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Theory of Supercrystalline Structures in Mixtures of ABC Triblock and ab, bc, and ac Diblock Copolymers

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SUMMARY: Theoretical analysis of the ability of forming mixed supercrystalline structures in the mixtures of **ABC** triblock copolymer with **ab**, **bc**, and **ac** diblock copolymers in the strong segregation limit is carried out. Effects of combined phase and microphase segregation are analysed. The possibility of changing the initial superstructure is demonstrated.

Introduction

During the last two decades block copolymers aroused considerable interest of both theoreticians and experimenters. It is well known that in the strong segregation limit microphase segregation with supercrystalline structure(s) formation occurs. The morphology of the superstructure formed by a diblock copolymer depends predominantly on the relative lengths of copolymer blocks. In the case of **ABC** triblock copolymers the difference between the energies of **A**·**B**, **B**·**C**, and **A**·**C** interactions also plays an important role [1, 2]. Hence, it becomes clear that by varying the block lengths and/or the chemical nature of blocks and their sequence in block copolymers one can obtain superstructures of different morphologies.

It was found that another way of regulating the morphology of diblock copolymer is available [3-7]. This approach consists in mixing two diblock copolymers, **ab** and **a'b'**, having chemically identical blocks with different lengths. The formation of the so-called mixed superstructure in which long and short blocks are mixed inside domains of the superstructure makes it possible to obtain the method of the "non-chemical" morphology control. On the basis of theoretical predictions, this effect was demonstrated experimentally [8].

The aim of the present work is to investigate theoretically the possibility of using this approach for controlling the morphology of the **ABC** triblock copolymer superstructure. For this purpose, the addition of some amounts of **ab**, **bc**, or **ac** diblock copolymers to the **ABC** copolymer is suggested (capital and small letters are used to distinguish between di- and triblock copolymers; **A** and **a**, **B** and **b**, and **C** and **c** are chemically identical blocks).

Method

The problem of finding the superstructure(s) formed in the block copolymer system is conventionally solved by the trial-and-error method. This approach assumes consideration of

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all situations that can arise in the system in principle and the choice of the thermodynamically most preferable situation. This approach is illustrated by the following scheme:

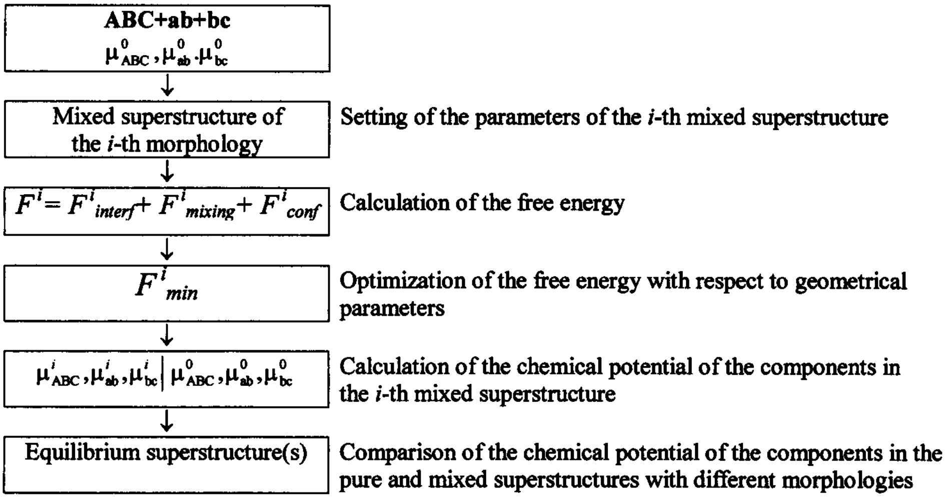


Fig. 1. Scheme of the trial-and-error method.

The calculation of the free energy of the i-th mixed superstructure is based on the concept of polymer brushes. Three terms: interfacial (F_{inetrf}), mixing (F_{mixing}), and conformational (F_{conf}) energies contribute the free energy. In this paper only such superstructures are considered in which only **A**·**B** and **B**·**C** (but not **A**·**C**!) contacts can take place. In strong segregation these interactions enter into F_{interf} via two coefficients of interfacial tension, $\gamma_{A/B}$ and $\gamma_{B/C}$.

The conformational contribution of chains forming the elements of a mixed superstucture is calculated on the basis of the well-developed polymer brushes theory. In the case of binary **ABC+ab** and ternary **ABC+ab+bc** mixed superstructures, the components are mixed on the molecular level. As a characteristic of the mixture composition, the quantities

$$f_1 = \frac{N_{ab}}{N_{ab} + N_{ABC}} \text{ and } f_2 = \frac{N_{bc}}{N_{bc} + N_{ABC}} \qquad (1)$$

will be used. These parameters and such characteristics of the components as blocks lengths and local characteristics (l_i – Kuhn segment length and a_i – monomer thickness of i-th block, i=**A**, **B**, and **C**) determine F_{conf}.

Results and discussion

Let us discuss the formation of a mixed lamellar superstructure from lamellae-forming tri- and diblock copolymers. The possibility of changing the initial lamellar morphology upon mixing will be considered below.

Lamellae-forming ***ABC*** *and* ***ab****: limited capacity of mixed lamella*

The solution of the problem of mixed superstructure formation implies answering the following question: can the **ABC** lamella ("host") accept the molecules of the **ab** diblock copolymer ("guests")? A detailed analysis of this problem is given in 9). Conformational free energy was calculated using a simple box (Alexander – de Gennes) model 11, 12) and the analytical self-consistent field (SCF) theory 1, 13, 14) of planar polymer brushes. Both these approaches gave qualitatively the same results: the "host" **ABC** superstructure can accept only a limited number of **ab** molecules. The box model allow us to obtain analytical estimation of this limiting value

$$f_1^{*(\mathrm{box})} = 1 - \left(\frac{\gamma_{\mathrm{B/C}}}{\gamma_{\mathrm{A/B}}} \frac{X_{\mathrm{ab}}}{X_{\mathrm{ABC}} - X_{\mathrm{ab}}} \right)^{1/3} \tag{2}$$

$$\text{where } X_{\mathrm{ABC}} = X_{\mathrm{A}} + X_{\mathrm{B}} + X_{\mathrm{C}},\ X_{\mathrm{ab}} = X_{\mathrm{a}} + X_{\mathrm{b}},\ \text{and } X_i = \frac{N_i a_i^5}{l_i}\ (i = \mathbf{A}, \mathbf{B}, \text{and } \mathbf{C}) \tag{3}$$

and the free energy of mixing was neglected (it can be done if the blocks are relatively long: $N_i >> 1$). The value of $f_1^{*(\mathrm{box})}$ is slightly lower than the real value of f_1^*. Hence, one can be sure that in the range of mixture composition $0 \le f_1 \le f_1^{*(\mathrm{box})}$ a single mixed superstructure will be formed in the mixture of two lamellae-forming components.

At a high diblock content in the mixture, phase separation into two microphase-segregated systems occurs. One of them is a "saturated" mixed lamella with the composition f_1^*. The other is a pure diblock lamella formed by an excess of the **ab** diblock.

It should be noted that if the values of the parameters satisfy the following inequality:

$$\frac{\gamma_{\mathrm{B/C}}}{\gamma_{\mathrm{A/B}}} < \frac{X_{\mathrm{ABC}} - X_{\mathrm{ab}}}{X_{\mathrm{ab}}}, \tag{4}$$

Eq. (2) gives meaningless value of $f_1^{*(\mathrm{box})} < 0$. This means that the diblock copolymer virtually does not mix with the triblock copolymer so that both of them form their individual lamellae in the mixture. The critical role of the $k = \gamma_{A/B}/\gamma_{B/C}$ ratio can be seen from Eqs. (2) and (4): higher interfacial tension at the **A/B** interface will favour the mixing of **ABC** with **ab**.

Lamellae-forming ABC, ab, and bc: cooperative incorporation of diblocks into the mixed lamella

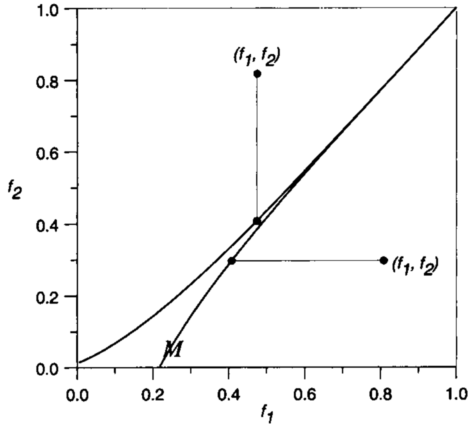


Fig. 2. Typical phase diagram of ternary mixture

A detailed analysis of this system is presented in ref. [10]. In contrast to the binary mixture **ABC+ab**, the presence of three components will always lead to the mixing of **ABC** with **ab** and/or **bc**. Fig.2 shows a typical example of the region of compositions of ternary mixed lamellae *M*.

The explanation of the behaviour of the ternary mixture with the aid of the diagram in Fig. 2 is rather simple. If the point (f_1, f_2) characterizing the composition of the prepared mixture falls within the region of composition *M*, all components form a single mixed lamellar superstructure with the same composition (f_1, f_2). If the point (f_1, f_2) lies above (or below) the composition region, all molecules of the **ab** (or the **bc**) diblock copolymer are incorporated into mixed lamellae, whereas only some of the **bc** (or the **ab**) molecules are in the mixed lamellae. It can be said that the **ABC/ab/bc** mixed lamella has a limited capacity with respect to the **bc** (or the **ab**) diblock copolymer but this capacity depends on the **ab** (or the **bc**) content. The addition of some amount of the **ab** (or the **bc**) diblock copolymer to the mixture will result in an increase of both diblock copolymers content in the mixed lamella and a decrease of the number of the **bc** (or the **ab**) diblock copolymer molecules in the pure phase. In this way the effect of cooperative incorporation of **ab** and **bc** diblock copolymers into ternary mixed lamella is manifested.

Lamellae- and cylinder-forming ABC and ab: changes of the initial morphology upon mixing

Now the second (and the main) problem stated in the Introduction will be discussed. Consider again the binary mixture **ABC+ab**. We will not restrict ourselves only to lamellae-forming components and lamellar superstructures. **ABC** triblock and **ab** diblock copolymers and their mixtures forming superstructures with cylindrical morphologies will also be taken into account (Figs. 3, 4, and 5). Moreover, only the **ABC** and the **ab** block copolymers with $N_A=N_a$ and $N_B=N_b$ will be considered. This situation can occur owing to incomplete triblock copolymer formation in the **ab+c→ABC** stage of the triblock synthesis. In addition, mixing free energy is neglected again.

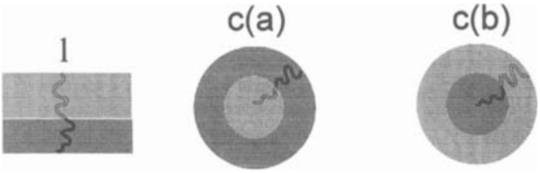


Fig. 3. Elements of pure diblock copolymer superstructures.

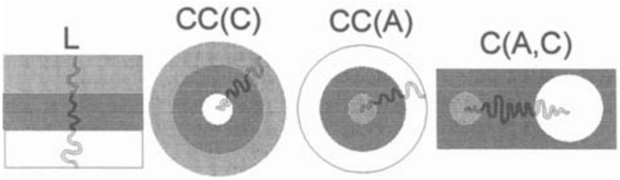


Fig. 4. Elements of pure triblock copolymer superstructures.

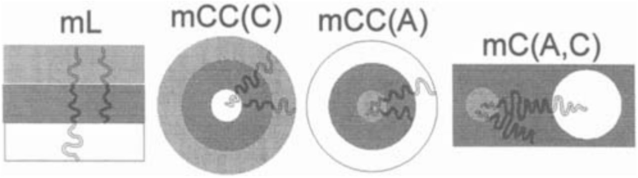


Fig. 5. Elements of mixed superstructures.

The analysis of this system has shown that its behaviour depends on the parameters of the block copolymers, as was already demonstrated for the case of lamellae forming **ABC** and **ab**. Let us focus on two interesting cases (Figs. 6 and 7). When the **ab** diblock is added to the **ABC** triblock copolymer in a small amount, it binds a definite amount of this copolymer to form the mixed superstructure. However, the morphology of this mixed superstructure is different from that of both pure **ABC** and **ab** copolymers! No initial superstructures can play the role of "host". Moreover, two opposite cases are possible: the formation of a mixed **mCC(C)** superstructure from two lamellae-forming **ABC** and **ab** block copolymers (Fig. 6), and the formation of the lamellar superstructure **mL** from two individual di- and triblock copolymers with cylindrical domains. When the amount of added **ab** is rather low, it can bind only a portion of **ABC** so that the rest of **ABC** still remains in the phase of its pure morphology. Hence, one can observe pure triblock and mixed superstructures (phases) coexisting in the mixture. Increase in the number of diblock molecules in the mixture will lead to complete binding and the disappearance of the pure triblock phase. All molecules will form mixed superstructures with new morphology. When the **ab** diblock content increases, the well-known effect of limited capacity of binary mixed superstructure with respect to **ab** diblock copolymer will be observed and the excess of **ab** will form its own pure phase.

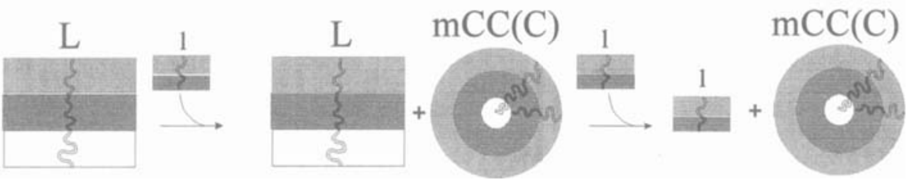


Fig. 6. Mixing of lamellae-forming tri- and diblock copolymers leading to the formation of cylindrical **mCC(C)** superstructure.

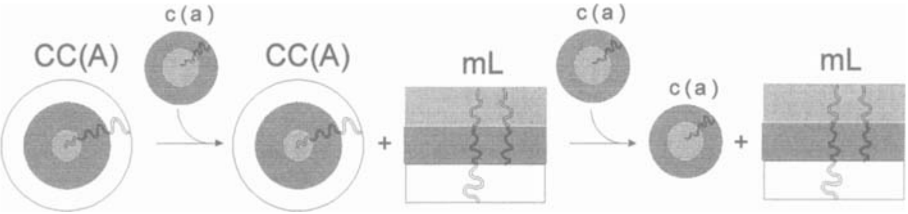
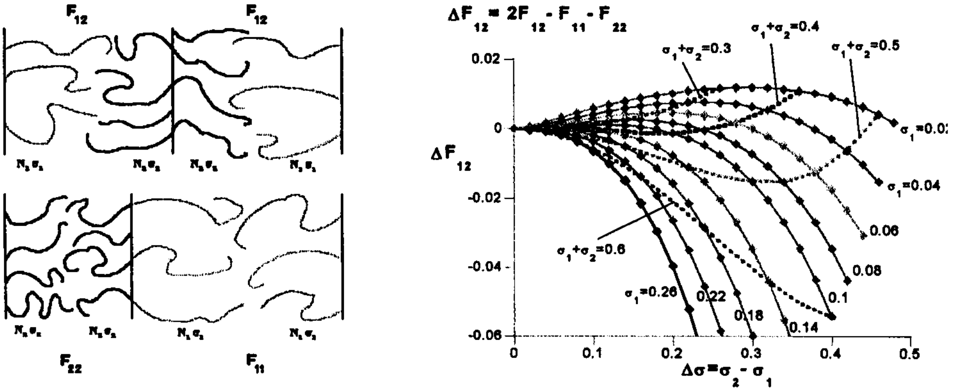


Fig. 7. Mixing of cylinders-forming tri- and diblock copolymers leading to the formation of lamellar superstructure

*Lamellae-forming **ABC** and **ac**: interpenetration of lamellae*

Because **ABC** and **ac** diblock copolymers form different interfaces in the pure lamellae (**A/B** and **B/C** in the pure **ABC** lamella and **A/C** in the pure **ac** lamella) they cannot mix on the molecular level. However, it is worth while to consider the arrangement of **ABC** and **ac** lamellae in this mixture. In the condition of complete segregation of two microphase-segregated structures, both superstructures, **...ACCBAABCCBA...** and **...accaacca...** have a centre of symmetry. The experiment has shown the existence of non-centrosymmetric structures: **...ABCcaABCcaABCca...** and theoretical estimations have established their thermodynamic preference [15)]. Since these estimations were based on some approximations, we carried out a direct calculation of the free energy of individual lamellae on the basis of the polymer brush concept. Mixed and individual lamellae are different in the type of oppositely directed brushes. In the centrosymmetric lamellar structures the brushes **...AA...**, **...CC...**, **...aa...**, and **...cc...** are brought into contact, i.e. in the all these cases both contacting brushes are completely equivalent (they consist of chains with equal lengths grafted at the same density). In the non-centrosymmetric structure the contacting brushes are **...Aa...** and **...Cc...**, i.e. they can differ both in chain length and grafting density. Hence, the model system of four brushes formed by the same polymer is considered (Fig. 8a). Two brushes of type 1 consist of chains with N_1 units grafted at a density σ_1, two brushes of type 2 consist of chains with N_2 units grafted at a density σ_2. The difference ΔF_{12} in the free energies for two variants of brush contact in the system was calculated by using SCF calculations [16)].



a b

Fig. 8. Contacting brushes in the **ABC+ac** mixture (a). Freeenergy of interpenetration (b).

The dependences of ΔF_{12} on $\Delta\sigma = \sigma_1 - \sigma_2$ for the case $N_1 = N_2$ are presented in Fig. 8b. Solid lines corresponds to different σ_1, dotted lines corresponds to $\sigma_1 + \sigma_2 = \text{const}$. As can be seen from Fig. 8b, ΔF_{12} is negative as a rule, although it is very small. The exceptions are the cases of very small σ_1, but the analysis shows that with increasing N, ΔF_{12} becomes less than zero. Hence, the difference in the grafting densities of oppositely directed and contacting brushes is the factor favouring the non-centrosymmetric packing of **ABC** and **ac** lamellae.

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