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Order-disorder- and order-order-transitions in AB and ABC block copolymers: description by a simple model

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Summary

Based on the description of AB-block copolymers as micellar structures given by Semenov, the phase diagram of AB-diblock copolymers is calculated taking the homogeneously mixed system as a reference state. The predicted value $(\chi N)_c=10.385$ for a symmetric AB-diblock copolymer compares very well to the result of the original Random Phase Approximation theory (10.495). The simplicity of the model allows its extension to predict order-order transitions in ABC-triblock copolymers.

Introduction

During the last two decades a lot of work has been done in the field of AB-diblock and ABA-triblock copolymers[1-6]. Much less attention was given to triblock copolymers with three different components[7-12]. It has been shown that in comparison to diblock copolymers, microphase separated ABC-triblock copolymers exist in many more morphologies. Furthermore, the sequence of the three blocks plays an important role in morphology control, if the thermodynamic interactions and/or the geometric requirements of the different pairs are sufficiently different. Meier[13] and Helfand & Wasserman[14-16] did basic theoretical work to describe the free energy of diblock copolymers in the so-called "strong-segregation"-limit. Later on Semenov gave a description of diblock copolymers accounting for both elastic and interfacial contributions to the free energy[17] based on former work by Alexander[18] and de Gennes[19] on polymers attached to surfaces. Following these ideas, descriptions of the free energy of triblock copolymers were given[11,12]. In this paper we will extend the model given before[11] to include partially mixed triblock copolymer morphologies, i.e. where two of the three blocks become miscible while being still microphase separated from the third one. This will be shown for the example of "symmetric" ABC-triblock copolymers where the volume fractions of A and C are equal and A and C become miscible. The necessary extension of the previous model is based on the inclusion of the free energy of mixing of the AC-phase, which will be given by a modified Flory-Huggins-Staverman[20-22] (FHS) approach. Before discussing the triblock copolymers, this simple model will be applied to diblock copolymers and its predictions will be compared with the original "weak-segregation"-theory[23].

Results and Discussion

Order-disorder transition in AB-diblock copolymers

The condition for the occurrence of a microphase separated structure in a block copolymer can be written as

(1) $$F_M - F_{mix} < 0$$

F_M is the free energy of the block copolymer arranged in ordered microdomains while F_{mix} is the free energy of the mixed system.

At the order-disorder transition (ODT) F_M equals F_{mix}. The system is treated to be incompressible, i.e. the total volume V_{tot} is given by the sum over all segmental volumes v_i

(2) $$V_{tot} = \sum_i N_i v_i$$

with N_i being the degree of polymerization of block i. In the following all energies are normalized by kT and entropies by k. The free energy of the mixed phase is given by

(3) $$F_{mix} = H_{mix} - T \cdot S_{mix}$$

where the enthalpic part given by the FHS-approach

(4) $$H_{mix} = N\phi_i\phi_j\chi_{ij}$$

$\phi_{i,j}$ are the volume fractions, N is the degree of polymerization of the whole chain and χ_{ij} is the segmental interaction parameter. The entropic contribution can not be given by the simple FHS-approach, due to the connectivity of the different blocks. Since the entropy of mixing becomes negligible for large N, we consider the ODT of diblock copolymers only in this limit:

(5) $$\lim_{N \to \infty} S_{Diblock}^{mix} = 0$$

To describe the free energy of the microphase separated system, only the energy associated with a single micelle is considered. The two contributions to the free energy of a certain morphology F_M are the surface energy F_M^{surf} and the elastic energy F_M^{elast}. F_M^{surf} is given by the product of the surface tension γ_{ij} and the interfacial area per chain, Σ_{ij}:

(6) $$F_M^{surf} = \sum_{i,j} \gamma_{ij}\Sigma_{ij}$$

The relationship between surface tension γ_{ij} and the segmental interaction parameter χ_{ij} is taken from the work of Helfand and Wasserman[15],

(7) $$\gamma_{ij} = \frac{\chi_{ij}^{1/2}}{(v_i v_j)^{1/4}} \cdot \frac{1}{2 \cdot 6^{1/2}} \cdot \left[a_i^{-1/2} + a_j^{-1/2} + \frac{1}{3} \cdot \frac{(a_i^{-1/2} - a_j^{-1/2})^2}{a_i^{-1/2} + a_j^{-1/2}} \right]$$

where a_i is the segmental length of component i. In this simple treatment we neglect contributions to the free energy by a finite interface thickness. Such contributions have been discussed by Semenov[24]. The elastic energy is related to the entropy of the block i:

(8) $$F_M^{elast} = \sum_i \frac{3}{2 \cdot a_i^2} \int \frac{dr}{dN} dr$$

with dr being the incremental change of the domain size R. Both F_M^{surf} and F_M^{elast} depend on the periodicity of the microphase separated lattice. To perform the free energy minimization the surface and the elastic contribution to F_M have to be expressed in terms of a single parameter which describes the spatial extension of the system as a function of N. All other dimensions are geometrically related to it. If R_B is used as the characteristic dimension (R_B being the half thickness of a B-lamella, or the radius of a B-cylinder or a B-sphere), F_M^{surf} and F_M^{elast} write as

$$(9) \qquad F_M^{surf} = \frac{N_B v_B}{R_B} \cdot K_M^{surf}$$

$$(10) \qquad F_M^{elast} = \frac{R_B^2}{N_B} \cdot K_M^{elast}$$

where K_M^{surf} and K_M^{elast} are constants at a given set of volume fractions ϕ_i, the chain parameters a_i, v_i and the surface tension γ (Tab. 1).

Upon minimization of the free energy with respect to R_B ($\frac{\partial F_M}{\partial R_B} \equiv 0$), R_B of the morphology can be determined and by substituting it into eqs. 9 and 10 the minimized free energy of the morpholgy is obtained[11]:

$$(11) \qquad F_M = \frac{3}{2} \cdot (2 \cdot N_B \cdot K_M^{elast})^{1/3} \cdot (v_B \cdot K_M^{surf})^{2/3}$$

The spinodal between disordered phase and ordered morphology is then given by

$$(12) \qquad F_M - F_{mix} = 0$$

Comparison of the model's prediction for diblock copolymers with the RPA theory

The Random Phase Approximation (RPA) applied by Leibler to the order-disorder transition of diblock copolymers predicts a critical value for the transition between the disordered to the ordered lamellar state for a symmetrical diblock copolymer (ϕ_B=0.5) at $(\chi N)_c \approx 10.5$, which is supposed to be a second order transition[23]. To compare this value with the simple model presented here, the product χN is determined from eq. 12 assuming infinite large N, $a_i = 1$ and $v_i = a_i^3$ (Fig. 1).

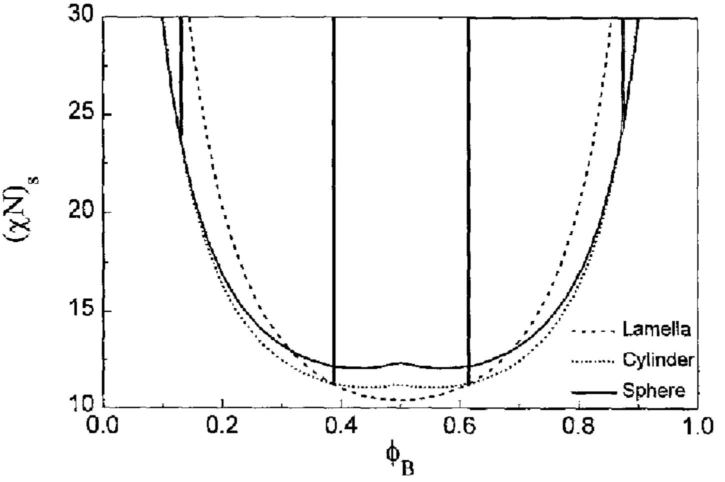

Fig. 1: Spinodals of typical diblock copolymer morphologies from eq. 12.

Table 1: Surface and elastic energy coefficients for different diblock copolymer morphologies:

Morphology	K_M^{surf}	K_M^{elast}
Lamellae (l)	γ_{AB}	$\frac{3}{2}\left(\frac{1}{a_B^2}+\frac{1-\phi_B}{\phi_B}\cdot\frac{v_A}{v_B a_A^2}\right)$
B-Cylinders in A-Matrix (c)	$2\gamma_{AB}$	$\frac{\pi^2}{16\cdot a_B^2}-\frac{3}{8}\cdot\ln(\phi_B)\cdot\frac{v_A}{v_B a_A^2}$
B-Spheres in A-Matrix (s)	$3\gamma_{AB}$	$\frac{3\pi^2}{80\cdot a_B^2}+\frac{1}{2}\cdot(1-\phi_B^{1/3})\cdot\frac{v_A}{v_B a_A^2}$

Table 2: Surface and elastic energy coefficients for different triblock copolymer morphologies:

Morphology	K_M^{surf}	K_M^{elast}
Lamellae (ll)	$\frac{1}{2}(\gamma_{AB}+\gamma_{BC})$	$6\left(\frac{1}{a_B^2}+\frac{\phi_A}{\phi_B}\cdot\frac{v_A}{v_B a_A^2}+\frac{\phi_C}{\phi_B}\cdot\frac{v_C}{v_B a_C^2}\right)$
Lamellae with AC-Mixture (ml)	$\frac{1}{2}(\gamma_{AB}+\gamma_{BC})$	$6\left(\frac{1}{a_B^2}+\frac{\phi_A}{\phi_B}\cdot\frac{v_A}{v_B a_A^2}+\frac{\phi_C}{\phi_B}\cdot\frac{v_C}{v_B a_C^2}\right)$
B-Cylinders at AC-Lamellae Interphase (lc)	$\gamma_{AB}+\gamma_{BC}+$ $\gamma_{AC}\cdot\left(\frac{1}{(\pi\phi_B)^{1/2}}-\frac{2}{\pi}\right)$	$\frac{3\pi^2}{8\cdot a_B^2}-\frac{3}{2}\cdot\ln(\phi_B)\cdot\left(\frac{\phi_A}{1-\phi_B}\cdot\frac{v_A}{v_B a_A^2}+\frac{\phi_C}{1-\phi_B}\cdot\frac{v_C}{v_B a_C^2}\right)$
B-Cylinders in AC-Mixture (mc)	$\gamma_{AB}+\gamma_{BC}$	$\frac{\pi^2}{4\cdot a_B^2}-\frac{3}{2}\cdot\ln(\phi_B)\cdot\left(\frac{\phi_A}{1-\phi_B}\cdot\frac{v_A}{v_B a_A^2}+\frac{\phi_C}{1-\phi_B}\cdot\frac{v_C}{v_B a_C^2}\right)$
B-Spheres at AC-lamellae Interphase (ls)	$\frac{3}{2}(\gamma_{AB}+\gamma_{BC})+$ $\gamma_{AC}\cdot\left(\frac{3^{1/2}}{2\pi^{1/3}\phi_b^{2/3}}-\frac{3}{4}\right)$	$\frac{8}{3\cdot a_B^2}+2\cdot(1-\phi_B^{1/3})\cdot\left(\frac{\phi_A}{1-\phi_B}\cdot\frac{v_A}{v_B a_A^2}+\frac{\phi_C}{1-\phi_B}\cdot\frac{v_C}{v_B a_C^2}\right)$
B-Spheres in AC-Mixture (ms)	$\frac{3}{2}(\gamma_{AB}+\gamma_{BC})$	$\frac{3\pi^2}{20\cdot a_B^2}+2\cdot(1-\phi_B^{1/3})\cdot\left(\frac{\phi_A}{1-\phi_B}\cdot\frac{v_A}{v_B a_A^2}+\frac{\phi_C}{1-\phi_B}\cdot\frac{v_C}{v_B a_C^2}\right)$

For infinite high molecular weight at $\phi_B = 0.5$ the result is $(\chi N)_c \approx 10.39$, which is rather close to the original RPA-prediction. Furthermore the transitions from lamellar to cylindrical and cylindrical to spherical morphology are located at $\phi_B \approx 0.385$ and 0.126, respectively. This is in reasonable agreement with experimental results on poly(styrene-block-isoprene) diblock copolymers[5].

Order-order transitions in "Symmetric" ABC-triblock copolymers with miscible end blocks

In ABC triblock copolymers various situations related to mixing of blocks may occur. Similar to the ODT in AB respectively ABA block copolymers an ordering transition from the completely homogeneous melt to an ordered state may be considered. However there also exist various possibilities for order-order transitions. Here we consider the cases of symmetric ABC triblock copolymers ($\phi_A = \phi_C$), where A and C may form a mixed phase. For example such a transition can occur between the following morphologies: "cylinder at lamellae interface" (lc) and "cylinder in mixed matrix" (mc); "sphere at lamellae interface" (ls) and "sphere in mixed matrix" (ms), "demixed lamellae" (ll) and "partially mixed lamellae" (ml). An example is shown in Fig. 2.

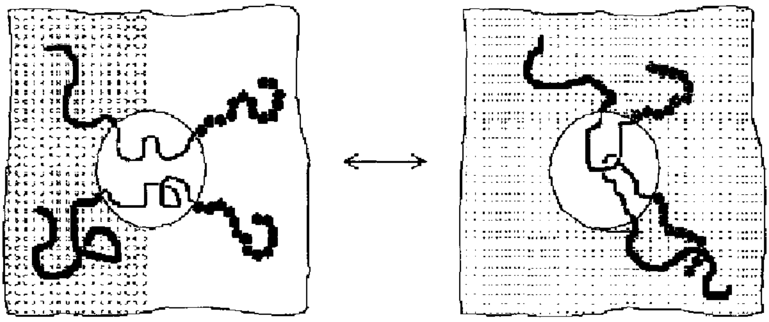

Fig. 2: Transition between (lc) and (mc) morphology

As done in the case of the diblock copolymers, we again consider only systems with a repulsive binary interaction, i.e. $\chi > 0$. This means that the enthalpic interactions between the A- and C-block stay repulsive throughout the following discussion.

One driving force for A and C to become miscible is the gain of mixing entropy on the interface with the B-block. Furthermore, the elastic energy of the B-chain is reduced significantly in case of spherical or cylindrical B-domains, when A and C form a single phase, because the B-chain has more conformational freedom (the two block junction points both can be located anywhere on the B-interface within an elemental volume of the morphology, when A and C are mixed). More conformational freedom means a smaller elastic contribution to the free energy of the B-block. In total the miscibility between A and C is controlled by the balance between repulsive segmental interactions between A and C, the gain of entropy at the interface to B and, in the case of the (ls)→(ms) and (lc)→(mc) transitions discussed here, the reduction of elastic energy of the B-chain. While in an AC-separated system the AB- and BC-junction points are placed in a regular order (each on the surface of a half sphere or half cylinder or different lamellae interfaces), these junction points can be located randomly on the cylinder or sphere surface in the AC-mixed state. Thus only the entropy change of the sphere, cylinder or lamellae surface has to be considered in a first approximation, which is the problem of arranging two kinds of segments on a two-dimensional lattice. The connectivity of the chain is here of no importance, since the conformational entropy is acounted for in the elastic part of the free energy. In this case the entropy gain of the system is given by:

$$\text{(13)} \qquad T \cdot S^{AC-mix}_{triblock} = -\frac{\phi_A}{\phi_A+\phi_C} \cdot \ln\left(\frac{\phi_A}{\phi_A+\phi_C}\right) - \frac{\phi_C}{\phi_A+\phi_C} \cdot \ln\left(\frac{\phi_C}{\phi_A+\phi_C}\right)$$

As before it will be assumed that all segmental lengths are the same ($a_i = 1$) and the segmental volumes are given by $v_i = a_i^3$. Dissimilarities in segmental lengths and volumes will have an influence on the free energy, as has been shown also by Lyatskaya et al.[12] for some ABC mircrophase morphologies.

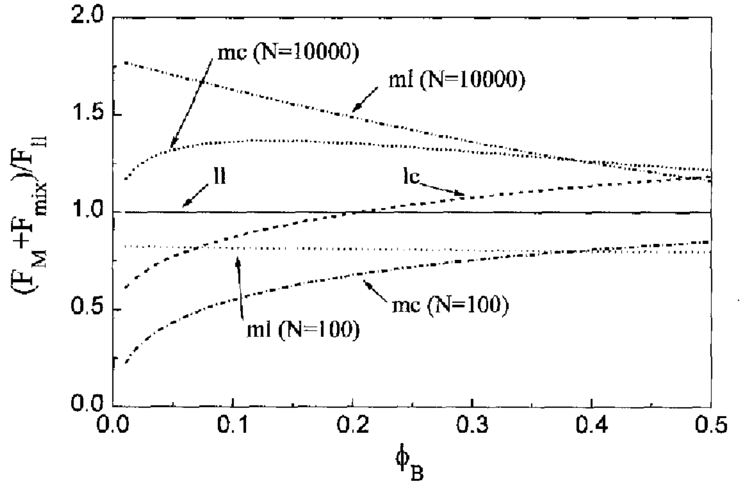

Fig. 3: Normalized free energy of different morphologies of symmetric ABC-triblock copolymers for two different chain lengths, $\chi_{AB} = \chi_{BC} = 0.05$, $\chi_{AC} = 0.005$

The free energy of the fully segregated (ll, lc) and partially mixed (ml, mc) morphologies are shown in Fig. 3 for $\phi_A = \phi_C$. The free energies are normalized with respect to the (ll)-morphology (again F_M contains surface and elastic contributions while F_{mix} is the free energy of mixing of the AC-phase). For N = 100 the free energy of the (ml)- and (mc)-morphologies (A,C mixed) are below F_{ll} and F_{lc}. The latter are independent of N in this reduced representation. For N = 10000 the morphologies with all three components being segregated are more stable. The transition occurs around N = 2000 (Fig. 4). At this chain length a sequence of morphologies (ml) → (ll) → (mc) → (lc) → (ms) is predicted when reducing ϕ_B from 0.5 to 0.05. This reflects the different contributions to the free energy (Tab. 2). Independent of the choice of the different interaction parameters, the transitions between (ms)- and (mc)-morphology and (mc)- and (ml)-morphology occur at the same ϕ_B as in the case of AB-diblock or symmetric ABA triblock copolymers ((s) ↔ (c) ↔ (l)).

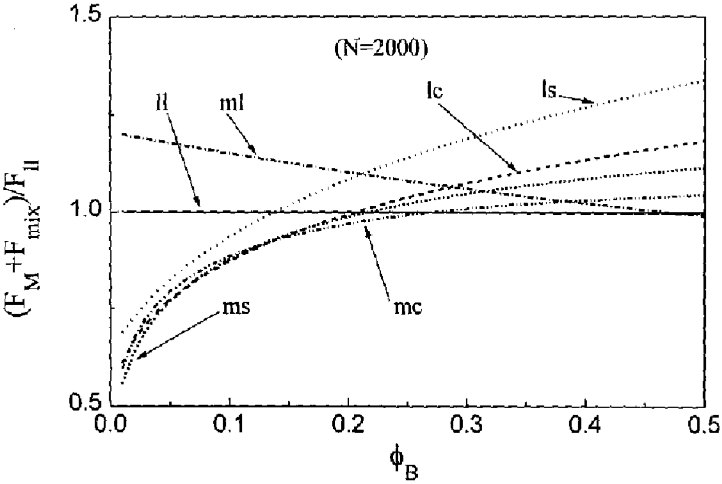

Fig. 4: Normalized free energy of different morphologies of symmetric ABC-triblock copolymers for a chain length of N=2000, $\chi_{AB} = \chi_{BC} = 0.05$, $\chi_{AC} = 0.005$

While in case of diblock copolymers the free energy of the chains can be described in terms of $(\chi N)_S$, three binary interactions have to be considered in ABC-triblock copolymers. The transition between two morphologies may be studied as a function of ϕ_B. In Fig. 5 this is shown for the transition between the (lc)- and (mc)-morphology. The smaller the interaction between A and C-block, the larger is the stability region of the (mc)-morphology. It must be noted that the stability limit for morphologies in which B forms cylinders is restricted to the range of approximately $0.1 < \phi_B < 0.35$. Beyond these limits spherical or lamellar morphologies have to be considered.

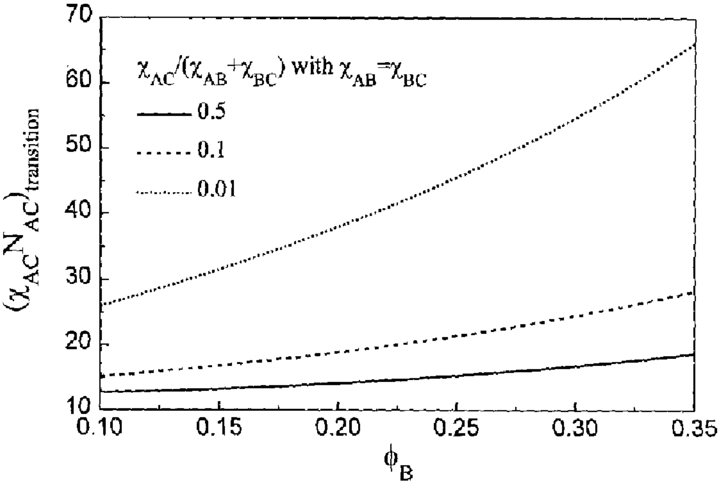

Fig. 5: Transition from (lc)- to (mc)-morphology of a symmetric ABC-triblock copolymer

While here it was found for ABC-triblock copolymers that a center B-block may enhance miscibility between the A- and C-end blocks, the situation is different for BAC-triblock copolymers. There the B-endblock hinders miscibility between A and C, because miscibility between A and C leads to an increasing elastic energy of these blocks (C chains have to swell A-chains which are attached at the B-interface). Experimental results on such a system are given elsewhere[25].

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