Scaling theory of supermolecular structures in block copolymer–solvent systems: 2. Supercrystalline structures

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The supermolecular structures formed in a block copolymer–solvent system were considered by using the scaling method. The equilibrium characteristics of the superstructures of different morphologies formed by two-block copolymers with non-crystallizable blocks were determined as a function of the molecular weight and composition of copolymer and the strength and concentration of the solvent in the system. The composition–concentration diagram of the system was obtained. The lamellar superstructure formed by a block copolymer with one crystallizable block was analysed. The results of the theory were compared with the experimental data.

(Keywords: concentrated solution of block copolymer; supermolecular structure; composition–concentration diagram of state)

INTRODUCTION

In a preceding paper[1] it has been shown that the block copolymer micelles in a selective solvent remain segregated without interpenetrating up to limiting high concentrations of block copolymer. This behaviour leads to regular micelle packing and the formation of a superstructure with well developed long-range order, which may be regarded as liquid-crystalline structure.

In contrast to the situation in a dilute solution in which micelles are of spherical shape, the morphology of the superstructure formed at high block copolymer concentration is determined by the composition of the block copolymer, its concentration and the degree of solvent selectivity. Thus, at approximately equal lengths of A and B blocks in a two-block copolymer ($q=N_A/N_B \simeq 1$), planar lamellae are formed ($i=1$), and at a considerable difference between block lengths $q \gg 1$ spheres of the minor component B ($i=3$) are formed. They are located at the nodes of the cubic lattice and surrounded with the matrix of the predominant component A. In the intermediate case of moderate q, the minor component B is concentrated in cylinders ($i=2$) hexagonally packed in the matrix A (*Figure 1*).

In this paper the scaling analysis of the previous paper[1] is continued by considering the free energy, the stability and geometric characteristics of superstructures with different morphologies ($i=1$–3) in relation to molecular parameters and to solvent concentration.

As before, a two-block copolymer, $A_{N_A}B_{N_B}$, will be considered. All the symbols used have been defined in ref. 1. We will assume that the polymer concentration C_A and C_B (or solvent concentration $1-C_A$ and $1-C_B$) in the corresponding elements of the superstructures are fixed. At $C_A=C_B=1$, the relationships obtained describe the superstructure in the absence of the solvent.

Some results of this work have already been published[2–4].

THEORY

Let us consider the conformational free energy ΔF of a chain of a block copolymer in a superstructure of type i. As before, we will restrict ourselves to the main power term in each of the components of ΔF (equation (1.1), i.e. equation (1) in ref. 1) but retain the numerical coefficients omitted in the previous paper:

$$\Delta F = \Delta F_A + \Delta F_B + \Delta F_S \tag{1}$$

As before, the interface free energy ΔF_S is determined by equation (1.2):

$$\Delta F_S = \bar{\phi}\sigma = \phi\sigma/a^2 \tag{2}$$

where σ is interface area per chain and $\bar{\phi}=\phi/a^2$ is the coefficient of corresponding surface tension.

As to conformational free energies ΔF_A and ΔF_B of the blocks A and B in the corresponding structural elements, these blocks may be treated as chains of blobs, grafted to the interface. As usual in semidilute solution the blob size is $\xi_j \simeq aC_j^{-\nu/(3\nu-1)}\,\bar{v}$, the number of blobs is $n_j = N_j C_j^{1/(3\nu-1)}$, $\nu=\frac{1}{2}$ or $\frac{3}{5}$, $j=$ A or B.

Taking into account the stretching of blocks B in a domain of size R_i, we obtain:

$$\Delta F^i_{B,el} = \alpha_i R_i^2/\xi_B^2 n_B \tag{3}$$

where α_i are numerical coefficients of the order of unity.

In the calculation of $\Delta F^i_{A,el}$, the non-uniformity of stretching of grafted chains for spherical ($i=3$) and cylindrical ($i=2$) morphologies will be taken into account. By using equation (1.20) for the free energy of stretching of part of a chain of δn blobs in a layer of thickness δr at a distance r from the domain centre and the condition

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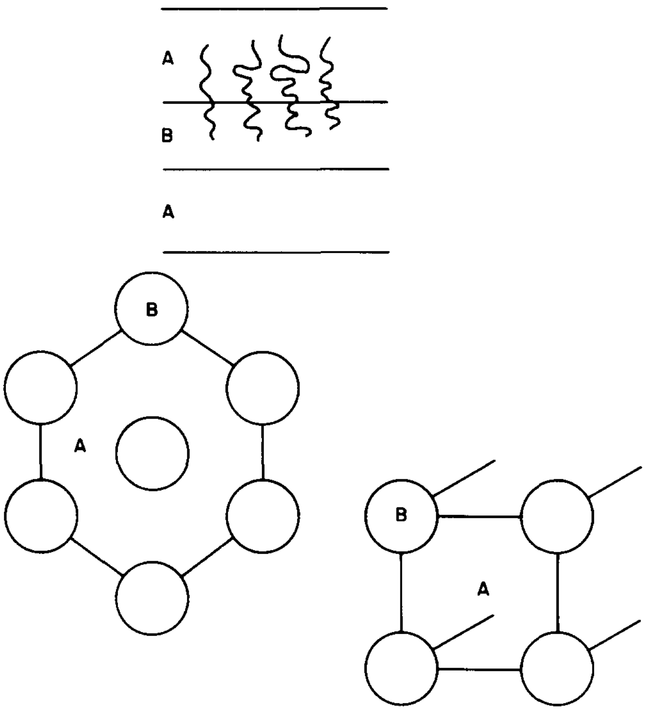

Figure 1 Superstructures consisting of block copolymers

of dense packing of blobs:

$$\delta n \xi_A^3 \simeq \delta r \sigma_i (r/R_i)^{i-1}$$

we obtain:

$$\Delta F^i_{A,el} = \beta_i \frac{\xi_A R_i^2}{\xi_B^3 n_B} \begin{cases} 1-[R_i/(R_i+D_i)]^{i-2} & i \neq 2 \\ \ln(1+D_i/R_i) & i=2 \end{cases} \quad (4)$$

Here D_i is the characteristic size of the matrix formed by blocks A around a given domain B:

$$D_i = R_i[(1+qC_B/C_A)^{1/i}-1] \quad (5)$$

β_i are numerical coefficients of the order of unity and $q = N_A/N_B$. Applying equation (5) we have:

$$\Delta F^i_{A,el} = \beta_i \frac{R_i^2}{a^2 N_B} C_B^{(2\nu-1)/(3\nu-1)} \left(\frac{C_B}{C_A}\right)^{\nu/(3\nu-1)} \times \begin{cases} 1-(1+qC_B/C_A)^{(2-i)/i} & i \neq 2 \\ \ln(1+qC_B/C_A) & i=2 \end{cases} \quad (6)$$

The concentration components $\Delta F^i_{j,\text{conc}} \simeq N_j C_j^{1/(3\nu-1)}$ are independent of the morphology and parameters of the structure and hence do not participate in minimization.

The minimization of ΔF^i taking into account equations (1)–(3) and (6) yields equilibrium values of the domain size R_i and the conformational free energy of the chain ΔF^i in the structure of i type. At fixed values of C_A and C_B we have:

$$R_i = a(i\phi/2)^{1/3} C_B^{(2-5\nu)/3(3\nu-1)} N_B^{2/3} Q_i^{-1/3} \quad (7)$$

$$\Delta F^i = 3(i\phi/2)^{2/3} C_B^{(1-4\nu)/3(3\nu-1)} N_B^{1/3} Q_i^{1/3} \quad (8)$$

where

$$Q_i = \alpha_i + \beta_i \left(\frac{C_B}{C_A}\right)^{\nu/(3\nu-1)} \begin{cases} 1-(1+qC_B/C_A)^{(2-i)/i} & i \neq 2 \\ \ln(1+qC_B/C_A) & i=2 \end{cases} \quad (9)$$

The values of numerical coefficients α_i and β_i have been calculated in ref. 5.

Equations (7)–(9) are the complete solution of the problem. In particular, they determine the molecular-weight, concentration and composition dependences of the parameters of the superstructure of morphology i.

Let us analyse in greater detail the results and compare them with both other available theoretical investigations and the extensive experimental data accumulated in the literature.

RESULTS AND DISCUSSION

Molecular-weight dependence

It can be seen from equations (7)–(9) that at a fixed composition of the copolymer $q = N_A/N_B \equiv \text{const}$ for a linear size of superstructure of any morphology (domain radius, lamella thickness and complete period), a single law should be obeyed:

$$R_i \sim N_B^{2/3} \qquad D_i \sim N^{2/3} \quad (10)$$

at an arbitrary fixed polymer concentration in the system including the melt.

Also we have for specific surface area σ_i and the conformational free energy ΔF^i:

$$\Delta F^i \sim \sigma_i \sim N^{1/3} \quad (11)$$

The analysis carried out in ref. 2 for lamellar structures has shown that equations (10) and (11) should also be approximately obeyed at a variable q, which is due to relatively slight variations of composition in the range of stability of lamellar structures. The same is also true for $i = 2$, 3, because of the weaker dependence of R_i on q (equations (7) and (9)).

The law in equation (10) is close to that obtained previously by Helfand[6] for lamellar superstructure on the basis of mean-field considerations: at $N \to \infty$, $R_1 \sim D_1 \sim N^{\nu'}$ where $\nu' = 9/14 = 0.64$. For $i > 1$, Helfand's theory[7] does not give single-power asymptotes, and the exponent ν' is a function of composition q; but the quantitative differences are slight.

A systematic experimental investigation of the molecular-weight dependence of the size of superstructures was carried out for melts of copolymers at $C_A = C_B = 1$. Numerous data for lamellar structures summed up in refs. 8 and 9 show that the exponent ν' is close to 2/3. The value of $\nu' = 2/3$ has also been confirmed in a special investigation of the exponent for narrow-disperse polystyrene–polyisoprene (PS–PI) polymers, $2 \times 10^4 < M < 2 \times 10^5$ (ref. 8). For polydisperse samples, the dependences in equation (10) were also obeyed when $\bar{M}_n$ was used as the parameter[10].

An example of the dependence with $\nu' = 2/3$ plotted from the experimental data in ref. 10 is shown in *Figure 2*.

For superstructures with other morphologies, the experimental results are less definite. Thus, the experimental data of several authors summarized in ref. 11 and the data in ref. 12 are characterized by considerable scattering, which prevents reliable determination of the exponents in the molecular-weight dependence of the parameters. However, the analysis of experimental data in refs. 11 and 13 for spherical domains formed by block PS–PI copolymers, $7 \times 10^4 < M < 7 \times 10^5$, of the highest molecular weight among the samples investigated in the

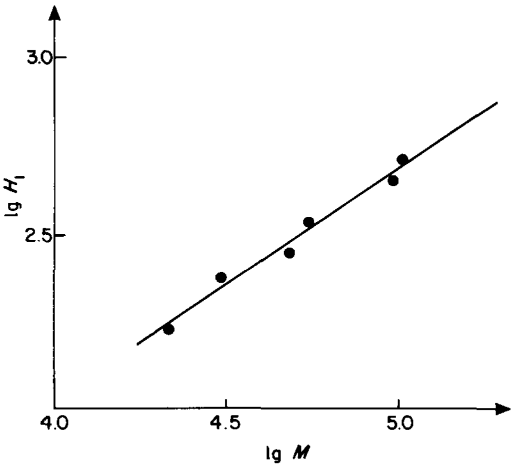

Figure 2 Molecular-weight dependence of the size of the lamellar structure[10]

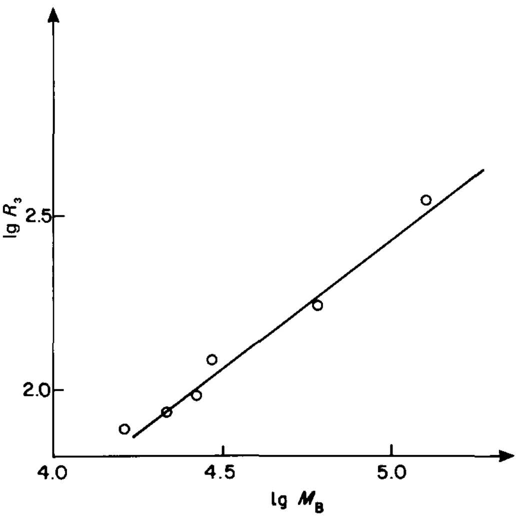

Figure 3 Molecular-weight dependence of the size of spherical domains R_3[11]

literature, have shown that the law $v' = 2/3$ is adequately obeyed (*Figure 3*).

Superstructures of three-block copolymers

So far we have considered only two-block $A_{N_A}B_{N_B}$ copolymers. However, the analysis may be extended to symmetrical three-block copolymers of ABA (or BAB) type. The simplest assumption is that in the formation of the superstructure the chains are folded in such a manner that the molecule of a three-block copolymer of molecular weight M may be regarded as two molecules of a two-block copolymer with molecular weight $M/2$. Hence, for AB and ABA copolymers with a fixed composition we have:

$$\begin{aligned} R_i(3; M) &= R_i(2; M/2) \\ D_i(3; M) &= D_i(2; M/2) \end{aligned} \tag{12}$$

where numbers 2 and 3 denote the block number in the copolymer.

It can be seen from *Figure 4* that the geometric characteristics of the superstructure of three-block polystyrene/polybutadiene PS–PB–PS and PB–PS–PB copolymers[14] fall on the same straight line as those of two-block PS–PB copolymers. The coordinate $M/2$ is used for three-block copolymers instead of M for two-block copolymers, in agreement with equation (12).

It is also of interest to consider the change in the parameters of the superstructure when the third block is bonded to a two-block $A_{N_A}B_{N_B}$ copolymer, i.e. on passing to $A_{N_A}B_{N_B}A_{N_A}$. In this case the composition of the copolymer changes, $q(2) = N_A/N_B$, $q(3) = 2N_A/N_B = 2q(2)$, and the total molecular weights are $M(2) = M_A + M_B$, $M(3) = 2M_A + M_B$. Taking into account the structural equivalence of the three-block copolymer and the two-block copolymer with molecular weight $M(3)/2$ we have for lamellar structures ($i = 1$):

$$\begin{aligned} \frac{R_1(3)}{R_1(2)} &= \frac{1}{2}\left(\frac{2+2q(2)}{1+2q(2)}\right)^{1/3} \\ \frac{D_1(3)}{D_1(2)} &= \left(\frac{2+2q(2)}{1+2q(2)}\right)^{1/3} \\ \frac{H_1(3)}{H_1(2)} &= \frac{R_1(3)+D_1(3)}{R_1(2)+D_1(2)} = \left(\frac{1+2q(2)}{2+2q(2)}\right)^{2/3} \end{aligned} \tag{13}$$

These results may be compared with the experimental data in ref. 15. According to experimental data, when a third PB block ($M = 2.5 \times 10^4$) was added to the two-block PS($M = 3.8 \times 10^4$)–PB($M = 2.5 \times 10^4$) copolymer, the thickness of the PB lamella formed by PB–PS–PB copolymer increased by a factor of 1.25 with simultaneous decrease in the thickness of the PS lamella and the period on the whole (to 0.60 and 0.88 of the initial values, respectively). The calculation according to equation (13) gives $D_1(3)/D_1(2) = 1.10$, $R_1(3)/R_1(2) = 0.55$, $H_1(3)/H_1(2) = 0.80$, in good quantitative agreement with experimental data.

Concentration dependence of the parameters of superstructures

Equations (5), (7) and (9) determine the dependence of R_i and D_i on volume fractions of the solvent $(1 - C_j)$ ($j = A, B$) in a structure of given morphology. It is clear that geometrical parameters depend on C_j both directly and via the surface tension coefficient $\phi = \phi(C_A, C_B)$. Hence, it is necessary to begin from the analysis of the concentration dependence of $\phi(C_A, C_B)$.

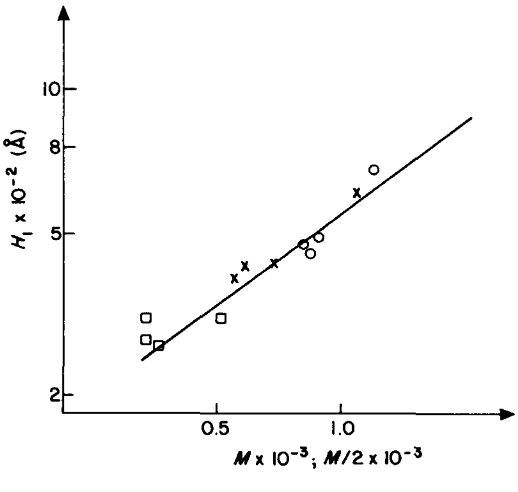

Figure 4 Molecular-weight dependence of the lamella period consisting of two- and three-block copolymers[14]

Surface tension coefficient. Let us begin from the case of a non-selective solvent when $C_A = C_B$.

The maximum surface tension at the boundary of two structural elements containing A and B blocks (and solvent) takes place when polymers A and B are incompatible and the excessive interaction constant χ_{AB} is very high. In the limit $\chi_{AB} \gg 1$, the interfacial layer between two semidilute solutions becomes limitingly thin ($\Delta \to 0$) and surface tension reduces to the sum of surface tensions of each solution near an impermeable wall:

$$\phi = \phi_A + \phi_B \tag{14}$$

The problem of a polymer solution near an impermeable wall has been solved[16] on the basis of simple scaling relationships, and the main results will be briefly considered here.

The effective repulsion of chain units by a wall leads to a decrease in their concentration C_s at the wall. This concentration may be determined from the condition of the equality of osmotic pressure at the wall $\pi_x \sim C_{sx}$ and in the bulk of solution $\pi_x \sim C^{\alpha_x}$ where $\alpha_x = 9/4$, 2 and 3 depending on the thermodynamic regime ($x = \mathrm{II}_+$, II_{mf} and II_θ) of the semidilute solution:

$$C_{sx} \simeq C^{\alpha_x} \tag{15}$$

The thickness of the depletion layer should be of the order of magnitude of the correlation radius ξ_x so that the concentration profile near the wall may be written in the scaling form:

$$C(z) = \begin{cases} C(z/\xi_x)^{\beta_x} = C_{sx} z^{\beta_x} & z \ll \xi_x \\ C & z \gg \xi_x \end{cases} \tag{16}$$

By using equations (15) and (16) and applying the values of α_x and the concentration dependence of ξ_x we find $\beta_x = 5/3$, 2 and 2 for regimes II_+, II_{mf} and II_θ, respectively.

A more detailed picture of the concentration profile near the wall may be obtained by using the self-consistent field method valid under regimes II_{mf} and II_θ. The calculation gives:

$$C(z) = C \tanh^2\left(\frac{z}{\xi}\right) \frac{v + 2wC}{v + 3wC - wC \tanh^2(z/\xi)} \tag{17}$$

where

$$\xi = a/[6(vC + 3wC^2)]^{1/2} \tag{18}$$

and $va^3 \simeq \tau a^3$ and wa^6 are the second and third virial coefficients of unit interaction. At $z/\xi \ll 1$, the expansion of equation (17) into a series leads to power relationships of equations (15) and (16) for regimes II_{mf} ($v \gg wC$) and II_θ ($v \ll wC$).

The surface tension coefficient ϕ is determined by the density of free energy of volume interactions $\pi_x \simeq C_{sx}$ and the width of the depletion region ξ_x:

$$\phi \simeq \pi_x \xi_x a^2 \simeq \begin{cases} v^{1/2} C^{3/2} & x = +, \mathrm{mf} \\ w^{1/2} C^2 & x = \theta \end{cases} \tag{19}$$

With decreasing χ_{AB}, the thickness Δ of the interface layer containing units of both types increases and the surface tension at the boundary of different elements decreases (*Figure 5*). It is possible to evaluate Δ on the basis of simple considerations by using the mean-field approximation (regimes II_{mf} and II_θ). It is known that according to the Flory–Huggins theory the phase separation of a mixture of two polymers A and B in a common good solvent obeys the condition:

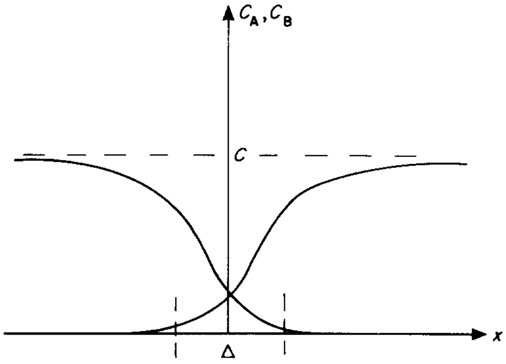

Figure 5 Scheme of the density profile of A and B units in the interdomain layer

$$C_c \chi_{AB} n = 2 \tag{20}$$

where C_c is the critical concentration of polymers and n is the degree of polymerization. It is natural to assume that the value of n also determines the successive number of units of any chain that may be located in a 'foreign' phase in the interface layer. Then its thickness is given by:

$$\Delta \simeq a n^{1/2} \simeq a(C\chi_{AB})^{-1/2} \tag{21}$$

in agreement with more detailed evaluations[17].

The formation of an interface layer leads to additional energetically unfavourable hetero-interactions, the energy of which in the mean-field approximation may be given by:

$$\Delta F_{AB} \simeq \chi_{AB} (\delta N)^2 a/\Delta \tag{22}$$

where $\delta N = \delta N_A = \delta N_B$ are the numbers of units of A and B type located in the interface layer (per unit area).

Assuming that the decrease in concentrations in the interface layer is described by the first of equations (16) we obtain:

$$\Delta F_{AB} \simeq \frac{\Delta}{a} \chi_{AB} C^2 \left(\frac{\Delta}{\xi}\right)^4 \tag{23}$$

This value is positive but the increase in the entropy of the system with the thickening of the interface layer leads to an overall decrease in the free energy. Under the equilibrium conditions both energetic and entropic terms are of the same order of magnitude. Hence, the value of ΔF_{AB} is the measure of the overall free energy decrease. The surface tension at the boundary of partially interpenetrating A and B solutions may be written in the form:

$$\phi \simeq \pi \xi a^2 - \frac{\Delta}{a} \chi_{AB} C^2 \left(\frac{\Delta}{\xi}\right)^4 \tag{24}$$

At weak penetration, when $\Delta \ll \xi$ (*Figure 5*), the addend in equation (24) may be neglected so that the concentration dependence of surface tension is still described by equation (19). In the other limiting case when the concentrations of each component at the corresponding boundaries of the interface layer attain limiting values $C_A = C_B = C$, equation (24) becomes incorrect, and the surface tension coefficient is given by[17]:

$$\phi = (\chi_{AB}/6)^{1/2} C^{3/2} \tag{25}$$

So far the limiting non-selective solvent was considered when $C_A = C_B = C$. In the case of a highly selective solvent, when $C_B = 1$ and $C_A < 1$, the main contribution to the concentration dependence of surface tension is provided by the change in the degree of contact of the solvent with the surface of the B structural element. Hence, the change in ϕ with concentration is not described by a power function so that in the scaling approximation this function may be regarded as a constant.

Selective solvent. Let the solvent exhibit high selectivity and be completely concentrated either in the matrix A ($C_A = C$, $C_B = 1$) or in the domain B ($C_B = C$, $C_A = 1$). It follows from equations (5), (7) and (9) that at $\phi = \text{const}\,(C)$ in both cases the swelling of the swelling block (decrease in C) should lead to an increase in both its thickness and the specific interface area σ but to a corresponding decrease in the thickness of the insoluble component. This conclusion is valid for all the range of qC_B/C_A values. It should be emphasized that the increase in σ is related to an increase in mutual repulsion of the chains in the swelling component with increasing swelling. This automatically leads to a decrease in the thickness of the structural element of the insoluble component (as a result of the retention of its volume), although it is not directly affected by swelling. For the particular case of insoluble spherical domains in a swelling matrix ($i = 3$, $C_B = 1$, $C_A < 1$, $qC_B/C_A \gg 1$), this effect has been considered in ref. 1 (concentration range $C_A > C_A^{**}$). Equations (5), (7) and (9) at $i = 3$ and $qC_B/C_A \gg 1$ give for this case:

$$
\begin{aligned}
R_3 &\simeq a\phi^{1/3} N_B^{2/3} C_A^{\nu/3(3\nu-1)} \\
D_3 &\simeq a\phi^{1/3} N_A^{1/3} N_B^{1/3} C_A^{-(1-2\nu)/3(3\nu-1)}
\end{aligned}
\tag{26}
$$

in complete agreement with the results in ref. 1.

The conclusions that selective swelling of the elements of the superstructure of any morphology should lead to (1) an increase in the dimensions of the soluble component, (2) an increase in the specific area of grafting and (3) a decrease in the dimensions of the insoluble component, are in complete agreement with a large number of experimental data[9] in which these effects are manifested.

In the case of spherical morphology ($i = 3$), the decrease in the size of the unswelling domain due to matrix swelling requires considerable rearrangement: decrease in the number of chains in the spherical domain (and the increase in the number of domains). For superstructures of other morphologies, these rearrangements are not so extensive: decrease in the thickness of the insoluble structural element is accompanied by its stretching in the perpendicular direction and may occur without chain redistribution between insoluble elements.

It is noteworthy that relatively strong effects, namely the increase in the size of the swelling structural elements and the thinning of the undiluted elements, are described by the theory even if the concentration dependence of the interface tension coefficient ϕ is neglected. A finer effect is the concentration dependence of the overall period of the structure, because one of the values decreases and the other increases. For lamellar structures the contributions of both values are close to each other. Hence (mainly for lamellar structures), even the sign of the concentration dependence of the overall period cannot be obtained theoretically without taking into account the dependence $\phi = \phi(C)$, although it is not a power dependence for a selective solvent. Good agreement with experimental data[9] according to which the period of lamellar structures always decreases with the swelling of elements of one type in a selective solvent (increase in $1 - C_A$) may be obtained with the assumption of a decrease in the coefficient ϕ at this swelling.

Non-selective solvent $C_A = C_B = C$. As follows from equation (9), in the case of a completely non-selective solvent $C_A = C_B = C$, the value of Q_i no longer depends on concentration C, and equations (7)–(9) give:

$$
\begin{aligned}
&R_i \sim D_i \sim \phi^{1/3} C^{-(5\nu-2)/3(3\nu-1)} \\
&\frac{\sigma_i}{a^2} \simeq \frac{aN_B}{CR_i} \sim \phi^{-1/3} C^{-(4\nu-1)/3(3\nu-1)}
\end{aligned}
\tag{27}
$$

It can be seen from equation (27) that with increasing swelling of the system (decrease in C) the specific area σ_i increases regardless of the morphology of the system. In this case taking into account the power concentration dependence $\phi(C)$, a decrease in the superstructure parameters R_i and D_i is obtained. According to equations (19) and (24), the resulting values of the exponent α in the dependence $R_i \sim C^{\alpha}$ are $\alpha = 1/12$, $1/6$ and $1/3$ under regimes II_+, $\mathrm{II}_{\mathrm{mf}}$ and II_θ, respectively. (It should be noted that the value of $\alpha_{\mathrm{mf}} = 1/6$ was obtained at $\nu = 1/2$ in equation (27) since in the mean-field region of a good solvent, $\mathrm{II}_{\mathrm{mf}}$, the chain size coincides with the θ dimensions.)

All the experimental data available in the literature on systems containing a non-selective solvent show that the specific area σ is actually an increasing function of the degree of swelling of the block copolymer.

The concentration dependences of dimensions R_i and D_i of superstructures are found to be less definite. On the one hand, the study[18] of lamellar structures ($i = 1$) formed by a two-block copolymer PS–PI ($M_A = M_B = 4.7 \times 10^4$) in toluene (non-selective solvent for PS and PI) in the range of volume fractions of the polymer $0.2 < C < 0.7$ showed that the thickness of A and B lamellae R_1 and D_1 and the overall period H_1 decrease with swelling. Moreover, this decrease is described by the power dependence $H_1 \sim C^{\alpha}$ where $\alpha = +1/3$. This value is in complete agreement with the above evaluation for regime II_θ. The values of the polymer–solvent interaction parameters $\chi_{AS} = 0.44$ and $\chi_{BS} = 0.4$ for PS and PI units respectively, reported in ref. 18, indicate that the conditions for both blocks are close to θ conditions.

However, at high concentrations of the block copolymer, $C > 0.6$–0.7, in ref. 18 and in a number of other papers[9] the increase in dimensions R_1 and D_1 with swelling has been established. The authors of ref. 18 relate this effect to incomplete equilibrium in the system at high concentrations.

Morphology of block copolymers: composition–concentration diagram

It follows from equations (8) and (9) that the conformational free energy of the chain in a structure of type i depends on the composition of the copolymer $q = N_A/N_B$ and the relative content of the solvent C_A/C_B (the function Q_i depends on these parameters).

Since the molecular-weight dependence of $\Delta F^i \sim N^{1/3}$ is identical for all morphologies ($i = 1$, 2 and 3), the comparison of ΔF^i values requires knowledge of numerical coefficients α_i and β_i in equation (9). These coefficients have been found by Semenov[5] for the case of superstructures in the melt ($C_A = C_B = 1$). When these data are applied, the functions become:

$$Q_i=\begin{cases}\dfrac{\pi^2}{8}\left[1+\left(\dfrac{C_B}{C_A}\right)^{\nu/(3\nu-1)} q\dfrac{C_B}{C_A}\right] & i=1\\[2ex] \dfrac{\pi^2}{16}+\dfrac{3}{8}\left(\dfrac{C_B}{C_A}\right)^{\nu/(3\nu-1)} \ln\left(1+q\dfrac{C_B}{C_A}\right) & i=2\\[2ex] \dfrac{3\pi^2}{80}+\dfrac{1}{2}\left(\dfrac{C_B}{C_A}\right)^{\nu/(3\nu-1)}\left[1-\left(1+q\dfrac{C_B}{C_A}\right)^{-1/3}\right] & i=3\end{cases} \tag{28}$$

Figure 6 shows the diagram of morphology of superstructures constructed according to equations (8) and (28). The diagram of states contains five regions. Regions I, II and III in *Figure 6* correspond to lamellae, cylinders and spheres formed by the component B of the copolymer. Regions II′ and III′ correspond to inverted cylinders and spheres when the component A forms the domains and the component B forms the matrix. The conformational free energy $(\Delta F^i)'$ of inverted structures is obtained directly from equations (8) and (28) by exchanging $C_A \rightleftarrows C_B$ and $N_A \rightleftarrows N_B$. The boundaries between the regions are determined from the condition:

$$\begin{gathered}\Delta F^i=\Delta F^{i+1}\\ (\Delta F^i)'=(\Delta F^{i+1})'\end{gathered} \tag{29}$$

(shaded values refer to inverted systems).

The case of the completely non-selective solvent $C_B=C_A=C$ $(C_B/C_A=1)$ including its absence $C=1$ is shown by a broken line in *Figure 6*. In this case the morphology of the system is determined only by the composition of the block copolymer. Thus, at $q_c^{-1}<q<q_c$ lamellae are formed; at $q_c<q<q_s$ and $q_s^{-1}<q<q_c^{-1}$ cylinders are formed; and at $q>q_s$ and $q<q_s^{-1}$ spheres appear. The numerical values of $q_c \approx 2.6$ and $q_s \approx 7$ coincide with the results in ref. 5 obtained for superstructures in the melt. Hence the change in C due to non-selective swelling at a fixed q cannot lead to a change in the morphology of the structure.

In the case of a selective solvent, $C_B/C_A \neq 1$, the unequal swelling of the components (change in C_B/C_A with increasing swelling of the system) leads to the possibility of a change in the supermolecular structure. The swelling of the matrix (increase in C_B/C_A) leads to the narrowing of regions I and II, whereas that of the domain (decrease in C_B/C_A) results in the broadening of these regions. Therefore transitions I→II→III, i.e. lamella→cylinder→sphere, are possible due to the matrix swelling and transitions III→II→I, i.e. sphere→cylinder→lamella, are possible due to the swelling of the domains.

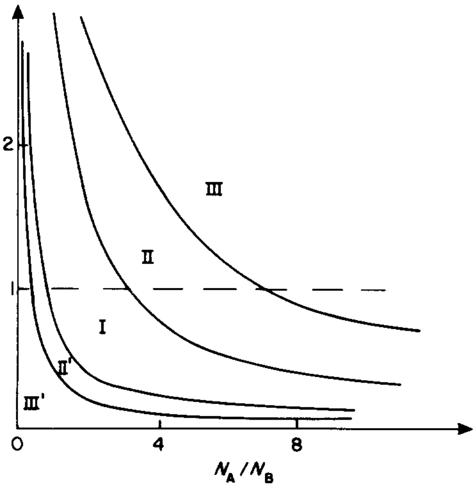

Figure 6 Concentration composition diagram of superstructures consisting of two-block copolymers

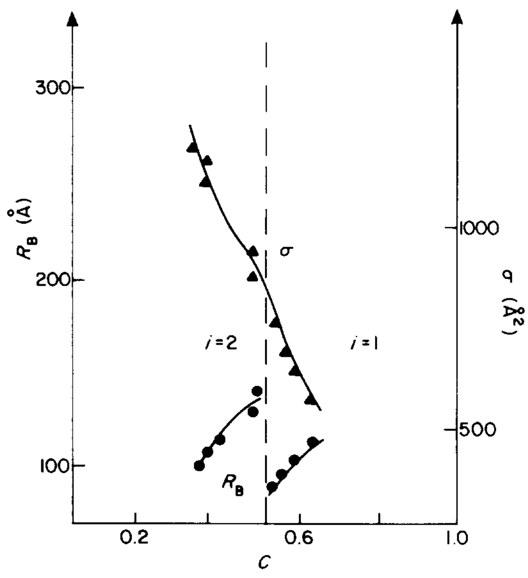

Figure 7 Cylinder–lamella concentration transition[19]

It follows from equations (8) and (29) that when the boundaries of the regions of the diagram are intersected, i.e. when the morphology of the superstructure changes, the specific area remains continuous:

$$\sigma_i=\sigma_{i+1} \tag{30}$$

which automatically leads to a jump in the size of the domain with a change in morphology:

$$R_{i+1}=R_i^{(i+1)/i} \tag{31}$$

The validity of equations (30) and (31) is independent of the details of calculation of free energies of blocks ΔF_A^i and ΔF_B^i and of the block number (they are also valid for three-block copolymers ABA or BAB) and is a direct consequence of the initial assumptions[1]: the equilibrium character of the supermolecular structure and the small thickness of the interface layer as compared to the size of structural elements $(\Delta \ll R_i, D_i)$. It is the small value of Δ that makes it possible to consider the free energy of the system as the sum of contributions of ΔF_A, ΔF_B and ΔF_S (see ref. 1 for further details).

The existence of concentration transitions leading to a change in the morphology of the superstructure has been reported by a number of authors[19,20]. *Figure 7* shows the lamella–cylinder concentration transition observed in ref. 19 in a structure formed by a three-block polyisoprene–polymethylstyrene–polyisoprene (ABA) copolymer with a fixed composition $(M_A{:}M_B=63{:}37)$ in decalin (preferential solvent for the A block). The change in the morphology of the structure took place at a weight concentration of the copolymer $C^*=50$–52%. Unfortunately, it is not possible to give the theoretical evaluation of C^* from the theory of two-block copolymers developed here because the position of the transition is determined by the coefficients α_i, β_i in Q_i depending on the block number. A primitive reduction of a three-block copolymer to the two-block copolymer with the same composition (for the sample investigated in ref. 19, $q \approx 2$) gives $C^* \approx 0.8$ (diagram in *Figure 6*).

It is possible, however, to compare with the theory other characteristics of the transition: the value of the jump in domain size and the slope of concentration dependence near the transition point. It can be seen from *Figure 7* that at the transition point the specific area per chain remains continuous $\sigma_1 = \sigma_2$ and the domain size undergoes a jump the value of which (R_2/R_1) is close to 2, in complete agreement with equation (31) at $i=1$. The slope of concentration dependences $\sigma_i(C)$ near C^* decreases at the lamella–cylinder transition, which is also in agreement with the theory.

Lamellar superstructure: block copolymer with one crystallizable block

The equilibrium characteristics of superstructures formed by two-block (and three-block) copolymers with non-crystallizable blocks have been obtained above. Here the lamellar structure formed by the copolymer with one block that can undergo crystallization will be considered (*Figure 8*). The crystalline layers in this structure are formed by folded chains B. The number of folds n_c per block and the specific interface, $\sigma/a^2 = n_c + 1$, are determined by the conditions of dense packing $C_B = 1$:

$$\frac{\sigma}{a^2} = n_c + 1 = \frac{N_B a}{R_1} \tag{32}$$

The amorphous block A can undergo swelling in a solvent $C_A \leqslant 1$. As before, the conformational free energy of the system is described by equation (1) and the free energy of block A and the interface free energy are described by equations (2) and (4). However, since the crystalline block B does not contribute to elastic stretching, equation (3) is replaced by:

$$\Delta F_B = \varepsilon_1 N_B + n_c(\varepsilon_2 - \varepsilon_1) = \varepsilon_1 N_B \times \delta\varepsilon n_c \tag{33}$$

where ε_1 is the energy of a unit in the crystalline state and $\delta\varepsilon$ is the excess energy at a kink in fold formation.

In other words, only two addends, ΔF_A and ΔF_s are retained in equation (1). Moreover, it follows from equations (32) and (33) that the value of ϕ in equation (2) is replaced by $\phi' = \phi + \delta\varepsilon$.

As a result of the minimization of ΔF we obtain:

$$R_1 = a\left(\frac{4\phi'}{\pi^2}\right)^{1/3} N_B N_A^{-1/3} C_A^{(4\nu-1)/3(3\nu-1)} \tag{34}$$

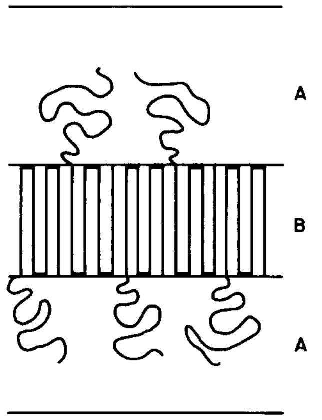

Figure 8 Scheme of a lamella formed by a block copolymer with one crystallizable block

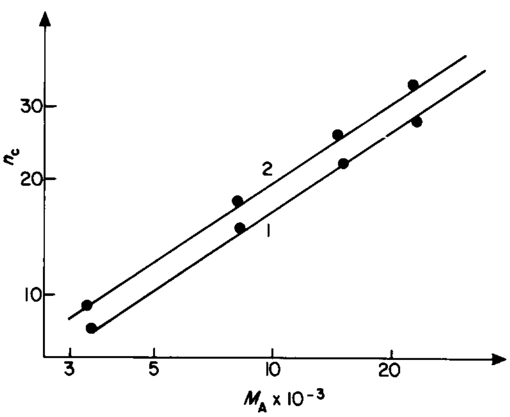

Figure 9 Molecular-weight dependence of the number of folds in a lamella in the absence (1) and the presence (2) of the solvent in the amorphous layer[22]

$$D_1 = a\left(\frac{4\phi'}{\pi^2}\right)^{1/3} N_A^{2/3} C_A^{-(5\nu-2)/3(3\nu-1)} \tag{35}$$

$$\frac{\sigma}{a^2} = n_c + 1 = \left(\frac{4\phi'}{\pi^2}\right)^{-1/3} N_A^{1/3} C_A^{(1-4\nu)/3(3\nu-1)} \tag{36}$$

These relationships coincide at $C_A = 1$ with the limiting case ($N \to \infty$) of the more detailed analysis in ref. 21.

Equations (34)–(36) determine the molecular-weight dependence of characteristics of the lamellar mesophase with one crystalline block. They show that, in contrast to the case of block copolymers with two amorphous blocks, equations (7)–(9), the thickness of the amorphous layer in semicrystalline block copolymers and the specific area σ/a^2 are determined only by the length of the amorphous block N_A (at any ratios of components A and B).

The dependence (36) is of particular interest. According to it, the number of folds of the crystalline component B is independent of N_B and is determined only by the characteristics of the amorphous layer: the block length N_A and the solvent content $(1 - C_A)$.

According to experimental data[22] for structures formed by polyoxyethylene–polystyrene (POE–PS) and polyoxyethylene–polybutadiene (POE–PB) copolymers, the number of folds of POE is actually independent of N_B and increases with N_A in both the absence and the presence of the solvent in the system (*Figure 9*).

However, the experimental dependence $n_c \sim N_A^{0.6}$ is found to be slightly stronger than according to equation (36), and at $M_B/M_A > 2$ the dependence of n_c on N_B also appears. It is possible that complete equilibrium is not attained in the structures being formed.

The increase in swelling $(1 - C_A)$ of the amorphous block, just as the increase in N_A, should lead us to an increase in fold number and the compression of the crystalline unswelling block.

The dependence of n_c on C_A is described by a power dependence $n_c \sim C_A^{-\alpha_x}$ with the exponent:

$$\alpha_x = \begin{cases} -7/12 & x = + \\ -2/3 & x = \text{mf}, \theta \end{cases} \tag{37}$$

The experimental dependence[22] of the specific area $\sigma = a^2(n_c + 1)$ on the volume fraction of the solvent $(1 - C_A)$ is shown in *Figure 10*. The tangent of the slope angle of the straight line passing through the experimental

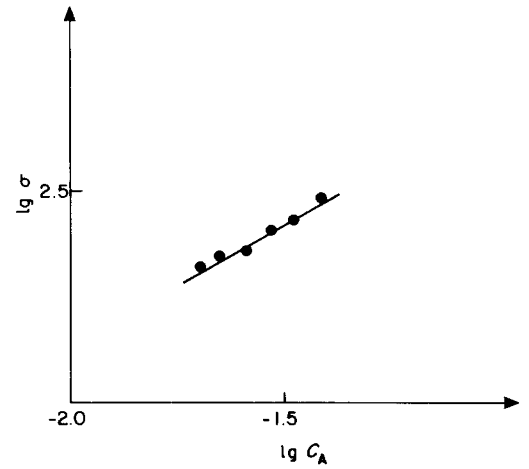

Figure 10 Dependence of specific area σ on solvent concentration in the amorphous layer

points is 0.6, in good agreement with the theoretical evaluations in equation (37).

The complete period of the lamella:

$$H_1 = R_1 + D_1 = a\left(\frac{4\phi'}{\pi^2}\right)^{1/3} N_A^{2/3} \times \left(C_A^{-(5\nu-2)/3(3\nu-1)} + \frac{N_B}{N_A} C_A^{(4\nu-1)/3(3\nu-1)}\right) \quad (38)$$

is determined by the sum of terms differing in the sign of the concentration dependence: increase in C_A leads to increase in R_1 and decrease in D_1. Hence, the behaviour of H_1 is determined by the sign of the derivative:

$$\frac{\partial H_1}{\partial C_A} \sim C_A \frac{N_B}{N_A} \frac{4\nu-1}{5\nu-2} - 1 \quad (39)$$

For the sample investigated in ref. 22 with $M_B/M_A = 1.5$ and $C_A < 0.45$, the value of H_1 should increase with decreasing C_A ($\partial H_1/\partial C_A < 0$), which is actually observed experimentally. It is of interest that in the range of weak dilutions the jump-like character of changes in the lamella parameters is very distinct. This character reflects the fact that n_c is an integer, which is particularly pronounced at low n_c values. In this case in the C_A ranges in which $n_c = \text{const}$, the value of H_1 increases with decreasing C_A as a result of the swelling of the amorphous block at a constant width of the crystalline layer.

Mutual influence of blocks

As has been shown above using a number of examples, the superstructures of block copolymers exhibit an interesting effect of the mutual influence of blocks of each component on the dimensions of structural elements of the other component.

Thus, in the section 'Superstructures of three-block copolymers', a transition from a two-block AB to a three-block ABA copolymer was considered. In this case the size M_B of the component B did not change but only the total amount of the component A increased by a factor 2. However, this resulted not only in the increase in the size of the structural element A (thickness D_1 of the lamella) but also in the decrease in the thickness of the element B. A similar result has also been observed in the concentration dependences of structural parameters: the swelling of one element in a selective solvent always leads not only to an increase in the size of this element but also to a decrease in that of the other unswelling element (see section on 'Concentration dependence of... the superstructures').

The reason for the mutual influence of block copolymer components is due to the fact that the specific area σ of the boundary of microphases in the superstructure is determined as a result of a compromise between two opposite trends: surface tension tends to decrease σ, whereas mutual side repulsion of blocks due to their resistance to the increase in grafting density, $1/\sigma$, tends to increase σ. The latter effect increases with the size of blocks of each component (increase in molecular weight and stiffness) and with increasing degree of their swelling. This increase leads to an increase in σ, which in turn, taking into account the constant volume of a structural element per block of the invariable component, leads to a decrease in the thickness of this element.

Hence, the size of each element of the superstructure depends not only on the molecular characteristics of its own blocks but also on those of blocks forming the other element.

The rearrangement of the morphology of the entire system during selective swelling of one block considered in the section on 'Morphology of block copolymers ...' is also an example of the mutual influence of blocks.

Finally, one of the most outstanding manifestations of the mutual influence of blocks has been considered in the section on 'Lamellar superstructure ...'. It was shown in this section that the number of chain folds of the crystalline component B is independent of M_B but is determined by the characteristics of the amorphous component: the block length M_A and the solvent content $(1 - C_A)$. This result was obtained here in terms of the equilibrium theory of block copolymers for which the semicrystalline structure with chain folds in the crystalline domain corresponds to the equilibrium state of the system. The authors believe, however, that the conclusion that the molecular weight (or the effective molecular volume) of the amorphous layer determines the fold number of the crystalline layer is of a more general character. It may be extended to the semicrystalline structures of homopolymers, the very existence of which is due to kinetic effects.

CONCLUSIONS

In this paper and in part 1[1] we have developed a general theory of supermolecular structures in two-block AB copolymer–solvent systems, which is mainly based on simple scaling concepts.

The supermolecular structures considered here, first the supercrystalline structures swelling in the solvent, are very interesting formations. They combine the existence of long-range supercrystalline order in the arrangement of A and B structural elements ~100 Å in size and the existence of the amorphous state within the elements of both types or one type. This regular microphase separation is a direct consequence of the chemical structure of two- (or three-) block copolymers in which the blocks are sufficiently large for the manifestation of polymer properties. Their incompatibility ensures phase separation, their fixation in one chain limits the transverse dimensions of each phase and moderate molecular-weight distribution determines the regular spatial arrangement of structural elements.

The scaling approach used in this work made it possible to establish several relationships between the morphology and characteristics of supermolecular structures on the one hand and the parameters of macromolecules, the content and properties of the solvent on the other. Moreover, it was possible to consider in a unified manner the behaviour of block copolymers in a wide range of concentrations varying from micellar solutions and superstructures with different contents of both the selective and the non-selective solvent to its complete absence.

This theory permitted the interpretation of a large number of experimental data accumulated in the literature and we hope that it may stimulate further investigations. We mean, first, the conformation–concentration diagram of the morphology of the superstructure constructed in this work. According to this diagram, the change in the concentration of the selective solvent can lead to the rearrangement of the morphology of the system.

To avoid misunderstanding, it should be emphasized that in this paper we restricted ourselves to the study of ordered supercrystalline structures under the condition distant from the point of transition to this ordered state. For this reason, the suggestion about the thin interphase layer, the properties of which do not depend on the molecular weight of individual blocks (see ref. 1), was chosen as one of the starting points of this work. The theory of the melt–superstructure transition has been considered in refs. 23 and 24.

In this paper we restricted ourselves to the consideration of traditional superstructures with planar lamellae, cylinders and spheres of one of the components. Recently it has been reported that a new type of structure has been detected: a bitetrahedral structure formed by star-branched block copolymers[25]. In a forthcoming paper (see also ref. 26) the approach developed here and the results of the theory of star-branched macromolecules[27–29] will be used for the theoretical analysis of these structures.

REFERENCES

1 Birshtein, T. M. and Zhulina, E. B. *Polymer* 1989, **30**, 170

2 Birshtein, T. M. and Zhulina, E. B. *Vysokomol. Soed. (A)* 1985, **27**, 1613

3 Zhulina, E. B. and Birshtein, T. M. *Vysokomol. Soed. (A)* 1986, **28**, 2589

4 Zhulina, E. B. and Birshtein, T. M. *Vysokomol. Soed. (A)* 1987, **29**, 1524

5 Semenov, A. N. *Sov. Phys.-JETP* 1985, **61**, 733

6 Helfand, E. and Wasserman, Z. R. *J. Polym. Eng. Sci.* 1977, **17**, 582

7 Helfand, E. and Wasserman, Z. R. *Macromolecules* 1978, **11**, 960; 1980, **13**, 995

8 Hashimoto, T., Shibayama, M. and Kawai, H. *Macromolecules* 1980, **13**, 1237

9 Gallot, B. in 'Liquid Crystalline Order in Polymers', (Ed. A. Blumstein), Academic Press, New York, 1978

10 Hashimoto, T. *Macromolecules* 1982, **15**, 1548

11 Hashimoto, T., Fujimura, M. and Kawai, H. *Macromolecules* 1980, **13**, 1660

12 Richards, R. W. and Thomason, I. L. *Macromolecules* 1983, **16**, 982

13 Todo, A., Kiuno, H., Miyoshi, K., Hashimoto, T. and Kawai, H. *J. Polym. Eng. Sci.* 1977, **17**, 587

14 Douy, A. and Gallot, B. *Makromol. Chem.* 1973, **165**, 297

15 Douy, A. and Gallot, B. *Cr. Acad. Sci. (C)* 1976, **282**, 895

16 De Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979

17 Naolandi, I. and Hong, K. M. *Macromolecules* 1983, **16**, 1443

18 Shibayama, M., Hashimoto, T., Hasegawa, H. and Kawai, H. *Macromolecules* 1983, **16**, 1427

19 Volkova, L. A., Andreeva, N. A., Podolsky, A. F., Bitsenko, M. I. and Eskin, V. A. *Vysokomol. Soed. (A)* 1982, **24**, 1180

20 Douy, A. and Gallot, B. *Makromol. Chem.* 1972, **156**, 81

21 DiMarzio, E. A., Guttman, C. M. and Hoffman, I. D. *Macromolecules* 1980, **13**, 1194

22 Gervais, M. and Gallot, B. *Makromol. Chem.* 1973, **171**, 157

23 Leibler, L. *Macromolecules* 1980, **13**, 1602

24 Erukhimovitch, I. Ya. *Vysokomol. Soed. (A)* 1982, **24**, 1942

25 Alward, D. B., Kinning, D. I., Thomas, E. L. and Fetters, L. J. *Macromolecules* 1986, **19**, 215

26 Birshtein, T. M. and Zhulina, E. B. *Vysokomol. Soed. (A)* 1988, **30**, 387

27 Daoud, M. and Cotton, J. P. *J. Physique.* 1982, **43**, 531

28 Birshtein, T. M. and Zhulina, E. B. *Polymer* 1984, **25**, 1435

29 Birshtein, T. M., Zhulina, E. B. and Borisov, O. V. *Polymer* 1986, **27**, 1079

NOTE ADDED IN PROOF

The scaling analysis scheme used in this paper assumes the determination of system characteristics in the form of power asymptotics. The conditions of transition from one asymptotic dependence to the other are determined by a crossover of the corresponding asymptotics. Thus, the boundaries of regions in *Figure 6* were obtained by crossover of the corresponding free energies (equation (29)).

It should be noted, however, that this approach inevitably leads to some simplification of the picture obtained. Thus, the boundaries between regions I, II, III, I′ and II′, shown in *Figure 6* by solid lines, are actually two-phase corridors. These two-phase regions are typical for first-order concentration phase transitions in polymer solutions. A more detailed analysis shows that the widths of two-phase corridors are proportional to $N^{-2/3}$, and hence are small at $N \gg I$. Consequently, these regions may be approximated by lines, as in *Figure 6*.