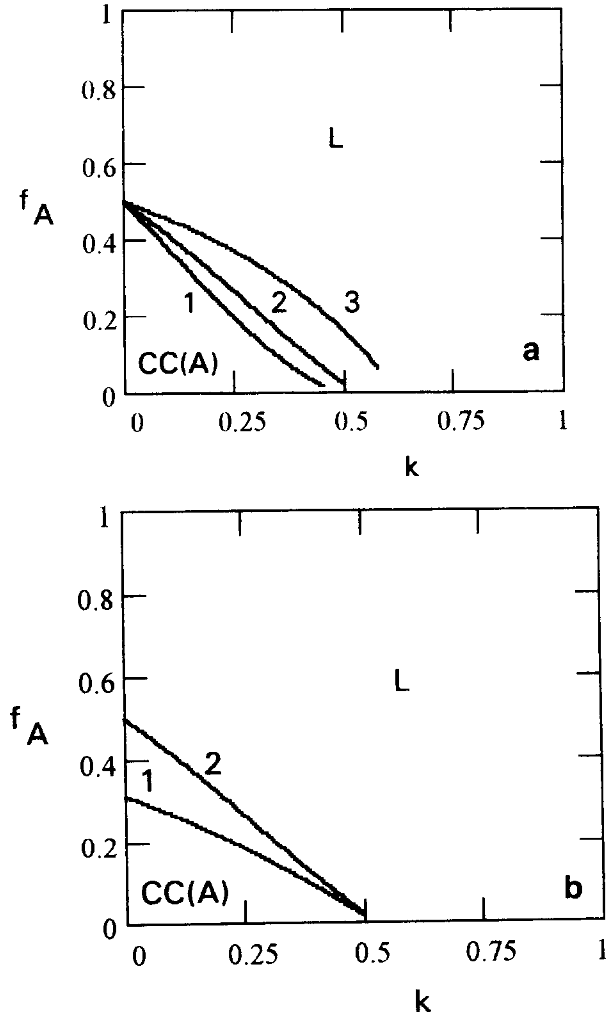

Figure 5 Volume fraction f_A of component A corresponding to the boundary between L and CC(A) morphologies in the triblock copolymer with $f_A=f_C$ *versus* k: (a) $Y_C=1$, $Y_B=0.7$ (1), 1 (2), 2 (3); (b) $Y_B=1$, $Y_C=0.5$ (1), 1 (2)

COMPARISON WITH EXPERIMENT

Comparison of theoretical results with experimental data is always a very delicate procedure owing to uncertainty in the values of the parameters being used in the theory. In our case these parameters are the widths and persistence lengths of the two blocks and the interfacial tension coefficients at the two interfaces. Another problem is that the theory developed does not take into account non-constant mean curvature of the interface, an effect indicated in recent experiments[14]. Nevertheless, we can realize a qualitative comparison of the theory and experiment without the strict demand of quantitative coincidence.

What we analyse here is the discrepancy in the observed morphologies formed by triblock copolymers ABC of 33/33/33 vol% with the single difference in the order of connectivity of the three blocks. As indicated in ref. 14, triblock copolymer P2VP–PI–PS of 33/33/33 vol% forms a superstructure of coaxial cylinders (CC) with P2VP as inner block, whereas triblock copolymer P2VP–PS–PI of the same volume fractions, analysed in ref. 13, forms well defined lamellae (L).

We tried to understand this discrepancy in terms of the diagram of *Figure 2*. It is seen from *Figure 2* that if the monomer units of each block had equal local characteristics, $Y_B = Y_C$, coaxial cylindrical superstructure can never be realized under the condition $f_{PS} = f_{P2VP} = f_{PI}$. So, we have to take into account the difference in block widths and persistence lengths. We can assume P2VP and PS to be approximately equal in monomer size and in stiffness, and thereby to have approximately equal values of $a_{PS} \approx a_{P2VP}$, $l_{PS} \approx l_{P2VP}$. This leads to the values $Y_C^1 = 1$ and $Y_B^2 = 1$, where the superscript 1 corresponds to cylinder-forming triblock copolymer P2VP–PI–PS and superscript 2 refers to lamellae-forming triblock copolymer P2VP–PS–PI. Approximate values of the other parameters used in the theory are $Y_B^1 = 0.7$, $Y_C^2 = 0.7$. We did not take into account the stretching energy of the outer block C in the superstructure of coaxial cylinders CC(P2VP), equation (7), because ref. 14 stated the lack of this effect. These approximations result in the dependences $k(Y_B, Y_C)$ shown in *Figure 6*. It is seen that at the values $Y_B^2 = 1$, $Y_C^2 = 0.7$ (P2VP–PS–PI) lamellar superstructure is realized at $k_2 > 0.05$, and at the values $Y_B^1 = 0.7$, $Y_C^1 = 1$ it is realized at $k_1 > 0.12$. Estimating, for example, $k_1 = \phi_{PS/PI}/\phi_{P2VP/PI} = 0.07$ and $k_2 = \phi_{PS/PI}/\phi_{P2VP/PS} = 0.15$, we can expect lamellar superstructure formation in the first case and cylindrical superstructure formation in the second case, which correlates with experimental data[13,14]. Let us discuss this effect.

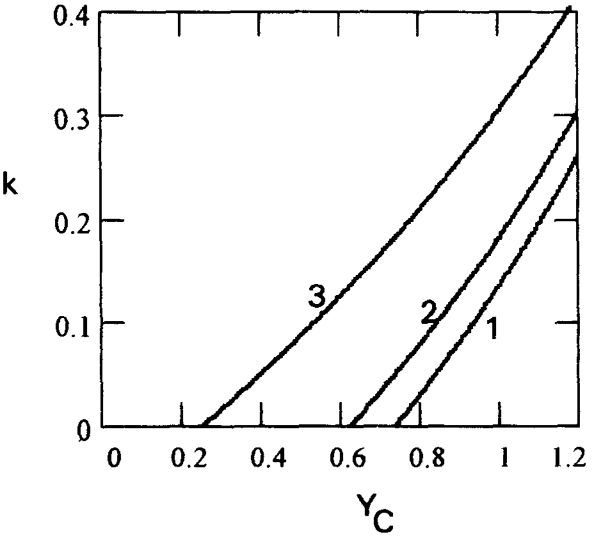

Figure 6 Dependence of k corresponding to the boundary between L and CC(A) morphologies in the triblock copolymer with $f_A = f_B = f_C$ on Y_C. $Y_B = 0.7$ (1), 1 (2), 2 (3)

In the case of triblock copolymer P2VP–PS–PI, the thinner PI block is located outside the domain that makes lamellar superstructure more stable than the coaxial cylinder CC(A) morphology with block A in the inner cylinder. The superstructure of coaxial cylinders CC(C) with C as the inner block cannot be realized in this case due to low value of parameter k (weak interfacial tension at interface B/C as compared with that at interface A/B). This leads to lamellar superstructure formation. In the case of triblock copolymer P2VP–PI–PS, we have a symmetrical triblock copolymer that forms a symmetrical lamellar superstructure at $k = 1$. The great difference in interfacial tension coefficients $\phi_{A/B}$ and $\phi_{B/C}$ leads to non-planar geometry of the superstructure and cylindrical CC(A) structure formation.

In summary, we can state that the difference in the interfacial tension coefficients at the two interfaces of triblock copolymer structures plays a vital role in superstructure formation, leading to cylindrical morphology in the case of a symmetric triblock copolymer (P2VP–PI–PS) with equal dimensions of monomers and persistence lengths of blocks A and C ($a_A = a_C$, $l_A = l_C$) and lamellar morphology in the case of an 'asymmetrical' block copolymer (P2VP–PS–PI) ($a_A \neq a_C$, $l_A \neq l_C$) at the same volume fractions of the components, 33/33/33 vol%.

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