Scaling theory of supermolecular structures in block copolymer–solvent systems: 3. New bitetrahedral superstructure of star-branched block copolymers

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The bitetrahedral (BT) superstructure formed by star-branched block copolymers with a large number of branches has been considered. A model for the description of the BT structure is proposed on the basis of the results of previously developed analytical theory of linear block copolymers and the theory of star-branched homopolymers. On the basis of this model, the equilibrium dimensions of the BT structure are calculated. The results of calculations are compared to experimental data.

INTRODUCTION

In the preceding papers[1,2], the theory of thermodynamic and geometrical characteristics of supermolecular structures of di- and triblock copolymers has been developed. These structures vary from micellar structures in dilute solutions to regular supercrystalline structures with a moderate content or absence of the solvent. Three morphologies of superstructures have been considered. Their existence is determined by the molecular-weight ratio of blocks and the concentration of selective solvent. They are lamellar superstructure, forming when blocks have similar dimensions, and cylindrical or spherical domains, consisting of the minor component and forming hexagonal or cubic lattices, respectively, in the matrix of the major component. These superstructures have been widely investigated in a great number of experimental papers.

Recently[3–5], a new non-canonical type of regular superstructure has been revealed. The authors of refs 3–5 have synthesized star-branched block copolymers consisting of a fixed number of branches $f = 2$ to 18. Each branch was a diblock copolymer of isoprene (inner part of the branch) and styrene (outer part of the branch) with a weight composition 70/30 and a narrow distribution in MW and compositions. Stars with the MW of branches $M_b = (2.3–10) \times 10^4$ have been investigated.

Linear block copolymers with this composition (i.e. single star branches, $f = 1$) form a supercrystalline structure of cylindrical (C) type with long cylindrical domains of polystyrene (PS) in the polyisoprene (PI) matrix. This structure has also been observed[3] in the case of block copolymer stars consisting of a small number of branches $f < f_0 = 6$; for the most investigated sample M_b is 3.3×10^4. At a large number of branches, a new type of supermolecular organization appeared in which both phases, those of PI and PS, are continuous: PS blocks are concentrated in 'broken' cylinders forming

two interpenetrating tetrahedral lattices in a continuous PI matrix[3–5] (*Figure 1*). According to the authors of refs 3–5, this structure will be called bitetrahedral (BT).

It is the aim of the present paper to develop the theory of the superstructure of star-branched block copolymers based on the combination of the theories developed by us previously: the theory of the superstructure of linear diblock copolymers[2] (see also refs 6 and 7), on the one hand, and the theory of star-branched homopolymers[8], on the other. Experimental investigations in refs 3–5 concern a dry polymer, whereas this theory, just as in ref. 2, is developed for the more general case of a concentrated solution of star-branched block copolymers including in the limit the case of a dry polymer.

RESULTS

C structure and stars

Let us represent, as usual[1,2], the conformational free energy of a block copolymer molecule (in the case of a star, that of its branch) in the superstructure in the following form:

$$\Delta F = \Delta F_A + \Delta F_B + \Delta F_s \qquad (1)$$

Here ΔF_A and ΔF_B are the free energies of stretching of a block A in the matrix A (predominant component, PI) and a block B in the domain B (minor component, PS), and the surface energy:

$$\Delta F_s = \gamma \sigma \qquad (2)$$

is determined by the surface area σ per chain and by the properties of the interphase layer (assumed to be narrow) on the domain boundary via the surface tension coefficient γ.

Let us assume as the starting point the fact that in linear ($f = 1$) block copolymers with this composition, the minimum of ΔF corresponds to the C structure of
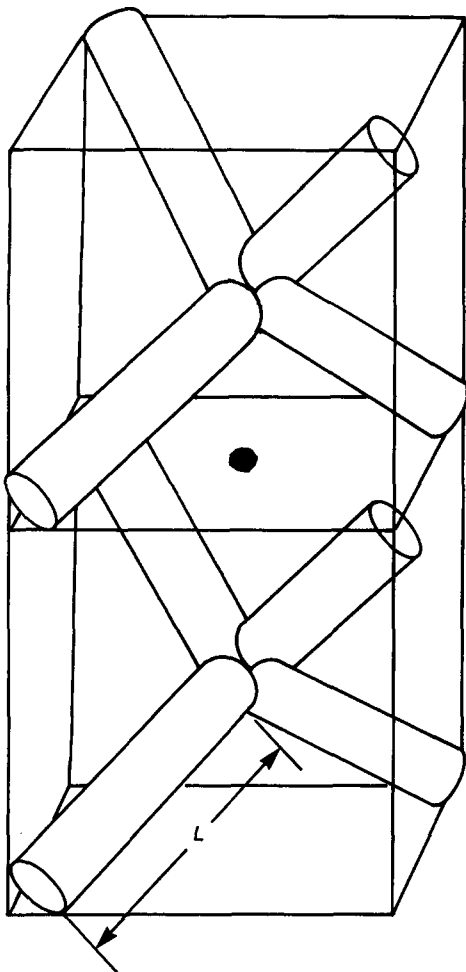
Figure 1 Scheme for a fragment of bitetrahedral structure formed by star-branched polymer. The centre of the superstar is shown by a point

the domains. In this structure[2] we have:

$$\Delta F_A = \frac{3}{8} \frac{R^2 c_B^{1/4}}{l^2 N_B} kT \ln\left(1 + \frac{N_A c_B}{N_B c_A}\right) \tag{3}$$

$$\Delta F_B = \frac{\pi^2}{16} \frac{R^2 c_B^{1/2}}{l^2 N_B} kT \tag{4}$$

where R is the radius of the cylinder. N_A and N_B are the numbers of segments in block A and B, l are the lengths of segments and chain thicknesses, assumed to be approximately equal, and c_A and c_B are the volume fractions of units in the matrix and the domain, respectively. The solvent is assumed to be thermodynamically good for one or both blocks. The matrix may be represented by a system of cylindrical layers with the outer radius $R (1 + N_A c_B/N_B c_A)^{1/2}$.

The minimization of ΔF according to equations (1)–(4) gives the radius of cylinders, R_C in the C structure of linear block copolymers:

$$R_C = \left(\frac{4}{\pi}\right)^{2/3} l \varphi^{1/3} N_B^{2/3} c_B^{-5/12} \left[1 + \frac{6}{\pi^2} \ln\left(1 + \frac{N_A c_B}{N_B c_A}\right)\right]^{-1/3} \tag{5}$$

where $\varphi = \gamma l^2/kT$. The numerical evaluations of φ carried out here by the comparison of experimental[9] and theoretical[1] results for the geometrical characteristics of superstructures of linear PI–PS block copolymers give $\varphi = 0.53$.

For the quantitative evaluation of R_C from equation (5), the value of $l = 6.5$ Å will be used. This is the mean value of PI $(l = 5$ Å$)$ $(l = 8$ Å$)$ blocks. Then the number of effective 'units' of PS and PI in a branch with $M_b = 3.3 \times 10^4$ is $N_B = N_{PS} = 36$, $N_A = N_{PI} = 129$, and the calculation according to equation (5) at $c_A = c_B = 1$ gives $R_C = 54$ Å. This value is in good agreement with the experimental value for cylinder radius in the C structure formed by stars with a small number of branches: $f < f_0 = 6$, i.e. $R_C \approx 50$ Å.

In the C structure considered here and existing in linear block copolymers, A and B blocks are stretched in the radial direction, the stretching of block A decreasing with the increasing distance from the cylindrical domain in the direction of the inner part of the matrix. On the other hand, it is known from the theory of star-branched homopolymers[8] that at $f \gg 1$ star branches are characterized by strong radial stretching, which is maximum in the star core and decreases with increasing distance from the core to the periphery.

Hence, for block copolymer stars with $f \gg 1$ and the predominant component A inside the star, a contradiction exists between the spherical symmetry of the star, on the one hand, and the cylindrical symmetry of the superstructure (with the outer component B in cylinders) optimum for linear block copolymers with a given ratio of phase volumes $V_A/V_B = N_A c_B/N_B c_A$, on the other. The star arrangement in the C structure requires their considerable deformation: the transformation of a spherically symmetrical star into a flat 'pancake' of the same volume.

Stars in the BT structure

Analysis shows that the structure revealed in refs 3–5 is a compromise satisfying both symmetry requirements formulated above: the component B is concentrated in cylindrical domains, but the arrangement of cylinders belonging to the two lattices is characterized by symmetry of a high order comparable to that of stars.

An important structural parameter is the number m of stars in an elementary cell. The experimental value of m can be easily determined proceeding from the structural characteristics found in refs 3–5.

Star number in a cell according to experimental data. The quantitative characteristics of the BT structure are the cylinder radius R (as in the C structure) and the length L of the domain. It follows from the geometry of the structure that their ratio is determined by the composition of the block copolymer:

$$\left(\frac{R}{L}\right)^2 = \Phi_B \frac{2}{3\sqrt{3}\pi} \tag{6}$$

where

$$\Phi_B = v_B M_B/(v_A M_A + v_B M_B) = N_B/(N_A + N_B)$$

is the volume fraction of the outer B blocks (PS) and v_A and v_B are the corresponding specific volumes of the components. In further discussion, the polymer composition Φ_B and the cylinder radius R will be considered as independent characteristics. The values of R and L determine the total volume of the elementary cell and the volume of elementary domains and, hence, the total

mass of blocks in the cell:

$$M_b fm = \frac{4\pi R^2 L}{v_B} = (12\pi^2)^{3/4} \frac{R^3}{v_B \Phi_B^{1/2}} \qquad (7)$$

For stars with the fixed number of branches f, equation (7) makes it possible to determine the experimental value of the number m of stars in a cell from the values of R and Φ_B.

The analysis of data in refs 3–5 shows that, in all investigated cases, the number m of stars in a cell is great. In fact, according to experimental data, the cylinder radius R and its length L in BT structure do not depend on the number of branches f in a star, at a fixed MW of the branch, being e.g. $R = 50$ Å and $L = 290$ Å for a sample with $M_b = 3.3 \times 10^4$ at all $6 \leqslant f \leqslant 18$. Equation (6) is used for the determination of the total number of branches in all the stars of the cell $mf = \text{const}(f) = 550$ and $m = 30$–90 at the above values of f.

Note that equations (6) and (7), just as the experimental data in refs 3–5, refer to the case of dry block copolymers. In the presence of solvent in the system, equations (6) and (7) are transformed into the equations:

$$\frac{L}{R} = \left(\frac{27\pi^2}{4}\right)^{1/4} \left(\frac{c_A - c_B}{c_A} + \frac{c_B}{c_A \Phi_B}\right)^{1/2} \qquad (8)$$

$$m = (12\pi^2)^{3/4} \frac{R^3 c_B}{l^3 N_B f} \left(\frac{c_A - c_B}{c_A} + \frac{c_B}{c_A \Phi_B}\right)^{1/2} \qquad (9)$$

(The volume of block B in equation (9) is represented in the form $v_B M_B = l^3 N_B$.)

Multibranch star in the BT structure. Now the theoretical evaluation of structural characteristics will be given assuming, as in ref. 2, the fixed morphology of the structure. In this case, however, in contrast to the situation for canonical morphologies, the fixation of the BT structure is insufficient for plotting directly the free energy of the system according to equation (1), because in principle different variants of star arrangement in the cell are possible.

It is natural to assume that ΔF_s and ΔF_B are determined only by the area of the interface σ and the radius of cylinder R and are described by equations (2) and (4), as before. Then the entire specificity of the free energy of the BT structure is determined by the term ΔF_A, i.e. by the free energy of the predominant polymer component located in the inner parts of the star and forming the matrix of the BT structure. The value of ΔF_A depends on the arrangement of stars in the cell, and a reasonable model should be introduced for its determination.

On the basis of the BT structure, it might be expected that its elementary unit is a symmetrical group of stars that contains $mf/3$ branches and which we will tentatively call a 'superstar'. The centres of superstars lie at the centres of faces of elementary cells (*Figure 1*, the point shows the centre of one of the superstars).

Let the superstar be a star consisting of a certain large number $\mathscr{F} = mf/3$ of branches. The symmetry about the star centre in the BT structure makes it possible to evaluate ΔF_A as a sum of the free energy $\Delta F_A^\circ(\mathscr{F})$ of blocks in an undeformed superstar consisting of $\mathscr{F}$ branches (see ref. 8 for further details):

$$\Delta F_A^\circ = \frac{3}{8\pi} \frac{\mathscr{F}}{c_A} \left(\frac{1}{\rho_0} - \frac{1}{\rho}\right) kT + \Delta F_A(\rho_0) \qquad (10)$$

and the correction, $\Delta F_A'$, related to the fixation of ends of blocks A (adjoining blocks B) on the surface of a cylinder consisting of the B component:

$$\Delta F_A' = kT \ln\left(\frac{4\pi\rho^2}{2\pi RL}\right) = kT \ln\left(\frac{R}{\rho} \frac{N_A c_B}{N_B c_A}\right) \qquad (11)$$

where

$$\rho = \frac{3}{4\pi} \left(\frac{\mathscr{F} l^3 N_A}{c_A}\right)^{1/3}$$

is the radius of a star consisting of blocks A in the presence of a solvent uniformly distributed on the matrix and having a concentration $(1 - c_A)$, $\Delta F_A(\rho_0)$ is the free energy of a branch part with maximum stretching in the core of a star of radius ρ_0 (see ref. 8 for further details) and R and L are the characteristics of cylinders consisting of the B component in the BT structure. The right-hand side of equation (11) takes into account the fact that:

$$V_A/V_B = 4\pi\rho^3/3\pi R^2 L = N_A c_B/N_B c_A$$

In order to determine the radius of cylindrical domains the free energy ΔF determined from equations (1), (2), (4), (10) and (11) should be minimized for R.

Let us consider first a hypothetical case in which the value of $\mathscr{F}$ is given by the conditions of chemical crosslinking, so that equation (9) should also be obeyed. Then the component ΔF_A° is independent of R and does not take part in minimization, $\Delta F_A^\circ = \text{const}(R)$ and $\Delta F_A' = kT \ln(R/l) + \text{const}(R)$. As a result of minimization, a cubic equation is obtained for R_{BT}:

$$\left(\frac{R_{BT}}{l}\right)^3 + \frac{8}{\pi^2} N_B c_B^{-1/4} \left(\frac{R_{BT}}{l}\right) - \frac{16}{\pi^2} \frac{\varphi N_B^2}{c_B^{5/4}} = 0 \qquad (12)$$

Its solution according to Cardan's formula is given by:

$$\frac{R_{BT}}{l} = \left(\frac{4}{\pi}\right)^{2/3} \varphi^{1/3} N_B^{2/3} c_B^{-5/12} 2^{-1/3}$$

$$\times \left\{\left[\left(1 + \frac{p^3}{q^2}\right)^{1/2} + 1\right]^{1/3} - \left[\left(1 + \frac{p^3}{q^2}\right)^{1/2} - 1\right]^{1/3}\right\}$$

$$\approx \left(\frac{4}{\pi}\right)^{2/3} \varphi^{1/3} N_B^{2/3} c_B^{-5/12} (1 - 2^{-2/3} pq^{-2/3}) \qquad (13)$$

where

$$p = 8N_B/3\pi^2 c_B^{1/4} \qquad q = 8\varphi N_B^2/\pi^2 c_B^{5/4}$$

and the right-hand side of equation (13) is written on the assumption that $p^3/q^2 \ll 1$.

Let us consider equation (13), restricting ourselves for simplicity to the case $c_A = c_B = 1$. Equation (13) determines the radius R_{BT} of cylindrical parts of the bitetrahedral structure as a function of the length of blocks of the minor component of the copolymer (as well as that of relative surface tension coefficient). Hence, at given N_B, φ values and the composition Φ_B of the copolymer, it is possible to determine the lengths L of cylindrical parts (lattice edges), equation (6), and the total mass of blocks in the cell, equation (7), i.e. in our case the number $\mathscr{F}$ of branches in the superstar. Hence, when the number $\mathscr{F}$ of branches in the superstar is fixed and N_B and Φ_B are given, the formation of the bitetrahedral structure with one superstar in the cell is possible only for superstars with a certain definite number of branches.

Substituting the above values of the parameters for the case $M_b = 3.3 \times 10^4$ at $c_A = c_B = 1$ into equation (13) and

taking into account that $pq^{-2/3} \sim N_B^{-1/3}\varphi^{-2/3}$, we find $R_{BT} = 62$ Å. The number of branches in a hypothetical superstar $\mathscr{F} = 1000$ is found from equation (7).

This system is naturally not realistic. However, the fact that the value of R_{BT} obtained here is close to the experimental value of $R_{BT} = R_C = 50$ Å shows that this picture reflects the main features of a real situation, namely the fact that the matrix element is not a single star consisting of approximately 10 branches but a very large system with a large number of branches.

Grouping of stars in the matrix. In the simplest variant, a group consisting of $m = \mathscr{F}/f$ f-stars might be represented in the form of a single $\mathscr{F}$-star by superimposing the centres of all f-stars at one point. However, in this case, according to equation (10) the value of ΔF_A° becomes a function of the variable value of m (and thus of R, from equation (9)), rapidly increasing with m. This fact is due to the increase in the degree of stretching of star branches and in star density when the number of branches increases.

Hence, it may be expected that a superstar should consist of f-stars the centres of which are located at a certain distance from the common centre of symmetry. Let us consider a possible model for this arrangement, taking into account for the sake of generalization the presence of the solvent in the matrix. Let the centres of these stars in a superstar consisting of $m/3$ stars be located on the surface in which the mean distance between the centres coincides with that between the centres r_0 of unperturbed stars in semidilute solution:

$$r_0 = l\left(\frac{fN_A}{c_A}\right)^{1/3} \qquad (14)$$

The radius of the sphere is determined by the condition

$$4\pi\rho_0^2 = \frac{m}{3}r_0^2 = l^2\frac{m}{3}\left(\frac{N_A f}{c_A}\right)^{2/3} \qquad (15)$$

Applying equation (9) we obtain:

$$\rho_0 = l\left(\frac{\pi^2}{12}\right)^{1/8}\left(\frac{R}{l}\right)^{3/2}\frac{N_A^{1/3}c_B^{1/2}}{c_A^{1/3}N_B^{1/2}f^{1/6}}\left(\frac{c_A - c_B}{c_A} + \frac{c_B}{c_A\Phi_B}\right)^{1/4} \qquad (16)$$

Considering a superstar as a system of $mf/3$ branches grafted onto a 'core' of radius ρ_0, taking into account branch stretching near the 'core' and applying the results of ref. 5, we obtain for the free energy:

$$\Delta F_A = \frac{1}{8\pi}\frac{mf}{c_A}\frac{l}{\rho_0}kT = \frac{3}{2}\left(\frac{\pi^2}{12}\right)^{1/8}\left(\frac{R}{l}\right)^{3/2}\frac{c_B^{1/2}f^{1/6}}{c_A^{2/3}N_A^{1/3}N_B^{1/2}}$$
$$\times\left(\frac{c_A - c_B}{c_A} + \frac{c_B}{c_A\Phi_B}\right)^{1/4}kT \qquad (17)$$

In this case the correction $\Delta F_A'$ according to equation (11) related to the fixation of blocks A at the boundary of domains B may be omitted because $\Delta F_A' \ll \Delta F_A$. When the overall energy ΔF determined from equations (1), (2), (4) and (17) is minimized for R, the equation for R_{BT} is obtained:

$$\left(\frac{R_{BT}}{l}\right)^3 + k_1\left(\frac{R_{BT}}{l}\right)^{5/2}f^{1/6} - k_2 = 0 \qquad (18)$$

where $k_1 > 0$ and $k_2 > 0$ are functions of N_A, N_B, c_A, c_B, Φ_B and φ, and the dependence on the branch number f

is expressed explicitly. Moreover, as can be seen from equation (18), this dependence is very weak. For the cases $M_b = 3.3 \times 10^4$, $c_A = c_B = 1$ and $f = 6$ to 18, equation (18) gives $R_{BT} = 50 \pm 2$ Å, which is in complete agreement with the experimental result $R_{BT} = 50$ Å at all $f \geqslant 6$. Correspondingly, the evaluations of mf and m from equation (7) lead to the same values as the analysis of experimental data carried out above: $mf \approx 550$ and $m = 30$–90 at $6 \leqslant f \leqslant 18$.

CONCLUSIONS

Good agreement with experimental data for the two alternative matrix models shows that each of these models takes into account the main feature of the BT structure: the content of a large number of stars (large number of branches) in an elementary cell.

Hence, the proposed approach makes it possible to reveal the main principles of the organization of new BT morphology of star-like block copolymers and to establish the relationship of the geometrical parameters of the BT structure to molecular characteristics. Unfortunately, the approximation adopted here does not make it possible to compare the values of ΔF_C and ΔF_{BT} for stars with given values of f and thus to determine the value of f_c corresponding to the transition from the C to the BT structure[3-5]. The reason for this is the assumption of the large value of branches $f \gg 1$ in each star, which ensures the validity of the approach used in this paper. Hence the analysis of the competition between BT and C structures is beyond the scope of our approach. This problem was considered in the publication of Anderson and Thomas[10] on the basis of the further extension of the theory of well defined structures forming in linear diblock copolymers systems[11]. As follows from the results of ref. 10, the BT structure can be formed not only by star block copolymers but also by linear block copolymers, in agreement with the results of ref. 12. On the other hand the theory of ref. 10 fails to predict the increase in thermodynamic stability of the BT structure with increasing branch number f, as is indicated by the experiments[3-5]. So we believe that these two approaches considering from different viewpoints the formation of BT structure in star block copolymers are complementary to each other.

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