Theory of supermolecular structures in polydisperse block copolymers: 2. Lamellar superstructure consisting of two-block copolymers

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The lamellar superstructure formed in polydisperse block copolymer melts has been considered. For the narrow interphase approximation, a mean-field analytical theory has been developed. This theory relates the equilibrium parameters of the superstructure to the characteristics of the copolymer molecules: the average molecular weight, the type of polydispersity and the surface tension. It is shown that, in a binary mixture of long block copolymers (with different molecular weights and compositions), the formation of a single lamella with common period is under certain conditions thermodynamically more advantageous than the segregation of the system into lamellae formed by the mixture components. The structure of the lamellar layers is investigated in detail. Theoretical and experimental data are compared.

(Keywords: lamellar superstructure; polydisperse copolymer melt; structure stability)

INTRODUCTION

Recently in the pioneering publication by Milner *et al.*[1] and in paper 1 of this series[2], a theory has been developed describing the structure and properties of layers of polydisperse polymer chains grafted at one end onto an impermeable planar surface. One of the main results of these works was the derivation of general analytical expressions making it possible to calculate the free energy and the layer height for an arbitrary form of the distribution function of molecular weights of the grafted chains (equations (1.46) and (1.45); the notation denotes the equations in paper 1[2]). These equations and some other results of ref. 2 make it possible to carry out a consecutive theoretical analysis of well determined supermolecular (lamellar) structures formed in solutions and melts of block copolymers polydisperse in both molecular weight and composition. Microphase separation in block copolymers is known to be based on the incompatibility of their components. The bonding of block ends at one point restricts the transverse dimensions of the resulting phases, causing their regular spatial alternation: the formation of a supercrystalline lattice. In narrow disperse block copolymer systems, the type of superlattice is determined by the ratio of molecular weights (or volumes) of blocks A and B. When the component volumes are approximately equal, a lamellar superlattice is formed. In the opposite case, spherical or cylindrical domains consisting of the minor component are formed in a matrix of the major component and located at the nodes of a cubic or hexagonal lattice.

The theory of microphase separation is particularly well developed for the case of a monodisperse block copolymer melt, all the molecules of which are of the same molecular weight and composition[3–8]. A considerable simplification of the initial equations describing the characteristics of the superstructures is the suggestion that the interphase layer between the A and B elements of the mesophase is narrow in comparison to domain size: the narrow interphase approximation (NIA). This approximation, according to which the joint points of A and B blocks are located within a narrow interphase (or interface) layer, makes it possible to consider the copolymer blocks to be 'grafted' onto the interphase. It should be borne in mind that the condition under which the NIA is valid is considerably distant from the disordered melt–mesophase transition point. Just under these conditions is the concept of a well determined supermolecular structure applicable. The use of the NIA and the development of the theory of grafted layers allows a considerable advance to be made in the theory of microsegregated block copolymers. In particular it is possible to obtain the analytical dependences of characteristic parameters of mesophases with different morphologies in melts[8] and solutions[9–12] of monodisperse block copolymers on their molecular weight and composition and the quantity and quality of the solvent.

As has been mentioned in the introduction to ref. 2, the aim of the work of this series is further development of the equilibrium theory of well determined superstructures: the analysis of the effect of polydispersity of the molecular weight and composition of block copolymer molecules on the morphology and characteristics of the mesophase. In the present paper we will consider the simplest case of lamellar mesophase formed in the melt of a two-block copolymer of AB type with an arbitrary type of polydispersity of molecular weight and composition. The approach will be based on the results and concepts developed in paper 1[2].

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A particular case of this system is a binary mixture of narrow disperse block copolymers with very different molecular weights. This type of polydispersity leads to fundamentally different possibilities for the formation of supermolecular structures. One of them is the formation of a single lamellar structure with a common period, the layers of this structure being formed by blocks A (or B) of different lengths mixed on the molecular level. The other possibility is the segregation of mixture components with the formation of lamellar structures, the layers of which consist of blocks of the same molecular weight. We will show that when each component of the mixture is lamellae-forming, the formation of a single lamellar structure is thermodynamically more advantageous than that of lamellae consisting of individual components The conformational structure of this single lamella will be considered, the general analytical dependences of its equilibrium characteristics will be obtained and the results will be compared with experimental data.

MODEL AND METHOD

Let us consider a lamellar mesophase formed in the melt of a polydisperse two-block copolymer of AB type under the conditions of microphase separation (*Figure 1*). The symbols used previously in the consideration of monodisperse systems[12] will be employed. A chain part of length equal to chain thickness a will be used as unit and the asymmetry parameter of the Kuhn segment $p = A/a$ is taken to be $p \geqslant 1$. It will be assumed that the molecular-weight distribution (*MWD*) of blocks A and B is given by the distribution functions $q_A(N_A)$ and $q_B(N_B)$ and the distribution of the overall molecular weight $N = N_A + N_B$ is determined by the function $q(N)$ so that:

$$\int_{N^{\min}}^{N^{\max}} q(N')\,dN' = 1 \qquad \int_{N_j^{\min}}^{N_j^{\max}} q_j(N_j')\,dN_j' = 1 \tag{1}$$

where $N_j^{\min} \gg 1$ and $N_j^{\max} > N_j^{\min}$ are the minimum and maximum values of molecular weights of block j ($j = \mathrm{A, B}$) in the mixture, and $N^{\min}$ and $N^{\max}$ are the minimum and maximum values of the overall molecular weight. The half-width of the lamellar layer of type j is denoted by H_j, $H = H_A + H_B$ is the half-period of the structure and σ is the mean area of the interphase per block copolymer molecule.

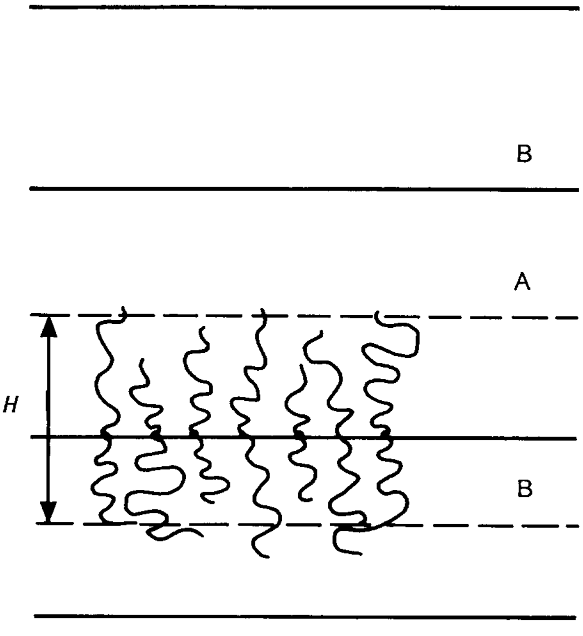

Figure 1 Scheme for a lamellar superstructure formed in a polydisperse melt of two-block copolymers

The equilibrium supermolecular structure in block copolymer systems is known to be determined by the balance of two factors. One of them is the tendency for the interface area to reduce (and the corresponding reduction of losses in the free energy of the system). Simultaneously this reduction in area leads to an increase in conformational restrictions for blocks in the elements of the mesophase causing block stretching normal to the surface of the interphase (and a corresponding increase in their conformational free energies).

The NIA makes it possible to consider copolymer blocks as grafted onto the interphase and to consider the free energy density of the mesophase as the sum of three terms:

$$\Delta F = \Delta F_S + \Delta F_A + \Delta F_B \tag{2}$$

where ΔF_S is the surface energy per unit volume a^3 determined by surface tension at the interface of the A and B components and by the half-period H:

$$\Delta F_S = \frac{\Phi' a^3}{H} = \frac{\Phi a}{H} \tag{3}$$

where Φ' is the surface tension coefficient ($\Phi = \Phi' a^2$ is the surface energy of unit surface). Here and below all energetic values are expressed in kT units. Under the conditions of high-molecular-weight block copolymers ($N_j^{\min} \gg 1$), the surface tension coefficient is determined by the chemical structure of A and B blocks (via the Flory interaction parameter χ_{AB}) and is independent of the molecular weights of the blocks, $\Phi' = \mathrm{const}(N_A, N_B)$, but may depend on the quality and quantity of solvent[9,13].

In the case of the melt considered here corresponding to the conditions of a dense layer ($\varphi(x) = 1$), the relationship between H_j and the *MWD* of the block $q_j(N_j)$ is determined by equation (1.43) at $\nu = 1/3$ and by the results given in table 1.1 (see paper 1[2] for further details) so that

$$H = \sum_j H_j = a\left(\frac{\sigma}{a^2}\right)^{-1} \sum_j \left(N_j^{\min} + \int_{N_j^{\min}}^{N_j^{\max}} q_j(N_j')\,dN_j'\right) \tag{4}$$

The number-average molecular weights in the mixture will be introduced:

$$\bar{N}_j = \int_{N_j^{\min}}^{N_j^{\max}} N_j' q_j(N_j')\,dN_j' = N_j^{\min} + \int_{N_j^{\min}}^{N_j^{\max}} dN_j' \varphi_j(N_j') \tag{5}$$

where

$$\varphi_j(N_j) = \int_{N_j}^{N_j^{\max}} q_j(N_j')\,dN_j' \qquad (j = \mathrm{A, B}) \tag{6}$$

This function represents the fraction of blocks of type j with a molecular weight higher than N_j. The number-average overall molecular weight is given by:

$$\bar{N} = \sum_j \bar{N}_j = H\sigma/a^3 \tag{7}$$

The densities of the conformational free energy of block stretching, ΔF_A and ΔF_B, are determined by equation

(1.44) and table 1.1 at $\nu = 1/3$ to give:

$$\Delta F_j = \frac{\pi^2}{8p}\frac{a}{H}\left(\frac{\sigma}{a^2}\right)^{-3} \times \left[N_j^{\min} + \int_{N_j^{\min}}^{N_j^{\max}} \mathrm{d}N_j \left(\int_{N_j}^{N_j^{\max}} q_j(N_j')\,\mathrm{d}N_j' \right)^3 \right] \quad (8)$$

Applying equations (5)–(7), equation (8) may be written in the following form:

$$\Delta F_j = \frac{\pi^2}{8p\bar{N}}\left(\frac{\sigma}{a^2}\right)^{-2}\left(\bar{N}_j - \int_{N_j^{\min}}^{N_j^{\max}} \varphi_j(N_j')[1-\varphi_j^2(N_j')]\,\mathrm{d}N_j'\right) \quad (9)$$

Then the total density of free energy of the system ΔF is given by:

$$\Delta F = \frac{1}{\bar{N}}\left[\frac{\Phi\sigma}{a^2} + \frac{\pi^2}{8p}\left(\frac{\sigma}{a^2}\right)^{-2} \times \left(\bar{N} - \sum_j \int_{N_j^{\min}}^{N_j^{\max}} \varphi_j(N_j')[1-\varphi_j^2(N_j')]\,\mathrm{d}N_j'\right)\right] \quad (10)$$

RESULTS

The characteristics of the lamellar structure are determined by the minimization of the total density of free energy ΔF with respect to the only independent parameter σ:

$$\frac{\sigma}{a^2} = \left(\frac{\pi^2}{4\Phi p}\bar{N}\right)^{1/3}(f[\varphi])^{1/3} \quad (11)$$

$$H_j = a\left(\frac{4\Phi p}{\pi^2}\right)^{1/3}\bar{N}_j(\bar{N}f[\varphi])^{-1/3} \quad (12)$$

$$H = a\left(\frac{4\Phi p}{\pi^2}\right)^{1/3}(\bar{N})^{2/3}(f[\varphi])^{-1/3} \quad (13)$$

$$\Delta F = \frac{3}{2}\left(\frac{\pi^2}{4p}\Phi^2\right)^{1/3}(f[\varphi])^{1/3}(\bar{N})^{-2/3} \quad (14)$$

where the type of the function $f[\varphi]$ is completely determined by the polydispersity character of the system considered here (by distribution functions $q_A(N_A)$ and $q_B(N_B)$):

$$f[\varphi] = 1 - \frac{1}{\bar{N}}\sum_j \int_{N_j^{\min}}^{N_j^{\max}} \mathrm{d}N_j'\varphi_j(N_j')[1-\varphi_j^2(N_j')] \quad (15)$$

Equations (11)–(15) determine in general form the equilibrium characteristics of the lamellar structure formed by the molecules of a two-block copolymer with an arbitrary distribution of molecular weight and composition. Examples of some specific *MWD* will be considered.

Monodisperse block copolymer

It can be easily seen that in the case of monodisperse block copolymer with molecular weight $N = N_A + N_B$ ($q_j(N_j') = \delta(N_j' - N_j)$), equations (11)–(15) give the known[8] results:

$$\frac{\sigma}{a^2} = \left(\frac{\pi^2}{4\Phi p}N\right)^{1/3} \quad (16)$$

$$H_j = a\left(\frac{4\Phi p}{\pi^2}\right)^{1/3}N_jN^{-1/3} \quad (17)$$

$$H(N) = a\left(\frac{4\Phi p}{\pi^2}\right)^{1/3}N^{2/3} \quad (18)$$

$$\Delta F(N) = \frac{3}{2}\left(\frac{\pi^2}{4p}\Phi^2\right)^{1/3}N^{-2/3} \quad (19)$$

In this case the detailed structure of lamellar layers (distribution functions of local chain stretching in layers and free end distribution) is determined by equations (1.15), (1.16), table 1.1 and equations (16) and (17). (Equations (16) and (17) relate the density $1/\sigma$ of 'grafting' of blocks onto the interface and the thickness H_j of lamellar layers to the values of N_A, N_B and Φ.) Thus, the function $E_j(X, X')$ determining the local stretching of a block of type j at a distance X from the nearest interface under the condition that the free end of the block is at a distance X' from it is given by:

$$E_j(X, X') = \frac{\pi}{2N_j}[(X')^2 - X^2]^{1/2} \quad (20)$$

The distribution function of free ends of blocks in lamellar layers is determined by equations (1.16) and (17):

$$g_j(X') = \frac{1}{H_j}\frac{X'}{[H_j^2 - (X')^2]^{1/2}} \quad (21)$$

Binary mixture of monodisperse copolymers

A binary mixture of monodisperse two-block copolymers of the AB type differing in molecular weights and compositions will be considered. For exactness, the component forming a block of the highest molecular weight among all four blocks will be designated by A. Let the value $(N_A + \Delta N_A)$ be the number of units in this block and N_A the number of units in the other A block. Let $(N_B + \Delta N_B)$ and N_B be the numbers of units in the two remaining blocks B. If these symbols are applied, the distribution functions $q_j(N_j')$ are given by:

$$q_j(N_j') = q_j\delta(N_j' - N_j - \Delta N_j) + (1 - q_j)\delta(N_j' - N_j) \qquad (j = \mathrm{A}, \mathrm{B})$$

where q_j is the fraction of blocks of type j with the highest molecular weight. Correspondingly, in this case the function in equation (15) is expressed by:

$$f[\varphi] = 1 - \frac{\Delta N_A}{\bar{N}}q_A(1 - q_A^2) - \frac{\Delta N_B}{\bar{N}}q_B(1 - q_B^2) \quad (22)$$

It follows from the definition of q_j ($j = \mathrm{A}, \mathrm{B}$) that two cases may be observed in a binary mixture of block copolymers: $q_A = q_B$ and $q_A = 1 - q_B$. In the former, symmetrical case, $q_A = q_B$, both blocks of one copolymer are larger than the corresponding blocks of the second copolymer. Using the symbols introduced above, the molecular weights of copolymer blocks are equal to $(N_A + \Delta N_A)$ and $(N_B + \Delta N_B)$ for one of the components and N_A and N_B for the second component. In the latter, non-symmetrical case, $q_A = 1 - q_B$, the molecular weights of blocks are equal to $(N_A + \Delta N_A)$ and N_B for the first component and N_A and $(N_B + \Delta N_B)$ for the second component of the mixture (*Figure 2*).

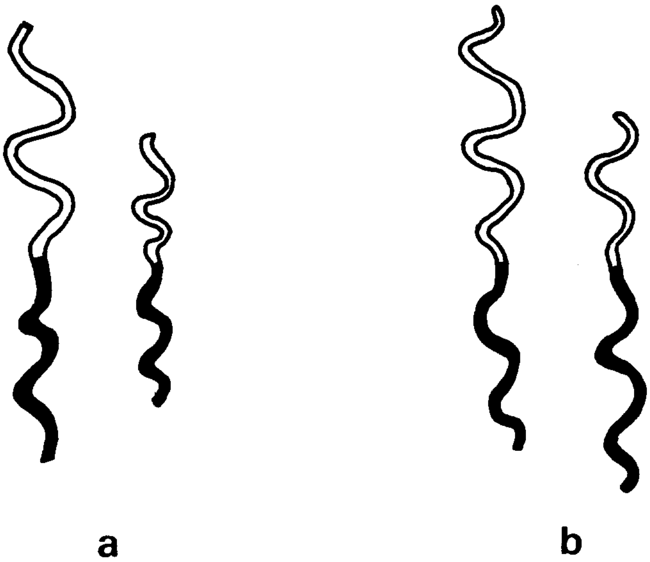

Figure 2 (a) Symmetrical and (b) asymmetrical situations which may be observed in a binary mixture of block copolymers with different compositions and molecular weights

Symmetric case $q_A = q_B = q$. In this case equation (22) gives:

$$f[\varphi] = \frac{1 - q^3 + q^3(N_2/N_1)}{1 - q + q(N_2/N_1)} = 1 - q(1 - q^2)\frac{\Delta}{\bar{N}} \quad (23)$$

where $N_2 = N_A + N_B + \Delta N_A + \Delta N_B$ and $N_1 = N_A + N_B$ are the total number of units in block copolymers of the mixture and $\Delta = N_2 - N_1$. Hence, in the symmetric situation, the function $f[\varphi]$ does not depend on the composition of the copolymer molecules and is determined only by the ratio of overall lengths $N_2/N_1 > 1$ of the copolymers. Correspondingly, in this case the specific area σ and the complete period $2H$ are not sensitive to the polydispersity of the composition of the components.

Non-symmetric case $q = q_A = 1 - q_B$. In the non-symmetric case, $q_A = 1 - q_B$, the polydispersity of composition is of considerable importance. Here we have $N_2 = N_A + \Delta N_A + \Delta N_B$, $N_1 = N_A + N_B + \Delta N_B$ and:

$$f[\varphi] = 1 - \frac{q(1 - q)}{\bar{N}}[\Delta N_A(1 + q) + \Delta N_B(2 - q)] \quad (24)$$

For simplicity, let $\Delta N_A = \Delta N_B = \Delta N$ and hence, $N_1 = N_2 = \bar{N}$. Then we have $f[\varphi] = 1 - 3q(1 - q)\Delta N/\bar{N}$ and the increase in the asymmetry of composition of block copolymers (increase in $\Delta N/\bar{N}$) may lead to considerable deviations of $f[\varphi]$ from unity even if the overall molecular weights of the components are equal. Consequently, in the non-symmetric case the characteristics of the lamellar mesophase are sensitive to the polydispersity of block copolymers with respect to both the molecular weights and the composition.

Structure of lamellar layers. As already mentioned, under the conditions of the NIA when the copolymer blocks are actually 'grafted' onto the interface, the structure of lamellar layers may be described from the viewpoint of the concepts of the structure of grafted layers developed in ref. 2. Thus, in the case of a binary mixture of monodisperse block copolymers considered here, each lamellar layer is a dense layer of polymer chains (copolymer blocks) with degrees of polymerization N_j and $(N_j + \Delta N_j)$, grafted at a density $1/\sigma$ onto a planar surface (interface). Note that the value of σ itself is determined from the molecular weights of blocks N_j and $(N_j + \Delta N_j)$, the mixture composition q_j and the surface tension Φ by using equations (11) and (22). In accordance with the concepts of ref. 2 of the structure of polydisperse grafted layers, each layer exhibits a complex structure. Shorter blocks accumulate in the regions of thickness $H_j^{(1)}$ adjoining the boundaries of the layer, whereas longer blocks form the central part of the layer of width $2(H_j - H_j^{(1)})$ (*Figure 3*). The width of the region where short blocks are accumulated $H_j^{(1)}$ is determined by equation (1.22) and table 1.1 at $\nu = 1/3$:

$$H_j^{(1)} = \frac{N_j a^3}{\sigma}(1 - q_j^2)^{1/2} \equiv H_j^0(1 - q_j^2)^{1/2} \quad (25)$$

where q_j is the fraction of longer blocks with molecular weight $(N_j + \Delta N_j)$ in a layer of type j. Both long and short blocks are stretched differently, and each block is stretched irregularly along its length. The functions of their local stretching are described by equations (1.12) and (1.13):

$$E_j^{(1)} = \frac{\pi}{2N_j}[(X')^2 - X^2]^{1/2} \quad (26)$$

$$E_j^{(2)} = \frac{\pi}{2N_j}\begin{cases}[u_j^2(X') - X^2]^{1/2} & 0 \leqslant X \leqslant H_j^{(1)} \\ [u_j^2(X') - u_j^2(X)]^{1/2} & H_j \geqslant X \geqslant H_j^{(1)}\end{cases} \quad (27)$$

where

$$u_j(X') = \frac{X' - \alpha_j[(X')^2 - (H_j^{(1)})^2(1 - \alpha_j^2)]^{1/2}}{1 - \alpha_j^2} \qquad \alpha_j = \frac{\Delta N_j}{N_j} \quad (28)$$

Superscripts (1) and (2) refer to short and long blocks, respectively. Note that equations (26)–(28) were first obtained in a work by Milner *et al.*[1], who applied a slightly different formalism in the consideration of polydisperse grafted layers. The distribution functions of free block ends and the density profiles of units of short and long blocks in lamellar layers are described by equations (1.21), (1.26), (1A.26) and (1A.25):

$$g_j^{(1)}(X') = \frac{X'}{H_j^0}\frac{1}{[(H_j^0)^2 - (X')^2]^{1/2}} \qquad 0 \leqslant X' \leqslant H_j^{(1)} \quad (29)$$

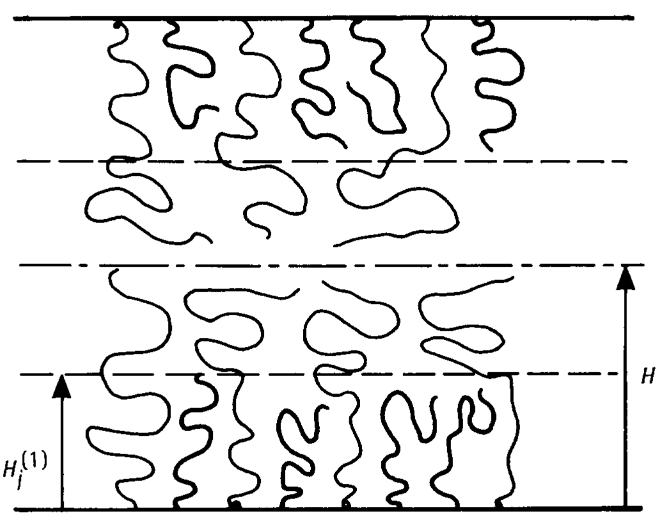

Figure 3 Scheme for the structure of lamellar layers in a lamellar structure formed in a binary mixture of block copolymers

$$g_j^{(2)}(X') = \frac{1}{H_j^0(1-\alpha_j^2)} \frac{u_j(X')}{[u_j^2(H_j) - u_j^2(X')]^{1/2}} \frac{\mathrm{d}u_j(X')}{\mathrm{d}X'} \qquad H_j^{(1)} \leqslant X' \leqslant H_j \tag{30}$$

$$\varphi_j^{(1)} = \frac{1}{2} - \frac{1}{\pi}\arcsin\left(\frac{2q_j^2 - 1 + (1-q_j^2)(X/H_j^{(1)})^2}{1-(1-q_j^2)(X/H_j^{(1)})^2}\right) \qquad 0 \leqslant X \leqslant H_j^{(1)} \tag{31}$$

$$\varphi_j^{(2)} = \begin{cases} 1 - \varphi_j^{(1)}(X) & 0 \leqslant X \leqslant H_j^{(1)} \\ 1 & H_j \geqslant X > H_j^{(1)} \end{cases} \tag{32}$$

where $H_j^{(1)}$, H_j^0 and H_j are determined by equations (25), (12) and (22).

Uniform block molecular-weight distribution

A relatively widespread situation will be considered in which the copolymer molecules have wide *MWD* of blocks A and B, which to a first approximation may be expressed by uniform distributions:

$$q_j(N_j) = \frac{1}{N_j^{\max} - N_j^{\min}} \equiv \frac{1}{\Delta_j} \tag{33}$$

In this case the distribution of the overall molecular weight is determined by the type of attachment of blocks A and B into a single block copolymer molecule. Some of these types will be considered below.

Fixation of the overall molecular weight. Let the molecular weights of blocks A and B be uniformly distributed over the same intervals $\Delta_A = \Delta_B$. Let us postulate that the overall molecular weight N of all block copolymer molecules formed as a result of joining of blocks A and B is fixed and assumes the value $N = N_A^{\min} + N_B^{\max} = N_A^{\max} + N_B^{\min}$. Then we have:

$$q(N') = \delta(N' - N)$$

In this case the molecules of the block copolymer have different compositions $\xi = N_A/N$ uniformly distributed in the range:

$$N_A^{\min}/N \leqslant \xi \leqslant N_A^{\max}/N$$

Fixation of the composition of block copolymer molecules. The known values of distribution ranges of the molecular weights of blocks Δ_A and Δ_B under the condition of a fixed composition (ξ = constant) determine the value of the composition of block copolymer molecules $\xi = \Delta_A/(\Delta_A + \Delta_B)$ and the range of the distribution function $q(N)$ of the overall molecular weight:

$$N_j^{\min}(\Delta_A + \Delta_B)/\Delta_j \leqslant N \leqslant N_j^{\max}(\Delta_A + \Delta_B)/\Delta_j$$

with the width $\Delta = \Delta_A + \Delta_B$. In this case the function $q(N)$ itself is given by:

$$q(N) = 1/\Delta$$

and the *MWD* of the molecules is uniform.

Random block attachment. Now the situation will be considered when the *MWD* of the molecules is determined by a random attachment of blocks A and B. It is clear that in this case the width of the range of *MWD* function $q(N)$ is given by:

$$\Delta = \Delta_A + \Delta_B \tag{34}$$

However, in this case the *MWD* function $q(N)$ is no longer uniform in contrast to the case of a fixed copolymer composition considered above. The resulting molecules will also exhibit a distribution in composition ξ.

Function $f[\varphi]$. A curious fact should be mentioned, namely that although the resulting *MWD* functions $q(N)$ are drastically different, the characteristics of the lamellar structures are determined only by the total value of widths of the *MWD* functions of blocks $(\Delta_A + \Delta_B)$. In fact, if equations (33) and (34) are applied, equation (15) gives:

$$f[\varphi] = 1 - \Delta/(4\bar{N}) \tag{35}$$

Hence, for an initially uniform *MWD* of blocks A and B and a given $\bar{N}$, the type of block bonding into a single molecule of the block copolymer does not affect the parameters of the lamellar structure.

As for the structure of lamellar layers, in this case they are dense layers of grafted chains (copolymer blocks) with a uniform *MWD.* Now the character of local block stretching and free end distribution in layers becomes different from that for the binary mixture considered above. Thus, in the case of a binary mixture the ends of long and short blocks were concentrated in the central region of the layer and in regions adjoining its boundaries, respectively. In contrast, now the range of localization of free ends of blocks of a given molecular weight becomes much more narrow, so that the position of the free end X' actually becomes fixed. The type of function of local chain stretching also changes. These problems have been considered in detail in ref. 1, where, in particular, closed equations were obtained describing the distribution profiles of free ends and those of local stretching in dense grafted layers with a uniform length distribution of grafted chains.

Binary mixture of block copolymers with a narrow disperse uniform distribution of blocks within each fraction

The case considered above concerned a binary mixture of monodisperse block copolymers of strictly fixed molecular weights N_1 and $N_2 > N_1$. In a real situation, however, even in narrow disperse fractions with average values of N_1 and N_2, a *MWD* of block copolymers always exists within each fraction about the values of N_1 and N_2. Hence, now the effect of this distribution on the characteristics of the lamellar mesophase will be considered.

Let us consider a mixture of two block copolymer fractions 1 and 2 with average molecular weights N_1 and $N_2 > N_1$ with the amount q of the higher-molecular-weight fraction 2 and the number-average molecular weight:

$$\bar{N} = (1-q)N_1 + qN_2$$

Let the molecular weights of blocks A and B within each fraction be uniformly distributed in the ranges $\Delta_j^{(1)}$ and $\Delta_j^{(2)}$ about the average values of $N_j^{(1)}$ and $N_j^{(2)}$:

$$N_1 = N_A^{(1)} + N_B^{(1)}$$

$$N_2 = N_A^{(2)} + N_B^{(2)}$$

For simplicity, the symmetric situation will be considered in which:

$$\begin{aligned} N_B^{(2)} - \Delta_B^{(2)}/2 &> N_B^{(1)} + \Delta_B^{(1)}/2 \\ N_A^{(2)} - \Delta_A^{(2)}/2 &> N_A^{(1)} + \Delta_A^{(1)}/2 \end{aligned} \tag{36}$$

In this case $q_j(N_j)$ is given by:

$$q_j(N_j)=\begin{cases}0 & N_j>N_j^{(2)}+\Delta_j^{(2)}/2\\ q/\Delta_j^{(2)} & N_j^{(2)}-\Delta_j^{(2)}/2<N_j\leqslant N_j^{(2)}+\Delta_j^{(2)}/2\\ 0 & N_j^{(1)}+\Delta_j^{(1)}/2<N_j\leqslant N_j^{(2)}-\Delta_j^{(2)}/2\\ (1-q)/\Delta_j^{(1)} & N_j^{(1)}-\Delta_j^{(1)}/2<N_j\leqslant N_j^{(1)}+\Delta_j^{(1)}/2\\ 0 & N_j\leqslant N_j^{(1)}-\Delta_j^{(1)}/2\end{cases} \tag{37}$$

and equation (15) gives:

$$f[\varphi]=1-\frac{\Delta}{\bar{N}}q(1-q)-q^3\frac{\Delta^{(1)}}{4\bar{N}}-(1-q^2)(1-q)\frac{\Delta^{(2)}}{4\bar{N}} \tag{38}$$

where $\Delta^{(1)}=\Delta_A^{(1)}+\Delta_B^{(1)}$, $\Delta^{(2)}=\Delta_A^{(2)}+\Delta_B^{(2)}$ and $\Delta=N_2-N_1=N_A^{(2)}-N_A^{(1)}+N_B^{(2)}-N_B^{(1)}\equiv\Delta_A+\Delta_B$. It can be seen that, in the case of a mixture of monodisperse block copolymers, $\Delta^{(1)}=\Delta^{(2)}=0$, equation (38) passes to equation (23), and in the second limiting case of uniform *MWD* of blocks in the ranges $\Delta_j^{(1)}=2\Delta_j(1-q)$, $\Delta_j^{(2)}=2\Delta_j q$ it transforms into equation (35).

Hence, a comparison of equations (38) and (23) shows that the existence of polydispersity within each fraction at a fixed $\bar{N}$ value leads to an additional decrease in $f[\varphi]$ and thus to an additional increase in linear dimensions of the lamella and decreases in the specific area σ and the free energy density of the system ΔF.

Thermodynamic stability of a polydisperse lamellar structure

As already mentioned in the 'Introduction', the molecular-weight polydispersity of block copolymers leads to two fundamentally different possibilities for the formation of the supermolecular structure. One of them is the formation of a single lamella formed by block copolymers with different lengths and compositions mixed on the molecular level. The other possibility is the segregation of the system with the formation of a set of lamellar structures formed by narrow disperse block copolymer fractions. In the former case the free energy density of the system ΔF is described by equation (14).

Let us calculate the free energy density, ΔF_0, in a system segregated into separate lamellae formed by narrow disperse block copolymer fractions. If the polydispersity within each fraction is neglected, which makes it possible to use equation (19) for the description of the free energy density of the lamella $\Delta F(N)$, formed by molecules of length N, and if the initial *MWD* $q(N)$ is taken into account, one obtains:

$$\Delta F_0=\frac{1}{\bar{N}}\int_{N^{\min}}^{N^{\max}}q(N')\Delta F(N')N'\,\mathrm{d}N'$$
$$=\frac{3}{2}\left(\frac{\pi^2}{4p}\Phi^2\right)^{1/3}\overline{(N^{1/3})}(\bar{N})^{-1} \tag{39}$$

Hence, the problem of the stability of the first or second states of the system is determined by the $\Delta F/\Delta F_0$ ratio. In the case $\Delta F/\Delta F_0<1$, a single structure with common period is the equilibrium structure, and in the opposite case, $\Delta F/\Delta F_0>1$, the system is separated into a set of lamellae formed by narrow disperse fractions of the mixture. When equations (14) and (39) are applied, the necessary condition for stability of a single lamellar structure is given by:

$$\frac{\Delta F}{\Delta F_0}=\frac{(\bar{N}f[\varphi])^{1/3}}{\overline{(N^{1/3})}}<1 \tag{40}$$

It can be seen that for a binary mixture of monidisperse block copolymer molecules with molecular weights N_1 and $N_2>N_1$ in which:

$$q(N)=q\delta(N-N_2)+(1-q)\delta(N-N_1)$$

inequality (40) is obeyed in both symmetric and nonsymmetric cases. Thus under the conditions of validity of equations (14), (23) and (24), a single lamellar structure is always thermodynamically more stable than a mixture of lamellae formed by monodisperse mixture components. It is clear that this conclusion should also be correct if the polydispersity within each fraction is taken into account (at least under the condition that the characteristic widths of the *MWD* within fractions are small compared to the total difference between the average molecular weights of the fractions $\Delta_j^{(1)}, \Delta_j^{(2)}\ll\Delta_j$). Below we will discuss the conditions of validity of equations (14), (23) and (24).

DISCUSSION

The theory of lamellar superstructure formed in the melts of polydisperse block copolymers developed in this work is based on some assumptions. One of them is the narrow interphase approximation (NIA) according to which the interphase (or interface) between A and B elements of the superstructure is narrow compared to the characteristic sizes of the elements themselves. This approximation is valid far from the transition point of the system into the disordered state. It is under these conditions that a distinct supermolecular structure with sharp boundaries is formed, and copolymer blocks may be regarded as 'grafted' onto the interface. Hence, only under the NIA conditions may block conformations be described from the standpoint of the theory of grafted polymer layers.

The second necessary condition for the validity of this theory to the description of supermolecular structures of block copolymers is a considerable stretching of all blocks in the elements of the superstructure with respect to their Gaussian dimensions. It is this block stretching that ensures the segregation of free ends of both 'opposite' blocks (i.e. blocks 'grafted' onto different boundaries of structural elements) and blocks of different lengths 'grafted' onto a common boundary and makes it possible to calculate the conformational free energy of the superstructure according to the scheme in refs. 2 and 8 and to obtain analytical dependences (11)–(15). The condition of block stretching, in turn, restricts the values of molecular weights of the block copolymers to which the concepts and the results of this work can be applied.

Monodisperse block copolymer

Let us begin from the case of a monodisperse block copolymer. According to the concepts of the structure of lamellar layers[8], the free ends of the blocks forming these layers are distributed throughout their thickness. Moreover, most free ends of the blocks are concentrated in the central part of the layers, $X'=H_j$. As a result of free end distribution, the blocks are stretched irregularly: their stretching, determined by the function $E(x,x')$

(equation (20)), is maximum near the lamellar boundary $x = 0$ and decreases with the approach to the free end of the block, $x = x'$. Let us evaluate the size δr of the unstretched end part consisting of δn units for the block whose free end is located in the layer centre, $x' = H_j$. Applying equation (20) and the requirements of the Gaussian dimensions of the end part (it is not stretched) one obtains:

$$\delta n = \frac{1}{p}\left(\frac{\delta r}{a}\right)^2 = \int_{H_j - \delta r}^{H_j} \frac{\mathrm{d}x}{E_j(x, H_j)} \approx \frac{2N_j}{\pi}\left(\frac{2\delta r}{H_j}\right)^{1/2} \qquad (41)$$

to give

$$\frac{\delta r}{H_j} \approx \frac{2}{\pi^{2/3}}\left(\frac{a(N_j p)^{1/2}}{H_j}\right)^{4/3} \qquad (42)$$

It is clear from equation (42) that the condition for the small size δr of the unstretched end part (end 'stretching' blob) compared to the halfwidth of the layer H_j is equivalent to that of block stretching with respect to the Gaussian size, $H_j > a(N_j p)^{1/2}$. The value of δr also determines the width of the region of mixing of free ends of 'opposite' blocks[11]. Hence the condition of block stretching with respect to Gaussian dimensions ensures the segregation of opposite block ends in lamellar layers and the applicability of equations (16)–(19) to the description of the characteristics of the lamellar structure formed by a monodisperse block copolymer.

Let us evaluate the molecular weight of the block copolymer molecule beginning from which the condition of block stretching in the superstructure, $H_j > a(N_j p)^{1/2}$, is obeyed (H_j is determined from equation (17)) and thus the scheme in refs. 2 and 8 is valid. For simplicity, let $N_A = N_B$ and $H_A = H_B$. Then taking into account equation (42) one obtains $N_j > N_{j0} = (\pi^2/2\Phi p)^2$. It should be borne in mind that according to the definition, N_j is the number of symmetric elements in a block, $N_j = L_j/a$, where L_j is the contour length of block j and a is its thickness. For transition to specific block copolymer systems, e.g. polystyrene–polyisoprene (PS–PI) or polystyrene–polybutadiene (PS–PB), the following values of the parameters $a = 6.5$ Å and $\Phi p = 0.5$ will be used as before[14]. Then taking into account the relationship of the molecular weight of the block M_j to N_j, a and specific volume v_j, $M_j = N_j a^3/v_j$, we obtain $M^0_{PS} \approx 1.5 \times 10^4$ and $M^0_{PB} \approx 1.3 \times 10^4$. Hence, the total molecular weight of the block copolymer, $M_A + M_B$, should be sufficiently high, $M > M_0 \approx 2.8 \times 10^4$, to justify the application of equations (16)–(19).

It should be noted that this estimate is in good agreement with numerous experimental data on the molecular-weight dependence of the period of lamellar structure in melts of narrow disperse PS–PI and PS–PB block copolymers (see e.g. ref. 15).

Binary mixture of monodisperse block copolymers

The approach developed in the present paper for describing the lamellar structure formed in a binary mixture of block copolymers with different molecular weights and compositions also assumes the stretching of all blocks (both short and long blocks) in structural elements. Only under the condition of stretching of all blocks are the equilibrium characteristics of a single lamellar structure formed by short and long chains mixed on the molecular level determined by equations (11)–(15). In the case of monodisperse block copolymer, the condition of block stretching with respect to Gaussian size restricts only the molecular weights of the blocks, $M_j > M^0_j$, whereas in the case of a binary mixture the mixture composition q plays the role of an additional restricting factor.

Let us consider in detail the conditions ensuring the block stretching of both mixture components in a single lamellar structure.

Conditions of block stretching. As mentioned above, under the conditions of block stretching the free end segregation is carried out in lamellar layers formed by long and short blocks. Thus, the ends of longer blocks are distributed in the central part of the layer of width $2(H_j - H^{(1)}_j)$. Moreover, their main part is concentrated near $x' = H_j$, whereas the ends of shorter blocks are distributed in layers of width $H^{(1)}_j$, adjoining the lamellar boundaries. The main part of the ends of short chains is concentrated near $x' = H^{(1)}_j$.

Let us evaluate the sizes of stretching end blobs $\delta r^{(1)}_j$ and $\delta r^{(2)}_j$ of short and long chains similarly to what has been done above for the case of a monodisperse block copolymer. Taking into account the functions of local stretching (26) and (27) and the condition of non-stretching of a chain part inside the stretching blob, one obtains:

$$\frac{\delta r^{(1)}_j}{H^{(1)}_j} \approx \frac{2}{\pi^{2/3}}\left(\frac{a(pN_j)^{1/2}}{H^{(1)}_j}\right)^{4/3} \qquad (43)$$

$$\frac{\delta r^{(2)}_j}{H_j} \approx \frac{2}{\pi^{2/3}}\left(\frac{a(pN_j)^{1/2}}{H_j}\right)^{4/3}\left(\frac{(q_j + \alpha_j)(1 + \alpha_j q_j)}{q_j}\right)^{1/3} \qquad (44)$$

where q_j is the fraction of longer blocks of length $N_j(1 + \alpha_j)$ in a layer of type j and $H^{(1)}_j$ is determined by equation (25). The small size of $\delta r^{(1)}_j$ and $\delta r^{(2)}_j$ as compared to the characteristic sizes of lamellar layers assumes block stretching and the segregation of free ends of both opposite long blocks and the short and long blocks 'grafted' onto a common boundary. Hence, the applicability of equations (11)–(15) to the description of a single lamellar structure is determined by the simultaneous fulfilment of four inequalities:

$$\begin{aligned} &\delta r^{(1)}_j < H^{(1)}_j \\ &\delta r^{(2)}_j < H_j - H^{(1)}_j \end{aligned} \qquad j = \mathrm{A, B} \qquad (45)$$

The first two inequalities ensure the stretching of short blocks (and the segregation of short and long blocks grafted onto a common boundary), whereas the second two ensure the stretching of longer blocks (and the segregation of free ends of opposite long blocks grafted onto different boundaries of the lamellar layer). It can be easily seen that when the content of one mixture component is small ($q_j \ll 1$ or $1 - q_j \ll 1$), one pair of inequalities (45) is always invalid. Hence, their simultaneous validity is possible only in the range of mixture compositions not very different from $q_j \approx 0.5$.

Symmetric block copolymers. Let us consider, for exactness, a binary mixture of symmetric block copolymers $\xi_1 = \xi_2 = 0.5$ of different molecular weights. In this case $N_A = N_B = N_1/2$, $\alpha_A = \alpha_B = \alpha$, $q_A = q_B = q$, where N_1 is the total number of units in the block copolymer of the lower molecular weight. In this case the four inequalities (45) reduce to two inequalities, and *Figure 4* shows the region S of values α and q in which both inequalities are fulfilled. The calculation was carried out

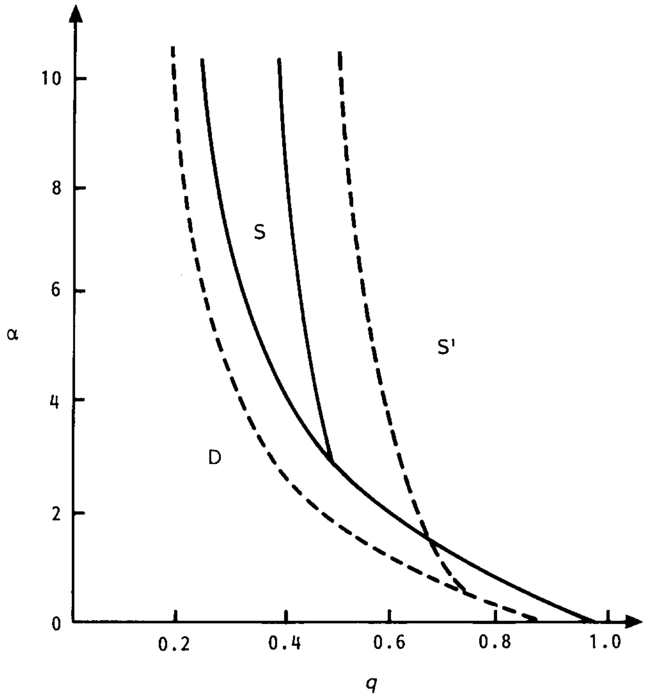

Figure 4 Region S of validity of inequalities (45) calculated for the values of $N_1/2 = 300$ (full curves) and $N_1/2 = 1000$ (broken curves)

by using the above value of $\Phi p = 0.5$, corresponding to systems PS–PI and PS–PB and for the values of $N_1/2 = 300$ (full curves in *Figure 4*) and $N_1/2 = 1000$ (broken curves in *Figure 4*). The region S′ adjoins the region S from the right. In the region S′ the first of inequalities (45) is not obeyed, and short blocks lose their stretching. The region D in which the second of inequalities (45) is not obeyed and the outer parts of long blocks lose their stretching is located to the left of region S. It can be seen from *Figure 4* that the requirement of block stretching with respect to Gaussian dimensions ensuring the applicability of equations (11)–(15) in the case of the binary mixture limits the molecular weights of the components to a much greater extent than in a monodisperse system. Thus, even at $N_1/2 = 300$ (which ensures the required block stretching of this component in the formation of its own lamellar structure, $N_1/2 > N_0 = (\pi^2/2\Phi p)^2$ we arrive in region S only when the second component of the mixture is of a still higher molecular weight, $\alpha \gtrsim 3$. In this case the width of the region S of allowed mixture compositions is small.

The region S becomes wider with increasing N_1 (broken curves in *Figure 4*) and in the limit $N_1 \to \infty$ virtually the entire range of mixture compositions q may be described in the framework of the approach developed there. Hence, in the limit $N_1 \to \infty$, equations (11)–(15) are asymptotically precise and the conclusion that the formation of a single lamellar structure is preferable to the fractionation of the mixture into two structures formed by the individual components is valid over a wide range of mixture compositions. In real systems however, in addition to the region of stability of a single structure S, region S′ and D in which equations (11)–(15) are no longer applicable also exist. Let us consider qualitatively the behaviour of the system in these regions of parameters.

Stability of a single structure. Let us consider first the region S′ to the right of region S in *Figure 4*. Here shorter chains lose their stretching, and the first of conditions (45) is not obeyed. It is evident that with the loss in stretching short chains become Gaussian coils located between the stretched chains of the major component (long blocks) and no longer contribute to the free energy of the layer as a whole. The retention of the contribution of short chain stretching in equation (8) may lead only to an increase in free energy. The same conclusion concerns the contribution of stretching of parts of long chains passing through the layer of short chains. However, this re-evaluation of the free energy is small because the main correctly evaluated contribution to the free energy is provided by the markedly stretched long chain layer. As a result, in the region S′ the free energy of the mixed layer is slightly lower than that calculated from equation (8). Consequently the conclusion of the stability of the single lamellar structure remains valid not only for the region S but also for the region S′ in *Figure 4*.

The situation is much less unequivocal in the region D in *Figure 4*, where the condition of stretching of peripheral parts of long blocks forming the central part of the lamellar layer is not obeyed. Since it is just the long chains that provide the main contribution to the free energy of the layer, the results of the calculations of the characteristics of the structure in this region of the parameters α and q from equations (11)–(15) cannot be considered correct. Hence, the problem of the stability or instability of a single lamellar structure in the region D remains unsolved.

It should be emphasized, however, that our results indicate that the single lamellar structure is stable in the regions S and S′. Moreover, this structure is doubtless stable when the differences in the molecular weights of the component blocks are small (small values of α). The number of units in a stretching blob of short chains, σ_1^2 (here $\sigma_1 = (\pi^2 N_1/2\Phi p)^{1/3}$ is the specific area per chain in an individual lamella consisting of short chains) provides a simple evaluation of the difference in the molecular weights of blocks $\alpha N_1/2 \approx \sigma_1^2$ at which the blocks may be considered to be 'quasi-monodisperse'. Consequently,

$$\alpha = \alpha_0 \simeq \left(\frac{\pi^2}{2\Phi p}\right)^{2/3} N_1^{-1/3}$$

is the threshold of resolution of polydispersity in the framework of this approach, and all the above results obtained for mixtures of block copolymers of different molecular weights assume the value of polydispersity $\alpha > \alpha_0$. (For PS–PB and PS–PI block copolymers taking into account the value of $\Phi p = 0.5$ we have $\alpha_0 \simeq 4.6/(N_1/2)^{1/3}$.

Characteristics of a single lamellar structure. Now the characteristics of a single lamellar structure under the conditions of its thermodynamic stability (regions S and S′ in *Figure 4*) will be considered. It is clear from equations (11)–(15) that the equilibrium characteristics of a single lamellar structure formed by a two-block polydisperse copolymer are determined by the product of two functions: the power function of the number-average molecular weight $\bar{N}$ ($\sigma \sim (\bar{N})^{1/3}$; $H \sim (\bar{N})^{2/3}$), and a weaker non-power function $f[\varphi]$ reflecting the character of polydispersity in this system. Hence, the power dependence on $\bar{N}$ predominates, and on its background is revealed a finer dependence of lamellar parameters on the character of the distribution of the block copolymers of the mixture with respect to molecular weight and composition.

Let us compare the characteristics of lamellar structures formed by polydisperse block copolymers with average molecular weight $\bar{N}$ with those of a monodisperse block copolymer with molecuar weight $N = \bar{N}$. It is clear, from comparison of equations (11)–(14) and (16)–(19) in which the evident condition $f[\varphi] < 1$ (equation (15)) is taken into account, that the specific area per chain σ and free energy density ΔF in a polydisperse lamellar structure are smaller than the corresponding characteristics of the mesophase formed by a monodisperse block copolymer with $N = \bar{N}$. Moreover, the size of lamellar layers H_j and the complete overall period of structure $2H$ exceed the corresponding dimensions of the monodisperse structure.

The reason for this is quite clear. In a lamella formed by a monodisperse block copolymer all blocks A or B have the same molecular weight N_A or N_B. If the end parts of some of these molecules are cut off and attached to the remaining chains, then the average molecular weight is retained and $\bar{N} = N = N_A + N_B$. However, in this case the peripheral parts of longer chains are under the conditions of effectively less dense grafting as compared to the initial monodisperse system and hence are less extended. On the whole, this leads to a gain in the conformational free energy of the system ($\Delta F_A + \Delta F_B$), a corresponding decrease in specific area σ and an increase in the transverse dimensions of the lamellar layers H_A and H_B and of the complete period of structure $2H$.

It should also be noted that since the free energy of the system is slightly re-evaluated in the region S′ (see above), the specific area σ in this range of parameters is slightly smaller and the transverse dimensions of the lamella are slightly greater than the values predicted by equations (11)–(15).

Comparison with experimental data. Extensive data on the structure of lamellar mesophases formed in block copolymer melts are available in the literature. The main attention has been devoted to the investigation of narrow disperse samples with the characteristic values of $M_w/M_n \simeq 1.1$–1.3. Analysis of numerous experimental data on PS–PI and PS–PB block copolymers shows (see e.g. ref. 15) that for narrow disperse block copolymers with relatively high molecular weights $M > 2 \times 10^4$, the power law is adequately obeyed for the period of structure $H \sim M^\alpha$ where $\alpha = 2/3$. (A special investigation of the value of the exponent α has been carried out in ref. 15 for a lamellar structure formed by narrow disperse PS–PI and PS–PB samples.) At moderate molecular weights, the dependence of H on M becomes steeper, however, which corresponds to higher values of the exponent $\alpha > 2/3$.

The polydisperse systems of block copolymers have been studied experimentally to a much smaller extent, and their results are often contradictory. Thus, in refs. 16 and 17 supermolecular structures formed in narrow disperse systems and binary mixtures of two- and three-block PS and PI copolymers have been studied. It has been shown in these papers that the structure formed in a binary mixture of lamellar-forming block copolymers of the same composition $\xi_1 = \xi_2 = 0.5$ and $M_1 = 2.7 \times 10^4$, $M_2 = 7.2 \times 10^4$ is characterized by a single period the value of which is determined by the number-average molecular weight of block copolymer in the mixture, $\bar{M} \sim \bar{N}$. On the other hand[18,19] the formation of two lamellar structures, i.e. mixture fractionation, has been observed in a binary mixture of PS–PI block copolymers with molecular weights $M_1 = 8.1 \times 10^4$ and $M_2 = 7.7 \times 10^5$. However, in a mixture of block copolymers with similar molecular weights $M_1 = 1.0 \times 10^5$ and $M_2 = 1.4 \times 10^5$, no fractionation has been observed and a single lamellar structure has been formed in the system[19].

It can be easily seen that in the latter case the polydispersity of the mixture $\alpha = (M_2 - M_1)/M_1 = 0.4$ is lower than the resolution limit of the components $\alpha_0 \simeq 4.6/(N_1/2)^{1/3} \simeq 0.7$. Hence, from the viewpoint of the concepts developed here the system is 'quasi-monodisperse' and thus a single lamellar structure should be formed in it at any mixture compositions.

As to the other two systems above, their behaviour is exactly opposite to the results of our theoretical investigation according to which the increase in the molecular weights of the components favours their compatibility in a single lamellar structure (*Figure 4*). As theoretical estimations show, a mixture of higher molecular weight with $\alpha = 8.6$ investigated in ref. 19 should be in the region of stability of a single lamellar structure (regions S and S′ in *Figure 4*) at $q \gtrsim 0.3$, whereas for a mixture of lower molecular weight[17], the region of stability of a single structure exists only at $q \gtrsim 0.85$. However, in the latter case a single structure was formed over the entire range of compositions whereas in the former case two types of lamellar structures were formed. Discussing these experimental results the author of ref. 18 assumes that the formation of the single structure is of a non-equilibrium character in the case of the mixture of the lower molecular weight[17]. We do not rule out this possibility but will also note that for this mixture the value of polydispersity is $\alpha \simeq 1.7$, which does not greatly exceed the limiting value of $\alpha_0 \sim N_1^{-1/3}$, the estimation of which gives $\alpha_0 \simeq 1$ for this system.

As to the formation of lamellar structures of two types[19] the results of the present work do not exclude the possibility of their formation in the region D of values of parameters in *Figure 4*. It should be emphasized, however, that even under the conditions of mixture segregation and the formation of two different lamellar structures, one of these structures should contain considerable fractions of both components. The reason for this is the existence of regions S and S′ in *Figure 4* in which the formation of mixed structures is thermodynamically advantageous. Unfortunately, the present work does not solve the problem of stability of the single lamellar structure in the region D of parameters in *Figure 4*. If the single lamellar structure is unstable in the region D and it is more advantageous for the system to form two structures, then according to the results of the present paper, one of them should have the composition approximately corresponding to the boundary between the regions D and S in *Figure 4*. We suppose that these problems require further theoretical and experimental investigations.

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