Theory of supermolecular structures in polydisperse block copolymers:
3. Cylindrical layers of bidisperse chains

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A theory of dry (containing no solvent) layers of polymer chains grafted onto the internal and external surfaces of an infinite cylinder has been developed. The geometric and thermodynamic characteristics of layers were investigated for two cases: for chains of the same length (monodisperse distribution) and for a mixture of chains of two different lengths (bidisperse distribution). It is shown that the thermodynamic advantage of mixing chains of different lengths demonstrated previously for the case of a planar layer is particularly pronounced for a concave cylindrical layer densely filling a cylindrical pore. The results obtained make it possible to investigate the thermodynamics of superstructures formed by mixtures of diblock copolymers of the AB type with different block length.

(Keywords: mean field theory; grafted chain layers; polymer mixtures; block copolymers)

INTRODUCTION

In the first paper in this series, an analytical theory of the structure and properties of planar layers of grafted polydisperse chains has been developed[1]. Using this theory, lamellar structures formed in the melts of polydisperse block copolymers under the conditions of strong segregation have been investigated[2]. A binary mixture of diblock copolymers of the AB type with different molecular weights and compositions has been studied in detail. It has been shown that in a mixture of high molecular weight lamellae-forming block copolymers, a single lamellar structure formed by block copolymers mixed on the molecular level can be thermodynamically stable. Equilibrium characteristics of this structure, i.e. its period, the thickness and a detailed organization of lamellar sublayers have been obtained. These parameters are functions of the free-end distribution of blocks and their local stretching in the sublayers depending on the mixture composition and the molecular weights of the blocks. The theoretical conclusions[2] have been compared to experimental results[3–5].

The extension of this investigation on the superstructures with different morphologies requires further development of the theory of layers of chains grafted onto both the internal and external surfaces of the matrices with different non-planar geometries. In this paper this is carried out for the case of layers of polymer chains grafted onto the surfaces of an infinite cylinder. A layer formed by a mixture of polymer chains with degrees of polymerization N_1 and N_2 (layer of bidisperse chains) will be taken as an example of a layer of polydisperse chains (as in ref. 1). We restrict ourselves to the analysis of 'dry' layers which contain no solvent and, in the case of concave layers, densely fill the cylindrical pore. It is this situation that exists in block copolymers under the conditions of well organized superstructure in the absence of solvent.

We begin with a brief consideration of monodisperse cylindrical layers of grafted chains. In this case, just as for bidisperse layers, we restrict ourselves to the case of a 'dry' layer, i.e. free of solvent. A detailed analysis of the structure and properties of cylindrical layers of monodisperse chains over a wide range of solvent strength (from an athermal solvent to a strong precipitant) will be given elsewhere. Some results for non-planar layers of monodisperse chains have previously been obtained[6–10]. In reference 10 weakly bending layers formed by grafted chains of two lengths have also been considered.

The results obtained here and in the previous papers in this series will be used as a basis for the theory of cylindrical and lamellar superstructures formed in binary mixtures of cylinder- and lamellae-forming block copolymers (see the next paper).

MONODISPERSE CYLINDRICAL LAYERS

A system of polymer chains consisting of N_1 units grafted at one end onto the surface of an infinite cylinder of radius R (*Figure 1*) is considered, with σ being the average grafting area per chain. As previously[1,2], part of a chain of length equal to the chain thickness a is chosen as a unit; the asymmetry parameter of the Kuhn segment A is $p = A/a \geqslant 1$. The chains in the layer are grafted relatively densely so that they are stretched. However, the grafting density is far from the limiting value, i.e. $\sigma/a^2 \gg 1$.

Theory

The equilibrium characteristics of a cylindrical layer of grafted monodisperse chains may be obtained on the basis of an analytical approach developed previously[1,11–16]. Thus, the conformational free energy of

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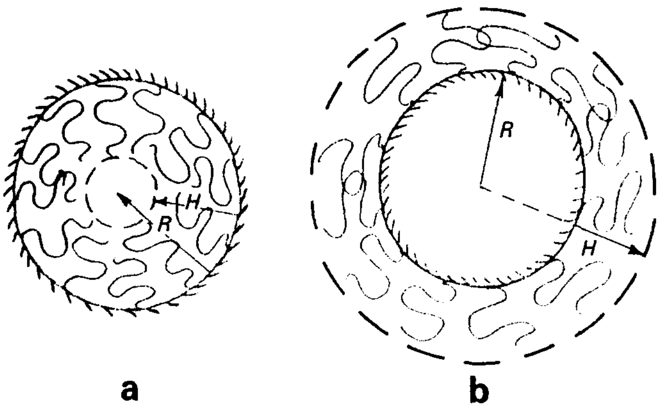

Figure 1 Cylindrical concave (a) and convex (b) chain layers

the layer per unit grafting area ΔF may be represented as:

$$\Delta F = \Delta F_{\text{el}} + \Delta F_{\text{conc}} = \frac{3}{2p\sigma}\int_0^{H_{10}} g(x')\,\mathrm{d}x' \int_0^{x'} E(x,x')\,\mathrm{d}x + \frac{a^2}{\sigma}\int_0^{H_{10}} \frac{\sigma(x)}{a^3} f[\varphi(x)]\,\mathrm{d}x \qquad (1)$$

where the first term takes into account the contribution of elastic chain stretching normally to the grafting surface, and the second term is the contribution of volume interactions between polymer units in a layer. Here, as previously[1], $E(x, x')$ is the function of local stretching of a grafted chain at point x under the condition that its free end is at a point $x' \geqslant x$; $g(x')$ is the distribution function of free ends of grafted chains; $f[\varphi(x)]a^{-3}$ is the density of volume interactions free energy, where $\varphi(x)$ is a density profile of polymer units; H_{10} is the layer height (subscript 10 implies that only N_1 chains are present in the layer) and

$$\sigma(x) = \sigma\frac{(R \pm x)}{R} \qquad (2)$$

is the effective area per chain at a distance x from the cylinder surface (the '+' sign corresponds to a convex surface, whilst the '−' sign corresponds to a concave surface). (Here and below all energetic values are expressed in kT units.)

The relation of the density profile $\varphi(x)$ to the functions $E(x, x')$ and $g(x')$ is determined by the equation:

$$\varphi(x) = \frac{a^3}{\sigma(x)}\int_x^{H_{10}} \frac{g(x')\,\mathrm{d}x'}{E(x,x')} \qquad \int_0^{H_{10}} \frac{\varphi(x)\sigma(x)}{a^3}\,\mathrm{d}x = N_1 \qquad (3)$$

In the case of the 'dry' layer we have

$$\varphi(x) = 1 \qquad (4)$$

and ΔF_{conc} in equation (1) becomes a constant.

The minimization of ΔF taking into account the additional normalization condition

$$\int_0^{x'} \frac{\mathrm{d}x}{E(x,x')} = N_1 \qquad (5)$$

makes it possible to determine the unknown functions $E(x, x')$ and $g(x')$ and to calculate the conformational free energy of the layer.

Equations (1), (3) and (5) are equivalent to the corresponding equations in references 1 and 12 in which the structure and properties of planar layers of grafted monodisperse chains are considered. The difference is only in the appearance of the dependence $\sigma(x)$ according to equation (2). The transition to the planar layer is carried out at $R \to \infty$. The characteristics of the planar layer are designated by indices 'lam' and '10' and are treated as the initial characteristics, so that the change in the characteristics of a planar layer upon its bending into a cylindrical layer is considered at a fixed grafting density (σ is a constant).

Let us introduce the following relative variables: the coordinate $z = x/H_{10}^{\text{lam}}$, the layer height $h = H/H_{10}^{\text{lam}}$ and the radius of the cylindrical surface $r = R/H_{10}^{\text{lam}}$. In the case of a 'dry' layer, when $\varphi(x) = 1$ and

$$H_{10}^{\text{lam}} = aN_1\left(\frac{\sigma}{a^2}\right)^{-1} \qquad (6)$$

the relative size of the cylindrical layer is given by

$$h = \pm(r - \sqrt{r^2 \mp 2r}) \qquad (7)$$

where the upper signs correspond to a concave surface, and the lower signs correspond to a convex surface. It is clear from equation (7) that in the case of a concave surface, the conditions $h \leqslant r^*$ and $r \geqslant r^* = 2$ should be met. (At $r = r^* = 2$ the inner cylinder space free of polymer units disappears, and all the inner part of the cylinder is densely filled with polymer units.) In the case of a convex surface the radius of the surface curvature does not impose any restriction on the layer height.

Concave cylindrical layer. Let us first consider the case of a concave cylindrical surface. The details of the calculation are given elsewhere[1,12] and only the main results are reported here.

(*1*) *Local stretching function.* The analysis of the variation problem in equations (1)–(5) shows that the local stretching function $E(x, x')$ of grafted chains in a concave layer does not depend on the layer geometry and the solvent quality and coincides with that of the local stretching in a planar layer.

$$E_{10}(x,x') = E_{10}^{\text{lam}}(x,x') = \frac{\pi}{2N_1}\sqrt{(x')^2 - x^2} \qquad (8)$$

(*2*) *Free-end distribution.* The function of the free-end distribution $g(z)$ is obtained by the inversion of integral equation (3) and the application of condition (4) and equation (8) as well as the normalization condition $\int_0^h g(z)\,\mathrm{d}z = 1$,

$$g(z) = \frac{2z}{h(2r-h)}\left(\frac{r-h}{\sqrt{h^2 - z^2}} + \ln\frac{h + \sqrt{h^2 - z^2}}{z}\right) \qquad (9)$$

It should be noted that the function $g(x')$ in equation (1) has the dimension of inverse length (it is normalized in the range of $0 \leqslant x' \leqslant H$) and the function $g(z)$ is dimensionless (it is normalized in the range of $0 \leqslant z \leqslant h$). This also concerns the pair of functions $u(x)$ (with the dimension of length) and $u(z)$ (a dimensionless function) considered below.

The first term in the function $g(z)$ in equation (9) gives the same functional dependence on z for a concave cylindrical layer as for a planar layer[9]. With increasing matrix curvature, $1/r$, the contribution of this term

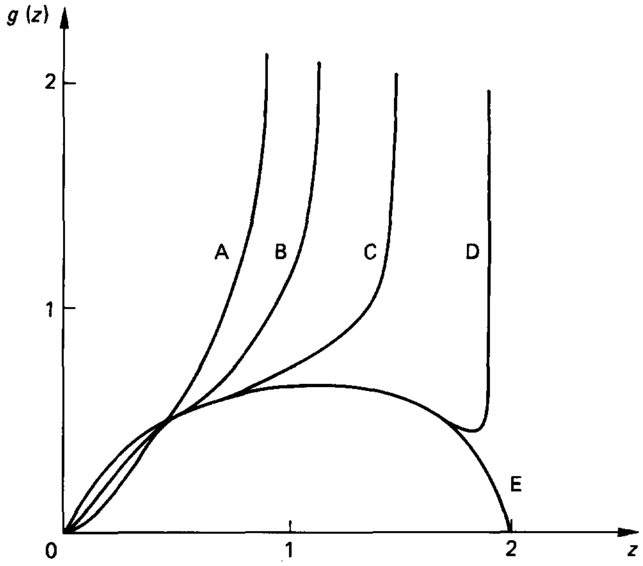

Figure 2 Distribution function of free chain ends, equation (9), in a concave cylindrical monodisperse dry layer for the values of $r=R/H_{10}^{\mathrm{lam}}=\infty$ (A), 3.6 (B), 2.25 (C), 2.006 (D) and 2 (E)

decreases and that of the second term increases. As a result, the function $g(z)$ becomes broader (*Figure 2*). According to equation (9), the average height of free ends [the first moment $g(z)$] is given by:

$$\frac{\bar{z}}{h}=\frac{1}{h}\int_0^h zg(z)\,\mathrm{d}z=\frac{\pi}{6}\frac{3-2h/r}{2-h/r} \tag{10}$$

and the distribution dispersion is given by:

$$D=\left[\frac{\overline{z^2}-(\bar{z})^2}{(\bar{z})^2}\right]\cong\frac{\sqrt{0.73-0.16h/r-0.35(h/r)^2}}{3-2h/r} \tag{11}$$

It is clear from these equations that with an increase in h/r from zero (planar layer) to unity ($r=h=r^*$), the value of $\bar{z}/h$ decreases from $\pi/4$ to $\pi/6$, and dispersion D increases from $\cong 0.3$ to $\cong 0.5$ (*Figure 3*).

Let us now consider the thickness h_1' of the sublayer in which the free ends of the fraction $q_1=1-q_2$ of grafted chains are located. Using the distribution function $g(z)$ of chain ends [equation (9)] yields:

$$q_2=\int_{h_1'}^{h} g(z)\,\mathrm{d}z$$

$$=\sqrt{1-(h_1'/h)^2}-\frac{(h_1')^2}{2r}\ln\frac{(h_1'/h)}{1-\sqrt{1-(h_1'/h)^2}} \tag{12}$$

It follows from equations (7) and (12) that at a given fraction of the chains q_1 the relative thickness of the sublayer h_1'/h increases with r. In the limit, $r\to\infty$, equation (12) gives an asymptotic dependence

$$h_1'/h=\sqrt{1-q_2^2} \tag{13}$$

characteristic of a planar layer[1].

(3) Free energy. Considering the results of equations (8) and (9), the elastic part of the conformational free energy of the layer per unit grafting area a^2 is given by:

$$\Delta F=\Delta F_{10}^{\mathrm{lam}}\frac{2(4-3h/r)}{(2-h/r)^3} \tag{14}$$

where

$$\Delta F_{10}^{\mathrm{lam}}=\frac{\pi^2}{8p}N_1\left(\frac{\sigma}{a^2}\right)^{-3} \tag{15}$$

It can be seen from equation (14) and *Figure 4A* that the free energy increases with the curvature of the cylindrical matrix $1/r$. It increases twice on passing from a planar layer $1/r=0$ to a layer of limiting thickness at $r=r^*=2$ and $h/r=1$.

Convex cylindrical layer. Let us now consider a layer of polymer chains consisting of N_1 units grafted onto the external surface of the cylinder (*Figure 1b*). The formal transition from a concave to a convex layer is carried out by the replacement of r by $-r$ in equations (8)–(13) [cf. equation (2)]. In this case the local stretching function $E(x,x')$ retains its shape [equation (8)]. However, the end distribution function $g(z)$ [equation (9)] changes markedly. The replacement of r by $-r$ leads to a change in the sign of the second term in equation (9), and hence to the appearance of a range of z values in which $g(z)<0$. This unrealistic result indicates that the so-called 'dead'

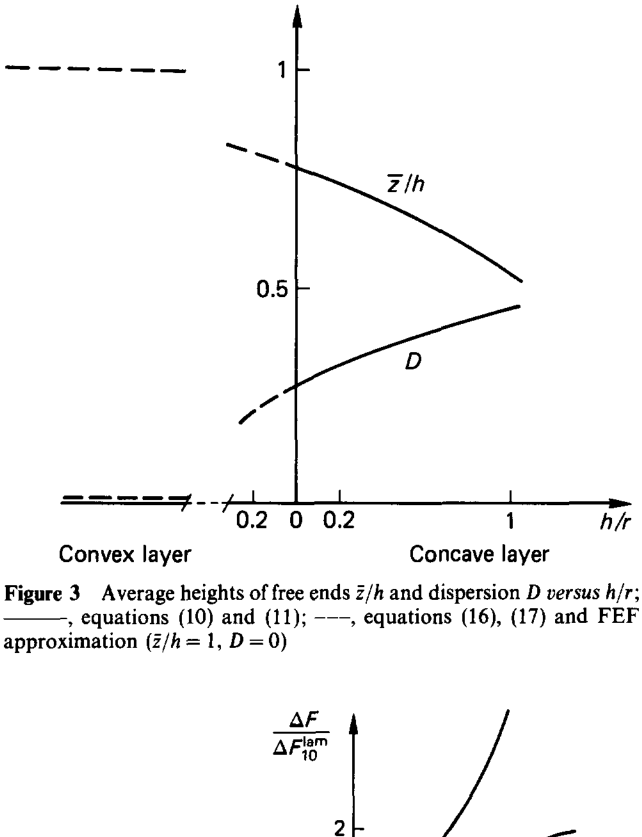

Figure 3 Average heights of free ends $\bar{z}/h$ and dispersion D *versus* h/r; ———, equations (10) and (11); ---, equations (16), (17) and FEF approximation ($\bar{z}/h=1$, $D=0$)

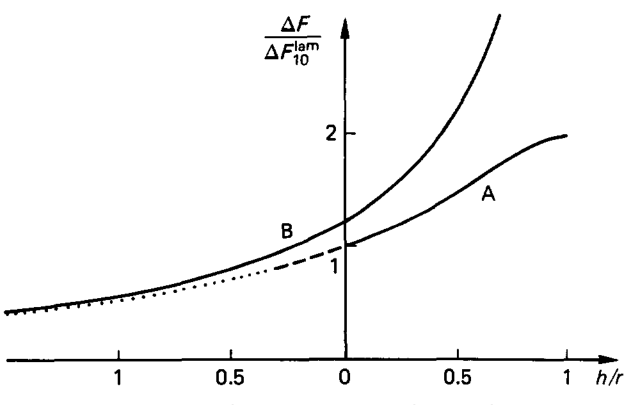

Figure 4 Free energy of concave and convex cylindrical layers. Curve A, ———, equation (14); ---, equation (18); · · ·, equation (18a). Curve B, FEF approximation, equations (21) and (46)

zone appears where the free ends of grafted chains are excluded, and adjoins the cylinder surface. The existence of these 'dead' zones in non-planar convex layers was first reported in reference 9. The correct solution of the problem of the convex layer requires, therefore, the inclusion of an additional condition $g(z)=0$ in the range of the dead zone, which greatly complicates equations (1)–(5).

However, it can be easily shown[10] [with the aid of equation (9) if r is replaced by $-r$] that the width of the dead zone decreases exponentially with decreasing matrix curvature $1/r$. This makes it possible to carry out the analytical continuation[10] of the results of equations (10), (11) and (14) for concave layers to the case of weakly convex layers $h/r \ll 1$. Thus, the expansion of equations (10), (11) and (14) for the small parameter h/r and the change in the sign of r give

$$\frac{\bar{z}}{h} \cong \frac{\pi}{4}\left[1 - \frac{1}{6}\left(\frac{h}{r}\right)\right] \cong 0.78(1 - 0.17h/r) \tag{16}$$

$$D \cong 0.28(1 + 0.56h/r) \tag{17}$$

$$\Delta F \cong \Delta F_{10}^{\mathrm{lam}}(1 - 0.75h/r) \tag{18}$$

Note that equation (18) has already been obtained in reference 10. The broken lines in *Figures 3* and *4* show the analytical continuations given by equations (16)–(18). The dotted line in *Figure 4* shows the analytical continuation of dependence (14) ($r \to -r$)

$$\Delta F = \Delta F_{10}^{\mathrm{lam}} \frac{2(4 + 3h/r)}{(2 + h/r)^3} \tag{18a}$$

in the whole range of h/r.

Let us now consider the convex layers of a considerable curvature for which $h/r > 1$ and the dead zone is wide. It is this situation that occurs in the superstructures of block copolymers. As mentioned in reference 9, the simplest assumption that the ends of all the grafted chains are fixed at the external boundary of the layer is a relatively good approximation for describing the characteristics of these layers

$$g(z) = \delta(h - z) \tag{19}$$

In fact, it can be seen in *Figure 3* and equations (10) and (16) that the mean height of free chain ends is monotonically displaced towards the periphery of the concave layer when the degree of concavity decreases. The same tendency remains upon passing from the planar layer into the range of increasing convexity of the surface. The dispersion of the end distribution function decreases simultaneously. It can be seen in *Figure 3* that the use of approximation (19) leading to $\bar{z}/h = 1$ and $D = 0$ is quite permissible for a convex layer at $h/r > 1$.

Taking into account equations (1)–(5) and (19) we obtain for strongly convex 'dry' layers $h/r > 1$ the local stretching function

$$E_{10} = \frac{a^3 r}{\sigma(r + z)} \tag{20}$$

and the conformational free energy

$$\Delta\tilde{F} = \Delta\tilde{F}_{10}^{\mathrm{lam}} \frac{2\ln(1 + h/r)}{(h/r)(2 + h/r)} = \Delta\tilde{F}_{10}^{\mathrm{lam}} \frac{r}{2} \ln(1 + 2/r) \tag{21}$$

where

$$\Delta\tilde{F}_{10}^{\mathrm{lam}} = \frac{3}{2}\frac{N_1}{p}\left(\frac{\sigma}{a^2}\right)^{-3} = \frac{12}{\pi^2}\Delta F_{10}^{\mathrm{lam}} \tag{22}$$

is the conformational free energy of a planar layer calculated under the approximation of free ends fixation of the external boundary (FEF approximation). Here and below the sign ($\sim$) refers to the values calculated with the aid of the FEF approximation.

LAYERS OF BIDISPERSE CHAINS

Let us now consider a 'dry' layer formed by a binary mixture of chemically identical polymer chains with degrees of polymerization N_1 and $N_2 > N_1$ grafted at a density of $1/\sigma$ onto the surface of a cylinder of radius R. As has already been mentioned, it is assumed that the grafting density causes all chains to be stretched. The effect of polydispersity on the characteristics of planar grafted layers has been investigated in detail elsewhere[1,16]. In particular, it has been shown that in the case of a bidisperse distribution in chain length, the free ends of short and long chains are segregated: the ends of shorter chains are distributed in the layer adjoining the grafting plane (short-chain sublayer), whereas the ends of long chains are concentrated in the peripheral part of the layer (long-chain sublayer). This effect is related to the tendency of the chains in equilibrium to minimize their stretching. It is clear that the same effect should also be observed in layers with other geometries. In particular, in a concave cylindrical layer, the ends of short chains should be located in a cylindrical layer of thickness H_1 adjoining the cylinder surface (short-chain sublayer), whereas the ends of long chains are concentrated near the cylinder centre (long-chain sublayer).

Concave layer of bidisperse chains

Theory. As before[1], let q_1 and q_2 be the fractions of chains of lengths N_1 and N_2 in the layer, and $\alpha = (N_2 - N_1)/N_1$ be the relative difference in the molecular weights of grafted chains. If the segregation of free ends is taken into account, the free energy functional (1) becomes:

$$\begin{aligned}\Delta F = {} & \frac{3}{2p\sigma}\int_0^{H_1} g_1(x')\,\mathrm{d}x' \int_0^{x'} E_1(x,x')\,\mathrm{d}x \\ & + \frac{3}{2p\sigma}\int_{H_1}^{H_2} g_2(x')\,\mathrm{d}x' \int_0^{x'} E_2(x,x')\mathrm{d}x \\ & + \frac{a^2}{\sigma}\int_0^{H_2} \frac{\sigma(x)}{a^3} f[\varphi_1(x) + \varphi_2(x)]\,\mathrm{d}x \end{aligned} \tag{23}$$

where subscripts 1 and 2 correspond to short and long chains, respectively. The additional relations (3) and (5) change correspondingly

$$\int_0^{x'} \frac{\mathrm{d}x}{E_i(x,x')} = N_i \qquad i = 1, 2 \tag{24}$$

$$\varphi_1(x) = \frac{a^3}{\sigma(x)}\int_x^{H_1} \frac{g_1(x')\,\mathrm{d}x'}{E_1(x,x')} \qquad \int_0^{H_1} \frac{\sigma(x)}{a^3}\varphi_1(x)\,\mathrm{d}x = q_1 N_1 \tag{25}$$

$$\varphi_2(x) = \frac{a^3}{\sigma(x)} \int_{\max(x,H_1)}^{H_2} \frac{g_2(x')\,\mathrm{d}x'}{E_2(x, x')}$$
$$\int_0^{H_2} \frac{\sigma(x)}{a^3} \varphi_2(x)\,\mathrm{d}x = q_2 N_2 \qquad (26)$$

The normalization conditions for functions $g(x')$ are given by

$$\int_0^{H_1} g_1(x')\,\mathrm{d}x' = q_1 \qquad \int_0^{H_2} g_2(x')\,\mathrm{d}x' = q_2 \qquad (27)$$

For the dry layer, we have

$$\varphi(x) = \varphi_1(x) + \varphi_2(x) = 1 \qquad (28)$$

The minimization of equation (23) and taking into account equations (24)–(28) determines the functions $E_i(x, x')$ and $g_i(x')$ and the thickness H_1 and H_2 of the concave cylindrical layer.

(*1*) *Local stretching functions.* The analysis of the variation problem in equations (23)–(28) shows that the functions of local stretching of short and long chains in a cylindrical layer completely coincides with those in a planar layer[1,12]. Thus, we have

$$E_1(x, x') = E_{10}(x, x') = \frac{\pi}{2N_1}\sqrt{(x')^2 - x^2} \qquad (29)$$

$$E_2(x, x') = \frac{\pi}{2N_1}\begin{cases}\sqrt{u^2(x') - x^2} & 0 < x < H_1 \\ \sqrt{u^2(x') - u^2(x)} & H_1 < x < H_2\end{cases} \qquad (30)$$

where the function

$$u(x) = \frac{x - \alpha\sqrt{x^2 - H_1^2(1-\alpha^2)}}{1-\alpha^2}$$
$$= H_{10}^{\mathrm{lam}}\frac{z - \alpha\sqrt{z^2 - h_1^2(1-\alpha^2)}}{1-\alpha^2}$$
$$= H_{10}^{\mathrm{lam}} u(z) \qquad (31)$$

has been obtained in reference 16 in the analysis of a planar layer of bidisperse chains. In the last equality the relative thickness of a short-chain sublayer $h_1 = H_1/H_{10}^{\mathrm{lam}}$ and the relative coordinate $z = x/H_{10}^{\mathrm{lam}}$ were introduced.

(*2*) *Layer thickness.* Let us consider in detail the characteristics of a layer under the conditions when the polymer units completely fill the interior of a cylinder of radius R. (This situation may be observed in cylindrical domains in the melts of bidisperse block copolymers forming a cylindrical superstructure.)

In this case the relative radius of the cylinder $r = R/H_{10}^{\mathrm{lam}}$ is related to long-chain fraction q_2 and the relative difference in the chain lengths α by the relationship

$$r = 2(1 + \alpha q_2) \qquad (32)$$

and

$$h_2 = H_2/H_{10}^{\mathrm{lam}} = r \qquad (33)$$

The condition of dense packing of polymer units inside a pore [equation (28)] makes it possible to calculate the functions of free end distribution $g_1(z)$ and $g_2(z)$ inversing integral equations (29) and (30) to the functions $E_1(x, x')$ and $E_2(x, x')$. Furthermore, using the normalization condition (27), the thickness of the short-chain sublayer H_1 will be determined. Omitting intermediate calculations, only the resulting equation relating the thickness $h_1 = H_1/H_{10}^{\mathrm{lam}}$ of a short-chain sublayer to α and q_2 is reported

$$\frac{q_2}{1 + \alpha q_2} = \frac{\sqrt{1 - (h_1/r)^2(1-\alpha^2)} - \alpha}{1-\alpha^2}$$
$$- \frac{h_1^2}{r^2}\ln\frac{(h_1/r)(1-\alpha)}{1 - \sqrt{1 - (h_1/r)^2(1-\alpha^2)}} \qquad (34)$$

Figure 5 shows the dependence of the ratio h_1/h on g_2 calculated from equation (34) for various values of α. Here, as before, h is the height of a layer of homodisperse chains of length N_1 [equation (7)] grafted onto a cylinder of radius r [equation (32)]. It is clear that the parameter α determining the degree of polymerization of long chains profoundly affects the shape of the dependence of h_1/h on composition q_2. With increasing α the curvature of this dependence and hence the relative thickness h_1/h at a given q_2 also increase. This change is partially due to an increase in the cylinder radius r [equation (32)] and is qualitatively equivalent to that observed for the layers of monodisperse chains grafted onto cylinders of various radii [equation (12)]. However, equations (12) and (34) are different, and the comparison of the relative thickness of the short-chain sublayer h_1/h and the relative thickness h'_1/h [equation (12)] of the part of the layer of monodisperse chains grafted onto a cylinder of radius $r = 2(1 + \alpha q_2)$ (*Figure 6*) shows that h'_1/h is always slightly higher than h_1/h. This difference increases with α and attains a maximum value at $\alpha \to \infty$ ($r \to \infty$) (cf. curves D and E in *Figure 5*) when equation (12) turns into equation (13). For equation (34) the asymptote at $\alpha \to \infty$ is different:

$$\frac{2}{h_1/h} = 1 + \frac{4q_2^2}{(h_1/h)^2} + \frac{h_1/h}{2q_2}\ln\left[1 + \frac{4q_2^2}{(h_1/h)^2} + \frac{2q_2}{h_1/h}\right] \qquad (34a)$$

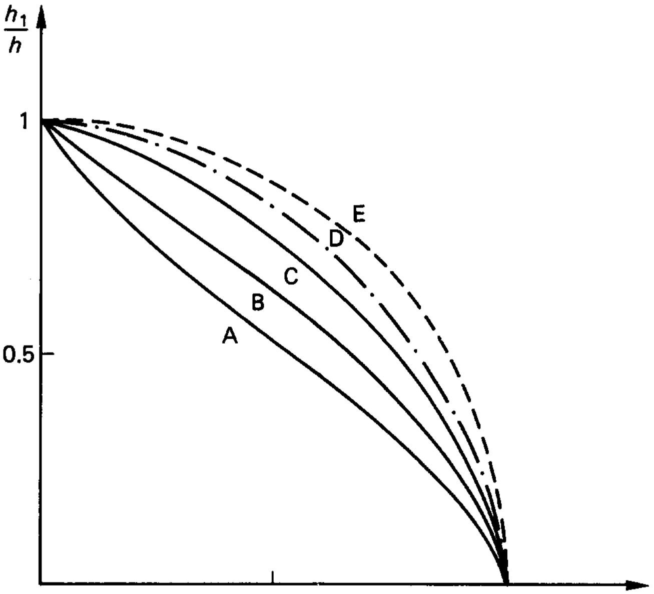

Figure 5 Ratio of the thickness h_1 of a short-chain sublayer in a bidisperse layer of grafted chains to the total thickness h of monodisperse layer, equations (7), (32) and (34), *versus* q_2 at different $\alpha = 0$ (A), 0.1 (B), 0.86 (C), ∞ (D). The asymptotic dependence h'_1/h on q_2 in a monodisperse layer, equation (13) is shown in (E)

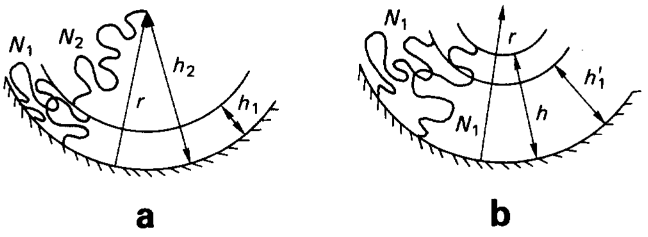

Figure 6 Scheme for concave cylindrical layers: (a) bidisperse layer with r, cylinder radius, h_2, thickness of long-chain sublayer and h_1, thickness of short-chain sublayer; (b) monodisperse layer with r, cylinder radius, h'_1, thickness of the sublayer in which the free ends of chain fraction $q_1 = 1 - q_2$ are located and h, total layer thickness

It will be recalled[1] that for a planar layer equation (13) remained valid for both mono- and bidisperse chains. The reasons for this and other differences in the behaviour of planar and concave layers will be discussed below.

(*3*) *Length of the tie part of long chains.* Let us introduce the average value βN_1 of the tie part of long chains in the short-chain sublayer:

$$\beta N_1 = \frac{1}{q_2}\int_{H_1}^{H_2} g_2(x')\,\mathrm{d}x' \int_0^{H_1} \frac{\mathrm{d}x}{E_2(x, x')} \tag{35}$$

In the case of a dry layer, the mean length βN_1 of the tie part is related to the thickness of the short-chain sublayer by a simple relationship

$$\beta = \left[\frac{h_1(1 - h_1/2r)}{q_2} - \frac{(1 - q_2)}{q_2}\right] \tag{36}$$

in which the dependence of h_1 on q_2 and α is determined by equation (34). *Figure 7* shows the dependence $\beta = \beta(q_2)$ for different values of α, calculated from equation (36). It is clear that at given q_2 the length of the tie chain increases with α (i.e. with r), which is equivalent to the increase in the sublayer thickness mentioned above. Equation (36) also describes [if h_1 is replaced by h'_1, equation (12)] the mean length of a chain part in a layer of monodisperse chains passing through the sublayer which adjoins the matrix and in which the ends of the fraction of q_1 chains are located. As before, the matrix radius is found from equation (32). As has been mentioned above, in the case of monodisperse chains, the sublayer thickness is always greater than for bidisperse chains (other conditions being equal). Correspondingly, the length of β is also slightly greater for monodisperse chains, the difference increasing with α. The maximum difference is observed when the layer of monodisperse chains becomes equivalent to a planar layer, and for this layer we have:

$$\beta = \frac{1}{q_2}\left(\sqrt{1 - q_2^2} - q_1\right) \tag{37}$$

(*4*) *Free energy.* The free energy of a layer of bidisperse chains is now considered. It should be emphasized that this is the principal thermodynamic characteristic in the theory of block copolymer superstructures. Intermediate calculations are omitted and only the resulting expression for the conformational free energy of the dry layer of bidisperse chains (the elastic component F_{el}) is reported:

$$\begin{aligned}\Delta F &= \left(\frac{\pi^2}{16}\right)\frac{R^2}{a^2 p N_1 \sigma} G(\alpha, q_2)\\ &= 2\Delta F_{10}^{\mathrm{lam}}(1 + \alpha q_2)^2 G(\alpha, q_2)\end{aligned} \tag{38}$$

where $\Delta F_{10}^{\mathrm{lam}}$ is the free energy of a planar layer of chains of length N_1, equation (15), and the function $G(\alpha, q_2)$ is rather cumbersome and contains the value $l_1 = h_1/r$ determined by equation (34) and the value $u \equiv u(z = h_2)$ determined by equation (31):

$$\begin{aligned}G(\alpha, q_2) = (1 + \alpha q_2)\{&\sqrt{u^2 - l_1^2}[6(1 + \alpha)u^2\\ &+ 0.5l_1^2 u(1 - 5\alpha - 10\alpha^2) - \frac{l_1^2(1 + \alpha)}{2}\\ &- u^3(6 - \alpha - 5\alpha^2)] + [-0.5l_1^4\alpha(1 + 5\alpha)\\ &+ 0.5l_1^2u^2(-10 + 3\alpha + 15\alpha^2)\\ &- 5(1 + \alpha)u^2(u^2 - l_1^2)\\ &+ u^4(6 - \alpha - 5\alpha^2)]\} - 3l_1^2\alpha q_2\end{aligned} \tag{39}$$

The dependence of ΔF on q_2 for various α is shown in *Figure 8*. It is clear that it is not monotonic and passes through a minimum which is displaced towards lower q_2 values and becomes deeper with increasing α. It should be recalled that in the case of a planar layer of bidisperse chains the conformational free energy per unit area

$$\Delta F_{\mathrm{L}} = \Delta F_{10}^{\mathrm{lam}}(1 + \alpha q_2^3) \tag{40}$$

increases monotonically with q_2 at any α values. The reasons for the qualitatively different behaviours of free energy in a planar and cylindrical layer will be considered below.

Convex layer of bidisperse chains

Theory. Let us now consider a dry convex layer formed by grafted chains of N_1 and $N_2 = N_1(1 + \alpha)$ units, with their fractions being equal to q_1 and q_2. As before, let H_1 and H_2 be the thicknesses of the short-chain sublayer and the entire layer, respectively. Restricting ourselves to the case of strongly convex layers, $h_2/r > 1$, and taking into account the results of the analysis for monodisperse

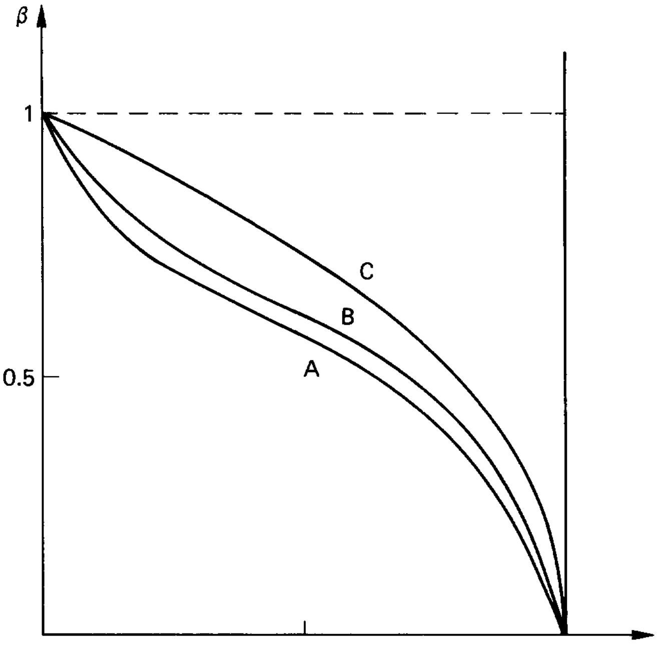

Figure 7 Mean length β of the tie part of long chains in a short-chain sublayer at different $\alpha = 0$ (A), 1 (B), ∞ (C), equation (36); ----, FEF approximation

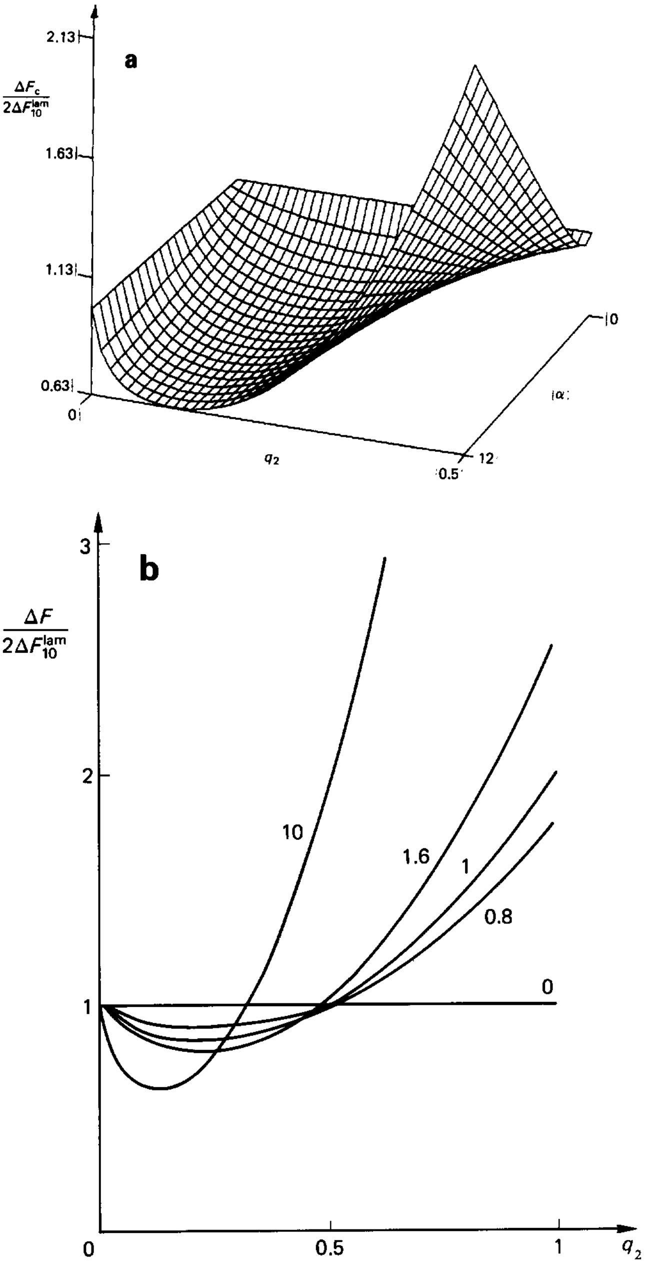

Figure 8 (a) Three-dimensional plot of relative free energy $\Delta F/2\Delta F_{10}^{\mathrm{lam}}$ in a system of coordinates q_2 and α and (b) the two-dimensional cross-sections at different α, equations (38) and (39). The values of α are shown on the curves

layers, it is reasonable to assume that the free ends of short and long chains are concentrated near $x' = H_1$ and $x' = H_2$ respectively, i.e.

$$g_i(z) = q_i \delta(z - h_i) \qquad (41)$$

where, as before, linear characteristics are divided by the height of a planar layer H_{10}^{lam}. In the framework of FEF approximation [equation (41)], it is also natural to assume the average length of the tie part of long chains in a sublayer of short chains to be equal to N_1, i.e. to take $\beta(q_2) = 1$ at all q_2 values (broken line in *Figure 7*). It should be noted that the results obtained above for a concave layer of bidisperse chains justify this approximation. As can be seen from *Figure 7*, the transition from strongly concave layers to a planar layer is accompanied by an increase in β. It is clear that the trend towards a further increase in β should be retained upon the transition from a planar to a strongly convex layer.

(*1*) *Local stretching functions.* According to the approximation $\beta(q_2) = 1$, a convex layer of bidisperse chains is divided into two cylindrical layers formed by monodisperse chains consisting of N_1 and $(N_2 - N_1)$ units grafted at densities of $1/\sigma$ and $q_2\sqrt{r}/\sigma\sqrt{r+2}$, respectively. Hence, it is possible to use the results for a monodisperse dry layer. The application of equation (20) gives the following equation for the local stretching functions of grafted chains:

$$\tilde{E}_1(z) = \frac{a}{\sigma}\frac{r}{(r+z)}$$
$$\tilde{E}_2(z) = \tilde{E}_1(z)\begin{cases} 1 & 0 < z < h_1 \\ q_2\sqrt{r}/\sqrt{r+2} & h_1 < z < h_2 \end{cases} \qquad (42)$$

Note that the jumps of functions $\tilde{E}_1(z)$ and $\tilde{E}_2(z)$ at the boundaries $z = h_1$ and $z = h_2$ are a consequence of the approximation that all free chain ends are fixed at the corresponding boundaries $z = h_1$ and $z = h_2$. In a precisely solved problem with a spatial free-end distribution, $E_1(z)$ and $E_2(z)$ would become equal to zero at the boundaries, as in the case for concave layers.

(*2*) *Layer thickness.* The condition of dense layer packing in a cylindrical layer determines the total layer thickness:

$$h_2 = H_2/H_{10}^{\mathrm{lam}} = -r + \sqrt{r^2 + 2r(1 + \alpha q_2)} \qquad (43)$$

The short-chain sublayer thickness [with the use of the condition $\beta(q_2) = 1$] is given by:

$$h_1 = H_1/H_{10}^{\mathrm{lam}} = -r + \sqrt{r(r+2)} \qquad (44)$$

This value is evidently independent of α and q_2 and coincides with the thickness h of a layer of monodisperse chains consisting of N_1 units grafted onto a cylinder of radius r [equation (7), lower signs].

(*3*) *Free energy.* Using the subdivision of a bidisperse layer into monodisperse layers and using equation (21), one obtains the conformational free energy:

$$\Delta\tilde{F} = \Delta\tilde{F}_{10}^{\mathrm{lam}}\left[\frac{r}{2}\ln(1 + 2/r) + \alpha q_2^3 \frac{r}{2}\sqrt{\frac{r}{r+2}}\ln\left(1 + \frac{2}{\sqrt{r(r+2)}}\right)\right] \qquad (45)$$

where $\Delta\tilde{F}_{10}^{\mathrm{lam}}$ is determined from equation (22).

DISCUSSION

The analytical theory developed here describes the conformational characteristics of dry layers with cylindrical morphologies formed by grafted polymer chains mono- or bidisperse in length. The theory is based on the concept of the considerable stretching of macromolecules in grafted layers normal to the grafting surface. This stretching is caused by volume interactions between units of grafted chains under the conditions of their marked overlapping. Compared to the planar grafted layer considered in the first paper in this series[1], the chains in concave cylindrical layers are more stretched and those in convex layers are less stretched (the grafting

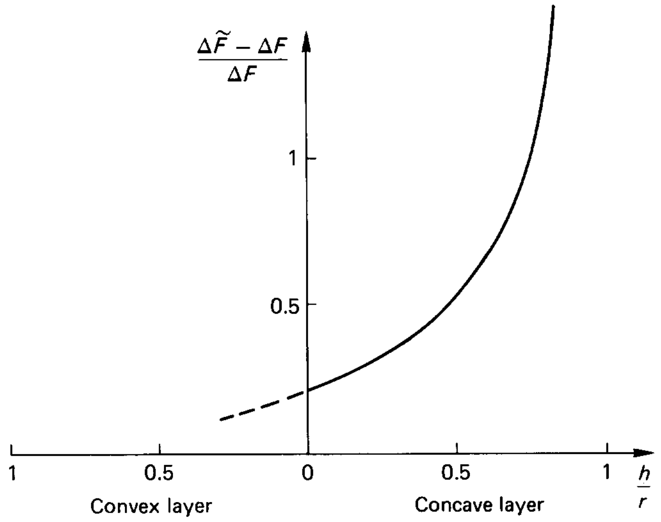

Figure 9 Relative error in the calculation of free energy $(\Delta\tilde{F}-\Delta F)/\Delta F$ in FEF approximation *versus* h/r; ———, equations (14) and (46); ---, equations (18) and (21)

density $1/\sigma$ is assumed to be constant). The reason for this is a decrease (or increase) in the space accessible to chains with increasing distance from the grafting surface. In the case of concave layers this causes the displacement of the mean position of free ends of grafting chains from the centre of the cylinder to the grafting surface (*Figure 3*). In contrast, in the case of convex layers, the mean position of ends is displaced from the grafting surface to the layer periphery.

The stretching of polymer chains with respect to their Gaussian size makes it possible to use the so-called Newtonian approximation[9] for describing the conformations of grafted chains. It is possible to obtain a precise solution for the case of concave[6,9] and planar layers[9,11,15] (for a discussion of the limits of the applicability of the theory, see ref. 1). In the case of convex layers, several approximations should be used, in particular, the FEF approximation in the case of considerable curvature.

Let us evaluate the error in the calculation of the conformational free energy $\Delta\tilde{F}$ of convex layers of monodisperse chains in the FEF approximation. For this purpose, let us first consider the free energy of a concave monodisperse layer with free ends at the outer boundary. This is given by equation (21) for a convex layer using the FEF approximation after replacing r by $-r$:

$$\Delta\tilde{F}=\Delta\tilde{F}_{10}^{\mathrm{lam}}\frac{-2\ln(1-h/r)}{(h/r)(2-h/r)}=\Delta\tilde{F}_{10}^{\mathrm{lam}}\frac{r}{2}\ln\frac{r}{r-2} \qquad (46)$$

Figure 9 shows the relative error of this approximation, $(\Delta\tilde{F}-\Delta F)/\Delta F$. As before, ΔF is calculated by equation (14), with the free ends distribution throughout the layer thickness being taken into account. It is clear from *Figure 9* that FEF approximation is inapplicable to markedly concave layers as it leads to a large error. The error decreases with decreasing concavity and for a planar layer is ~20%. The broken line in *Figure 9* shows a further decrease in the error of the FEF approximation for weakly convex layers. This dependence is obtained by the analytical continuation of the expansion of $(\Delta\tilde{F}-\Delta F)/\Delta F$ on h/r near $1/r=0$ (with a subsequent change in the sign of r). It is evident that for strongly convex layers $h/r>1$, the FEF approximation provides sufficient precision for the ΔF calculation. Some additional evaluations confirming this conclusion are given in the Appendix.

After this paper had been completed, we received a preprint of a paper by Ball and co-workers[17] which investigated the equilibrium characteristics of a convex grafted cylindrical layer formed by long monodisperse chains. These authors had developed a system of integral equations which made it possible to obtain, in particular, a precise solution for the free energy of the system taking into account the existence of a 'dead' zone free from ends inside of which $g(z)=0$. The results of this work have shown that in the case of a maximum curvature of a cylindrical surface, $R\to 0$, the precise solution coincides with the expression for free energy [equation (21)] obtained in the FEF approximation.

It seems to us more essential that the authors just notice that the true free energy should be lower than the FEF approximation, equation (21), but higher than the analytical continuation of equation (14) to the region of convex layers, equation (18a). The reason for this is the fact that the fixation of free ends on the external surface of the layer limits the class of functions in which the minimum of the functional (1) of free energy is obtained. In contrast, the absence of limitations of the sign of function $g(z)$ broadens the class of functions as compared to the physically possible class $[g(z)\geqslant 0]$. It can be seen from *Figure 4* that in the region of convex layers both approximate dependences are close to each other. Hence, the precise solution lying between them may be approximated with good precision by any of these approximate dependences, in particular, by equation (21).

This result may be extended to the case of bidisperse chain layers. It can be seen from equation (45) determining the conformational free energy of the convex bidisperse chain layers, that at $r\to\infty$, i.e. upon the transition to a planar layer, we have:

$$\Delta\tilde{F}=\Delta\tilde{F}_{\mathrm{L}}=\Delta\tilde{F}_{10}^{\mathrm{lam}}(1+\alpha q_2^3)=\frac{12}{\pi^2}\Delta F_{10}^{\mathrm{lam}}(1+\alpha q_2^3) \qquad (47)$$

instead of the rigorous equation (40). Hence, FEF approximation in a planar bidisperse layer under the condition $\beta(q_2)=1$, leads only to an increase in the numerical coefficient by 20% ($1\to 12/\pi^2$, just as for a monodisperse layer) but the functional dependence of $\Delta\tilde{F}$ on all the parameters contained in $\Delta\tilde{F}$ (N_1, σ, α and q_2) remains unchanged. This suggests that for convex bidisperse layers the relative error $(\Delta\tilde{F}-\Delta F)/\Delta F$ does not exceed that for monodisperse layers. It follows from the plot in *Figure 9* that the real evaluation of error in the case of strongly convex layers ($h/r>1$) hardly exceeds 10%.

Below we shall discuss the structure and properties of cylindrical layers of grafted bidisperse chains. As to the monodisperse chains layers (see the pioneering work in ref. 9 where the main results for dry curved layers were obtained and also ref. 10) only one interesting fact concerning the free energy of a concave layer of limiting curvature, i.e. a layer densely filling all the cylinder space, will be mentioned. It follows from equations (14) and (15) that the free energy of this layer per chain is:

$$\Delta F_{10}\frac{\sigma}{a^2}=2\Delta F_{10}^{\mathrm{lam}}\frac{\sigma}{a^2}\sim N_1/\sigma^2 \qquad (48)$$

Let us consider the variation in this value with the change in chain length N_1. There are two reasons for this change. If σ is constant (i.e. the linear density of chains grafting $\kappa = 2\pi R/\sigma$ is not constant), then the free energy of the chain increases in proportion to N_1. If κ is constant (i.e. the total number of chains grafted onto a cylinder is fixed), then $N_1/\sigma^2 \sim \kappa^2 = \text{constant}(N_1)$. In other words, if the cylinder is filled with grafted chains, and then each chain increases its length and a completely filled cylinder of a larger radius is obtained, then the free energy of each chain (and of the entire cylinder) does not change. Note that this invariability of the free energy is characteristic only of the cylindrical layer and is a consequence of its geometry.

Structure of bidisperse layers

Let us compare the structural characteristics of cylindrical and planar layers formed by polymer chains of two lengths. As has been shown elsewhere[1], the thickness of the short-chain sublayer in a planar case is independent of the long chain degree of polymerization (at fixed N_1 and σ values). The same refers to the average length βN_1 of parts of tie chains in this sublayer: β depends only on the fraction q_2 of tie chains and does not depend on N_2.

A different situation is observed in the case of dry concave layers completely filling the cylinder. The main effect is caused by the fact that in this case the cylinder radius is a function of N_1, α and q_2, i.e. the relative radius r is a function of α and q_2 [equation (32)]. Hence, the dependences of the characteristics of the monodisperse layer on r considered earlier are also manifested here as the dependences of these characteristics on q_2 and α. One of these characteristics is the thickness of the short chain sublayer H_1 (or the length βN_1 of the parts of tie chains in the sublayer). A direct influence of r on the sublayer thickness leads to an increase in its relative thickness h_1 (and the mean length of the parts of tie chains β) with increasing r (or α) at a fixed q_2 value (*Figures 6* and *7*).

Moreover, an additional effect exists caused by the influence of the polydispersity of grafted chains. At fixed values of r, σ and q_2, the thickness of the short-chain sublayer h_1 is a function of the length of long chains. Thus, the sublayer thickness h_1 is minimal at a maximum possible value of $N'_2 = N_2 = N_1(1+\alpha)$ when all the cylinder space is densely filled with polymer units [equation (34)]. With decreasing $N'_2 < N_2$, i.e. when the end parts of long chains are 'cut off' and the radius of the void in the centre of the cylinder increases, the thickness of the short-chain sublayer increases and attains maximum value at $N'_2 = N_1$, i.e. in a monodisperse layer of chains consisting of N_1 units [in this case $h_1 = h'_1$ is determined as the thickness of a sublayer in which the ends of the fraction $q_1 = 1 - q_2$ of grafted chains are distributed, equation (12)]. The effect is relatively slight and in a certain sense, paradoxical. In fact, when the ends of long chains filling the inner part of the cylinder are cut off, the tie chains, i.e. the parts of long chains located in the sublayer of short chains, become longer. Thus, the cutting of the ends of long chains leads to additional 'drawing in' of long chains inside the short-chain sublayer. It may be shown that this effect is due to the properties of the long-chain sublayer. If this sublayer is compact and has no void at the cylinder centre, then, as has been discussed above, the conformation free energy of this sublayer depends only on the linear grafting density and does not depend on the position of the boundary between the two sublayers. The dependence on the position of the boundary appears when the cylinder is hollow and contains a void. This leads to the additional displacement of the boundary between the two sublayers towards the centre of the cylinder. This effect increases with r.

Free energy of a bidisperse layer

The most important result of our work is the form of the free energy dependence on the composition of a dry layer consisting of two-length chains. *Figure 10* shows the characteristic dependences $\Delta F(q_2)$ for the planar layer (curve B), and for concave (curve A) and convex (curve C) layers grafted onto a cylindrical surface of the same radius $r = 2(1 + \alpha q_2)$. It can be seen from *Figure 10* that in all three cases the dependences $\Delta F(q_2)$ lie below the straight lines $\Delta F' = q_1 \Delta F(q_1 = 1) + q_2 \Delta F(q_2 = 1)$ determining the mean free energy obtained in the cases of segregation of chains with different lengths in a grafted layer (broken lines in *Figure 10*). This fact indicates that the mixing of chains of different lengths in a layer is always thermodynamically advantageous. It should be emphasized that this is not a result of a gain in the trivial mixing entropy of grafted chains (this weak effect is not taken into account). As has been shown for a planar layer[1,15] this gain is due to the fact that short chains located between long chains decrease the effective density of grafting in the long-chain sublayer. This, in turn, leads to a decrease in their stretching and steric interactions with one another. The same effect also occurs for curved layers but is weaker for a convex layer because of the increase in the available space with increasing distance from the matrix and stronger in the concave layer for the opposite reason. [It can be seen from *Figure 10* that

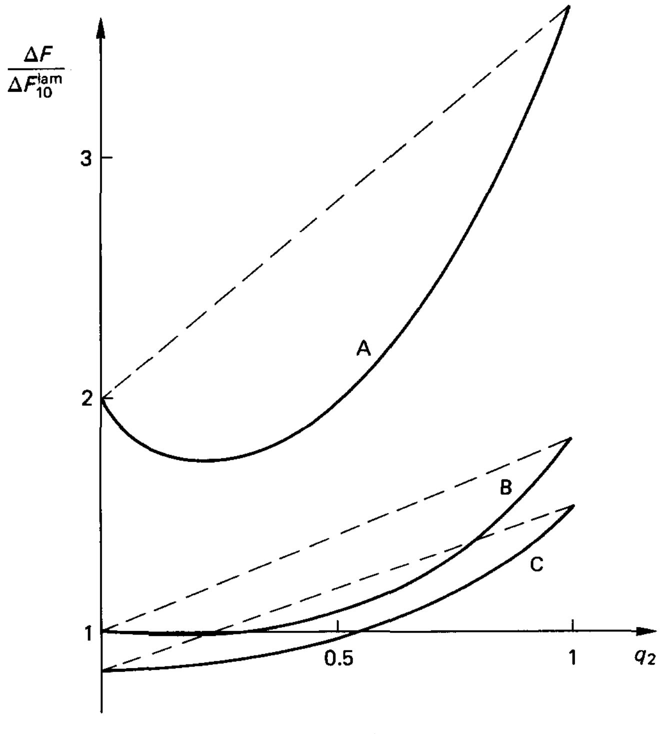

Figure 10 Relative free energy $\Delta F/\Delta F_{10}^{\text{lam}}$ of a bidisperse layer *versus* q_2 for (A) concave cylindrical, (B) planar and (C) convex cylindrical layers for a value of $\alpha = 0.8$ and the radius of cylinder $r = 2(1 + \alpha q_2)$. ---, Dependences $q_1 \Delta F(q_1 = 1) + q_2 \Delta F(q_2 = 1)$

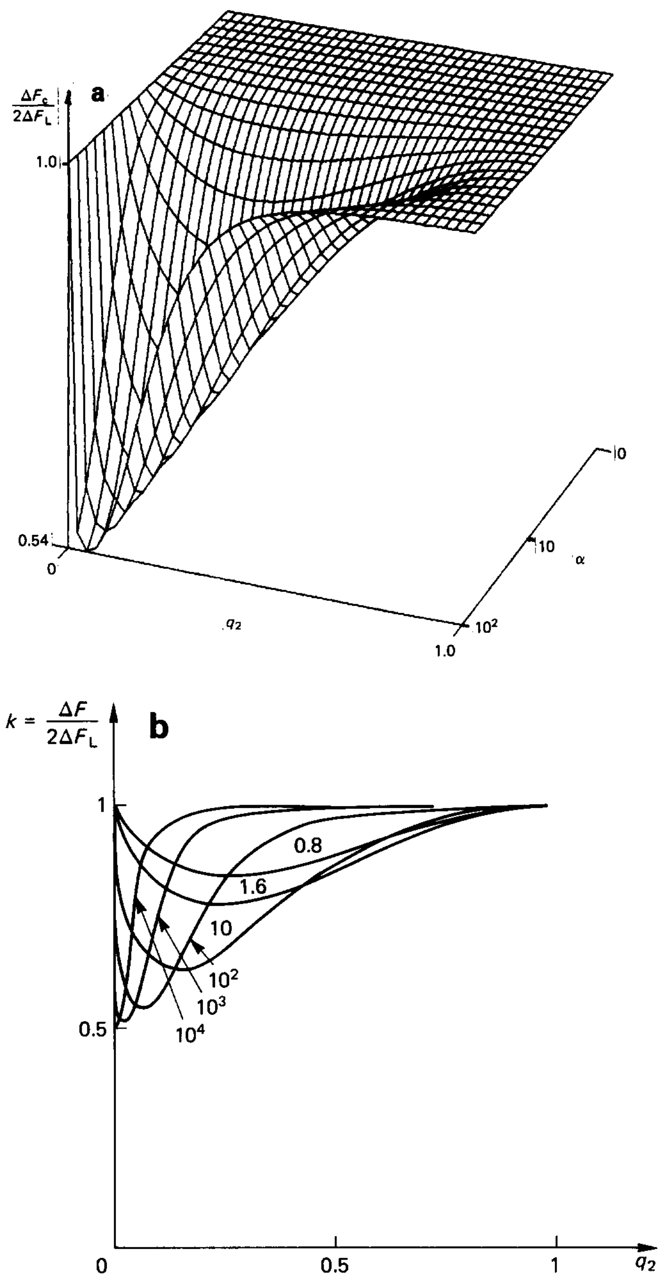

Figure 11 (a) Three-dimensional semilogarithmic plot of relative free energy $k = \Delta F/2\Delta F_L$ in a system of coordinates q_2 and α; (b) the two-dimensional cross-sections at different α, equations (38)–(40). The values of α are shown on the curves

at fixed layer composition, q_2 is constant, the difference $(\Delta F' - \Delta F)$ increases in the sequence: convex < planar < concave.]

It is clear from *Figure 10* (see also *Figure 8*) that in contrast to the monotonic dependences $\Delta F(q_2)$ in planar and convex layers (curves B and C), in the case of a concave layer $\Delta F(q_2)$ goes through a pronounced minimum (curve A).

In the case of a concave bidisperse layer densely filling the inner part of the cylinder, the cylinder radius is related to the fraction q_2 of long chains and to the relative difference in lengths α by equation (32). The increase in q_2 at a fixed α leads to increasing shallowness of the short-chain sublayer. This leads to a decrease in the conformational free energy of the short-chain sublayer. Simultaneously, the conformational free energy of the long-chain sublayer increases with increasing linear density of their grafting, which, in turn, increases with q_2. The summation of these two contributions to free energy leads to the appearance of the minimum on the dependence $\Delta F(q_2)$.

Figure 11 shows the dependences of one-half of the free energies ratio $k = \Delta F(\alpha, q_2)/2\Delta F_L(\alpha, q_2)$ on q_2 for different values of α. Both free energies are related to the dry bidisperse chain layers: $\Delta F(\alpha, q_2)$ characterizes the concave cylindrical layer $(r = 1 + \alpha q_2)$; $\Delta F_L(\alpha, q_2)$ characterizes the planar layer $(r \to \infty)$. At $q_2 = 0$ (concave cylindrical and planar monodisperse layers of short chains) we have $k = 1$: free energies differ by a factor of two at $h/r = 1$ [equation (14)]. With increasing q_2, when, as before, the main contribution to ΔF is still provided by short chains, k decreases tending towards 1/2 (short-chain sublayer becomes shallower, and its conformational energy approaches the free energy of the planar layer). With further increase in q_2, when the main contribution to free energy begins to be provided by long chains, k passes through a minimum, then increases and at $q_2 = 1$ (both concave cylindrical and planar monodisperse layers contain only long chains) becomes again equal to unity. With increasing α, the dependences $k(q_2)$ become sharper, the depth of the minimum increases and its width decreases. In the limit $\alpha \to \infty$, we have $k \to 0.5$ at $q_2 \to 0$.

In the next paper in this series[19], the results obtained here will be used for the investigation of stable morphologies in mixtures of lamellar- and cylinder-forming block copolymers and it will be shown that the extreme character of the dependence of ΔF on the fraction q_2 for concave layers leads to a non-trivial form of the diagram of states of superstructures in block copolymer mixtures. It should be emphasized that the results obtained here are valid under the conditions of stretching of all chains.

ACKNOWLEDGEMENT

We are grateful to R. C. Ball *et al.*[17] for providing a preprint of their paper.

REFERENCES

1 Birshtein, T. M., Lyatskaya, Yu. V. and Zhulina, E. B. *Polymer* 1990, **31**, 2185
2 Zhulina, E. B. and Birshtein, T. M. *Polymer* 1991, **32**, 1299
3 Hadziioannou, G. and Skoulios, A. *Macromolecules* 1982, **15**, 267
4 Hasegawa, H., Shibayama, M., Hashimoto, T. and Kawai, H. *Polym. Prepr. Jpn.* 1981, **30**, 2110
5 Hashimoto, T. *Macromolecules* 1982, **15**, 1548
6 Birshtein, T. M. and Zhulina, E. B. *Polymer* 1989, **30**, 176
7 Birshtein, T. M. and Zhulina, E. B. *Polymer* 1984, **25**, 1435
8 Daoud, M. and Cotton, J. P. *J. Physique.* 1982, **43**, 531
9 Semenov, A. N. *Sov. Phys. JETP* 1985, **61**, 733; *Zh. Eksp. Teor. Phys.* 1985, **88**, 1242
10 Milner, S. T. and Witten, T. A. *J. Physique.* 1988, **49**, 1951
11 Skvortsov, A. M., Pavlushkov, I. V., Gorbunov, A. A., Zhulina, E. B., Borisov, O. V. and Priamitsyn, V. A. *Vysokomol. Soedin.* 1988, **A30**, 1615
12 Zhulina, E. B., Priamitsyn, V. A. and Borisov, D. V. *Vysokomol. Soedin.* 1989, **A31**, 185
13 Zhulina, E. B., Borisov, O. V., Priamitsyn, V. A. and Birshtein, T. M. *Macromolecules* 1991, **24**, 140
14 Milner, S. T., Witten, T. A. and Cates, M. E. *Europhys. Lett.* 1988, **5**, 413
15 Milner, S. T., Witten, T. A. and Cates, M. E. *Macromolecules* 1988, **21**, 2610
16 Milner, S. T., Witten, T. A. and Cates, M. E. *Macromolecules* 1989, **22**, 859

17 Ball, R. C., Marco, J. F., Milner, S. T. and Witten, T. A. *Macromolecules* 1991, **24**, 693
18 Birshtein, T. M. and Karaev, A. K. *Vysokomol. Soedin.* 1988, **A30**, 1001
19 Lyatskaya, Yu. V., Zhulina, E. B. and Birshtein, T. M. *Polymer* 1992, **33**, 343

APPENDIX

In order to give an additional characterization of convex layers of a considerable curvature, an approach developed previously[18] for a planar layer preceding the development of the analytical theory may be used. In reference 18, a numerical solution of the equations of the type of equations (1) and (3)–(5) has been carried out by approximating the function $g(z)$ by a fixed number n of discrete values:

$$g(z)=\sum_{i=1}^{n} g_i\delta(z-z_i) \qquad z_n=h \tag{A1}$$

The values of g_i and z_i were determined by the minimization conditions. The transition to a precise solution should be carried out at $n \rightarrow \infty$. The comparison of the results of reference 18 with the conclusions of the analytical theory[12–15] shows that a series of characteristics of planar layers, in particular, the value of $\bar{z}/h$, determining the mean position of free ends in a layer and the value ΔF of the free energy of the layer are approximately linear functions of $1/n$. Therefore, the transition from the unimodal function $g(z)$ determined by equations (19) or (A1) at $n=1$ (FEF approximation, all ends are fixed on the outer boundary) to a bimodal function determined from equation (A1) at $n=2$ (part of the ends is fixed on the outer boundary of the layer and the other part is fixed at some height inside the layer) leads to the appearance of approximately half the difference between the precise solution and the solution from the FEF approximation. Thus, for a dry planar layer at $n=2$ we have[18] $\bar{z}/h=0.89$ [the precise value 0.78 is given by equation (10)] and $\Delta\tilde{F}(n=2)/\Delta\tilde{F}(n=1)=0.89$ [precise value 0.78, cf. equation (22)]. For a layer of chains grafted onto the surface of an infinitely thin cylinder ($h/r \rightarrow \infty$), the scheme in reference 18 does not lead to an energy gain in passing from $n=1$ to $n=2$, which confirms the possibility of the FEF approximation.