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# Domains in Melts of Comb−Coil Diblock Copolymers: Superstrong Segregation Regime

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ABSTRACT: Conditions for the crossover from the strong to the superstrong segregation regime are analyzed for the case of comb−coil diblock copolymers. It is shown that the critical interaction energy between the components required to induce the crossover to the superstrong segregation regime is inversely proportional to $m_b = 1 + n/m$, where $n$ is the degree of polymerization of the side chain and $m$ is the distance between successive grafting points. As a result, the superstrong segregation regime, being rather rare in the case of ordinary block copolymers, has a much better chance to be realized in the case of diblock copolymers with combs grafted to one of the blocks.

## 1. Introduction

Microphase separation in copolymers of immiscible polymer components A and B has been an area of intensive research over the past decades.[1−6] Theories have been developed to deal with the different regimes that can be distinguished, e.g., weak, strong, and intermediate segregation regime. Apart from these more common regimes, it was found that in the case of extremely strong immiscibility between the components of a diblock copolymer with one block (e.g., A chains) being rather small, the behavior of the system changes qualitatively from that of the usual strong segregation regime: a superstrong segregation regime emerges.[7] In this regime the A chains become practically completely extended within the corresponding microdomain. Calculations and experimental studies show that the superstrong segregation regime is not characteristic for ordinary block copolymers; however, it can be used for the description of aggregates and multiplets in associating polymers.[8]

These results apply for linear block copolymers. But recently, interest has shifted to the nature of the microphase-separated structures of block copolymers of a more complex linear[9,10] and nonlinear architecture.[6,11,12] For this paper comb−coil diblock copolymers consisting of a nonlinear comb copolymer block and a linear block will be of direct interest. A peculiar subset of these kind of systems, where the side chains are not covalently bonded but attached by strong physical interactions (hydrogen bonding and ionic bonding), have been studied in detail recently.[13−15] In this paper we consider the microphase formation in a melt of comb−coil diblock copolymers and study the conditions for the crossover from the strong to superstrong segregation regime.

## 2. Results and Discussion

We will consider the microdomain structure formed by comb−coil diblock copolymers consisting of a comb-like A block and a linear B block (see Figure 1). The main characteristic parameters of the A block are the degree of polymerization of the backbone $N_A$, the degree of polymerization of the side chains $n$, and the number of monomer units between the grafting points $m$. The B block is characterized by a single parameter $N_B$ which is the degree of polymerization of this block.

In correspondence with the main objective of this paper, let us assume that the monomer units of the A blocks are incompatible with the monomer units of the B blocks and that the immiscibility between the A and B blocks is strong enough to make a narrow interface between the A and B phases; i.e., the structure formed corresponds to the strong segregation limit.

**Spherical Micelles.** Let us first assume that $N_A \ll N_B$ and that the A blocks (as minority component) form spherical micelles with radius $R$ and aggregation number $Q$.

In ref 2 it was shown that in the strong segregation regime of ordinary block copolymers with immiscible linear A and B blocks both the A chains within the spherical micelles and the B chain parts in the region close to the micellar core are significantly stretched. This is the case for the system under consideration as well.

To estimate the aggregation number $Q$ and the radius of micelle $R$, let us consider the free energy $F$ of the system. This free energy can be presented as a sum of three terms:

$$F = F_{\mathrm{surf}} + F_{\mathrm{conf-A}} + F_{\mathrm{conf-B}} \tag{1}$$

where $F_{\mathrm{surf}}$ is the free energy of the micellar interface and the contributions $F_{\mathrm{conf-A}}$ and $F_{\mathrm{conf-B}}$ are due to the losses in conformational entropy of A and B chains.

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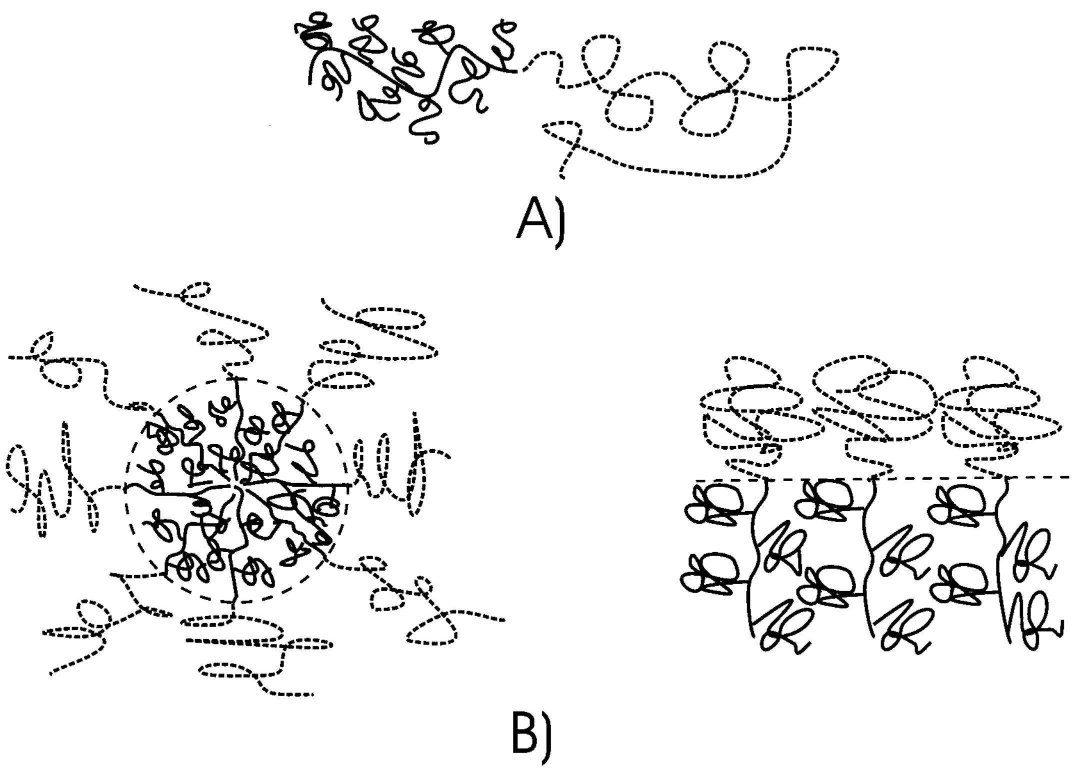

**Figure 1.** Schematic presentation of comb–coil diblock copolymer (A) and the superstrong segregated microstructure that may be formed by such macromolecules (B).

The interfacial free energy $F_{\mathrm{surf}}$ can be written as

$$F_{\mathrm{surf}} = 4\pi\gamma \frac{R^2 N}{Q} \tag{2}$$

where $N$ is the total number of chains in the system and $\gamma$ is the interface tension coefficient determining the degree of immiscibility of A and B blocks. The contribution $F_{\mathrm{conf-B}}$ describes the loss in conformation entropy of the linear B blocks. These losses are caused by the expansion of B chains in the interfacial region due to the high density of B chains in the neighborhood of the surface of A micelles. As shown in ref 7, the contribution $F_{\mathrm{conf-B}}$ can be written as

$$F_{\mathrm{conf-B}} = \frac{3}{8\pi}\frac{kT}{R^2}\frac{v_{\mathrm{B}}}{l_{\mathrm{B}} a_{\mathrm{B}}} NQ \tag{3}$$

Here $l_{\mathrm{B}}$, $a_{\mathrm{B}}$, and $v_{\mathrm{B}}$ are the Kuhn segment length, the length, and the volume of the monomer units of the B chains, respectively.

Finally, $F_{\mathrm{conf-A}}$ is the conformational free energy of the A blocks. Generally speaking, the term $F_{\mathrm{conf-A}}$ includes two contributions: a contribution from the conformational entropy of the backbone chain and one from the conformational entropy of the side chains, assuming, as we will, that the backbone monomer units and the monomer units of the side chains have no energetic interaction with each other. Because of the well-known Flory theorem,[16,17] the excluded-volume interactions are screened within the A micelle. As a consequence, the side chains have a conformation close to that of an ideal chain, and the following analysis shows that their conformations remain close to ideal even in the case of dense grafting of side chains (up to $m \sim 1$). To see this, we assume that the side chains form a dense tube with radius $D$ around the backbone. Equating the volume per single side chain, which is at least $D^2 m^{1/2} a$, with the total volume of the monomer units of a side chain, $na^3$, gives $D \sim n^{1/2}a/m^{1/4}$. This latter represents the minimum value of $D$ required to accommodate the side chains. Since this value is smaller than $n^{1/2}a$ up to $m \sim 1$, the conformation of the side chains will remain close to ideal. It implies that for $m \geq 1$ the contribution to the free energy due to elastic deformation of the side chains is negligible in comparison to the contribution of backbone of A chains.

Thus, the free energy $F_{\mathrm{conf-A}}$ includes only the elastic free energy contribution of the A backbone chains. In the simplest way this term can be written as the free energy of expansion of a backbone chain with $N_{\mathrm{A}}$ units multiplied by the total number $N$ of polymer chains in the system:

$$F_{\mathrm{conf-A}} \sim kTN \frac{R^2}{N_{\mathrm{A}} a_{\mathrm{A}} l_{\mathrm{A}}} \tag{4}$$

where $l_{\mathrm{A}}$ and $a_{\mathrm{A}}$ are the Kuhn segment length and monomer unit length of A chain, respectively.

Since in the case under consideration the excluded-volume interactions are screened, the persistence length of the backbone is not expected to increase with increasing density of side chain grafting up to $m \sim 1$ (note that an increase in stiffness of the backbone of comb copolymers immersed in a solvent is caused by excluded-volume interactions between side chains).[3,18,19]

By taking into account the fact that different A chains are expanded differently within the spherical micelle, one can rewrite the contribution (4) as (see ref 7)

$$F_{\mathrm{conf-A}} = \frac{3\pi^2}{80} kTN \frac{R^2}{N_{\mathrm{A}} a_{\mathrm{A}} l_{\mathrm{A}}} \tag{5}$$

The value $R$ of the radius of the A micelle is directly connected to $Q$ by the space-filling condition. For the case where the volume of the monomer units of the backbone $v_A$ is equal to the volume of the monomer units of the side chains, the condition of space filling takes the form

$$\frac{QN_A m_b v_A}{\frac{4\pi}{3}R^3} = 1 \tag{6}$$

where $m_b$ is the number of monomer units of the comb block per monomer unit of the comb backbone chain:

$$m_b = 1 + \frac{n}{m} \tag{7}$$

Using eqs 2−6 together with the notations $s_i = v_i/a_i$ and $L_i = N_i a_i$ ($i$ = A, B) ($s_i$ is the cross section; $L_i$ is the total contour length of corresponding blocks), the total free energy $F$ can be rewritten as

$$F = \left(\frac{36\pi}{s_A L_A}\right)^{1/3} m_b^{2/3}\left[\frac{\gamma}{kT}\frac{L_A s_A}{Q^{1/3}} + \frac{3\pi}{320}Q^{2/3}\frac{s_A}{l_A}\theta\right] \tag{8}$$

where $\theta = 1 + (40/3\pi^2)(s_A l_B/s_B l_A)(1/m_b)$. For the case $s_A \sim s_B$, $l_A \sim l_B$, and $m_b \gg 1$, the value of parameter $\theta$ is close to unity.

Minimization of the free energy $F$, eq 8, with respect to $Q$ gives the equilibrium value for the aggregation number $Q$:

$$Q = \frac{\gamma}{kT}\frac{160}{3\pi}\frac{L_A l_A}{\theta} \tag{9}$$

From eqs 6 and 9 we find for the equilibrium value of the micelle size, $R$

$$R = \left(\frac{\gamma}{kT}\frac{40}{\pi^2}\frac{L_A^2 l_A s_A}{\theta}m_b\right)^{1/3} \tag{10}$$

From eq 9 it is clear that for large values of $m_b$ the aggregation number $Q$ is almost independent of the structural parameters of the coil block B. In this case the parameter $\theta$, which in general depends on $l_B$ and $s_B$, is with high accuracy close to unity. Such a result seems quite natural. As with an increase of $m_b$ the radius of the A micelle $R$ increases (see eq 10), the density of B blocks in the neighborhood of the A micelle and thus the degree of expansion of these blocks drop. As a result, at high enough values of $m_b$, the contribution $F_{\text{conf}-B}$ becomes negligible in comparison with the free energy $F_{\text{conf}-A}$ of the A blocks.

With an increase in the degree of immiscibility $\gamma$, both the aggregation number $Q$ and the radius $R$ of the micelle increase up to the crossover to the superstrong segregation regime where the size of the micelle $R$ becomes comparable with the length $L_A$ of a fully stretched backbone of the A block:[7]

$$R \sim L_A \tag{11}$$

A simple calculation gives the following estimate for the critical value $(\gamma/kT)_{SS}$ at the crossover point to the superstrong segregation regime:

$$\left(\frac{\gamma}{kT}\right)_{SS} \sim \frac{\pi^2}{40}\frac{L_A\theta}{m_b l_A s_A} \tag{12}$$

At $\gamma/kT > (\gamma/kT)_{SS}$ (within the superstrong segregation regime) the size of the micelle $R_{SS}$ is a linear function of the contour length $L_A$ of the A blocks. Also, the aggregation number $Q_{SS}$ no longer increases with a decrease of temperature:

$$R_{SS} = L_A$$

$$Q_{SS} = \frac{4\pi}{3}\frac{L_A^2}{m_b s_A} \tag{13}$$

Equations 12 and 13 demonstrate that both the critical value $(\gamma/kT)_{SS}$ and the aggregation number $Q_{SS}$ in the superstrong segregation regime decrease as a function of $m_b = 1 + n/m$.

The characteristic sizes of the structure $R$ and of the critical value $(\gamma/kT)_{SS}$ for crossover to the superstrong segregation regime in the case of lamellar and cylindrical structures have the same scaling dependencies on $L_A$ and $m_b$ as in eqs 11−13. To show this, we now consider the formation of lamellar structure.

**Lamellar Structure.** In the case of a lamellar structure the free energy $F$ is given (by ignoring all irrelevant numerical factors) as

$$\frac{F}{kT} = \frac{{R_A}^2}{N_A l_A a_A} + \frac{{R_B}^2}{N_B l_B a_B} + \gamma\sigma \tag{14}$$

Here $\sigma$ is surface area of interface between A and B blocks per chain.

The self-consistent space-filling conditions are

$$R_A\sigma = N_A m_b v_A \tag{15}$$

$$R_B\sigma = N_B v_B \tag{16}$$

Minimization of free energy (14)−(16) with respect to $\sigma$ give us the equilibrium value of characteristic size of lamellar structure $R_A$ and $R_B$:

$$R_A \sim \left(\frac{\gamma}{kT}\right)^{1/3}\frac{N_A m_b v_A}{\left(\frac{N_A m_b^2 v_A^2}{l_A a_A} + \frac{N_B v_B^2}{l_B a_B}\right)^{1/3}}$$

$$R_B \sim \left(\frac{\gamma}{kT}\right)^{1/3}\frac{N_B v_B}{\left(\frac{N_A m_b^2 v_A^2}{l_A a_A} + \frac{N_B v_B^2}{l_B a_B}\right)^{1/3}} \tag{17}$$

Let us consider case $N_A m_b v_A \cong N_B v_B$, where the volume fractions of monomer units in the linear and comb blocks are equal to each other. In this case, the thicknesses of the layers of the comb and the linear blocks are equal to each other as well: $R_A = R_B = R$. The period of the structure $R$ is now given by

$$R \sim \left(\frac{\gamma}{kT}\frac{L_A^2 l_A s_A}{\theta_l}m_b\right)^{1/3} \tag{18}$$

where $\theta_l = 1 + l_A s_B/m_b l_B s_A$. For the case of $m_B \gg 1$, the value of $\theta_l$ is close to unity and the period of the structure $R$ is determined by the structural parameters of the comb block only. Analysis shows that in this particular case, as in a case of spherical micelles, the free energy $F$ of elastic deformation of the linear B block is negligible in comparison with elastic free energy of the A block due to the much higher stretching of the comb A block.

The crossover from the strong segregation regime ($R \sim L_A^{2/3}$) to the superstrong segregation regime ($R_{SS} \sim L_A$) proceeds at

$$\left(\frac{\gamma}{kT}\right)_{SS} \sim \frac{L_A\theta_l}{m_b l_A s_A} \tag{19}$$

In the superstrong segregation regime the characteristic period $R$ is determined by the length $L_A$ of the backbone of the comb block, which is much shorter (in the case of high values of $m_b$, see eqs 16−18) than the length $L_B$ of coil block. In this regime period $R$ does not increase with further increase of parameter of immiscibility $\gamma$.

The crossover to the superstrong segregation regime proceeds when the comb block is fully stretched, and in the general case the crossover point depends on the ratio $f = N_A m_b v_A / N_B v_B$ of the volume of monomer units in the comb and the linear blocks:

$$\left(\frac{\gamma}{kT}\right)_{SS} \sim \frac{L_A}{m_b l_A s_A}\left(1 + \frac{1}{f}\frac{l_A s_B}{m_b l_B s_A}\right) \tag{20}$$

At $f > 1$ the conditions for crossover coincides with condition (19), whereas with decrease of parameter $f$ below unity the critical value $(\gamma/kT)_{SS}$ increases.

Note that the eq 20 gives for a wide range of parameter values the same scaling dependence of critical value $(\gamma/kT)_{SS}$ of the crossover to the supercritical regime as eq 12. An increase in the degree of polymerization of the side chain $n$ or a decrease in the distance $m$ between the grafting points leads to softening of the conditions for the crossover from the strong to the superstrong segregation regime. In general, the period of the structure significantly increases with an increase in the degree of polymerization of the side chains or their grafting density.

In conclusion, we see that the possibility to reach the superstrong segregation regime is strongly enhanced for diblock copolymers involving comb blocks.

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