Theory of supermolecular structures of polydisperse block copolymers: 1. Planar layers of grafted chains

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This is the first of a series of papers which develops the theory of superstructures of block copolymers, taking into account the polydispersity of their components. In this paper, the mean-field theory describing the detailed structure and properties of planar grafted layers, formed by chains of two molecular weights, is developed. Several conclusions are drawn on the structure and properties of grafted layers with arbitrary character of polydispersity of molecular weight.

(Keywords: block copolymers; supermolecular structure; planar layer; grafted chain)

INTRODUCTION

Di- and triblock copolymers are known to form supercrystalline structures with different morphologies[1,2]. A surprising property of these structures is the fact that their formation does not require high degrees of monodispersity of copolymers. Moreover, the formation of regular structures in binary mixtures of block copolymers with different molecular weights and compositions is observed experimentally[3]. The aim of this and subsequent papers is to develop the theory of superstructures of block copolymers taking into account the polydispersity of their components.

In a previous series of investigations[4–10], the theory of well defined superstructures of monodisperse block copolymers with the same molecular weight and composition of all molecules has been developed. The initial point of the theory was the concept of a narrow interphase layer, the thickness of which is much smaller than the characteristic dimensions of the elements of the superstructure (lamellae thickness or the dimensions of the domains and interdomain layers) and is independent of the molecular weight of the copolymer components. In this case, which corresponds to the condition of strong segregation of block copolymer components, the theory of grafted polymer layers becomes a part of the theory of block copolymer superstructures. This theory of grafted polymer layers considers the conformations and thermodynamic properties of chains grafted onto an impermeable matrix of a fixed geometry. This impermeable matrix is formed by the interphase surface, its geometry is determined by the morphology of the superstructure, and different blocks are represented as chains 'grafted' onto this surface. The theory of grafted polymer chains also became an indispensable part of the theory of solutions of regularly branched polymers[11–14], the theory of stabilization of colloid dispersions by polymers[15], etc.

In recent years, considerable progress has been attained in the theoretical investigations of grafted polymer layers with different morphologies (geometries). The scaling consideration made it possible to establish the main power laws relating the characteristics of the layer to molecular parameters[16–19]. For planar layers (corresponding to lamellar mesophase), the naive scaling consideration does not make it possible to analyse the inner structure of the layer, which was first investigated on the basis of computer simulation[20,21] and the sublayer approximation[22] and subsequently on the basis of the mean-field theory developed by two groups of researchers[23–29]. This theory provided analytical expressions for the non-power distribution functions of free chain ends, the degree of chain stretching and their local ordering, the density profile of polymer units, both under the conditions of an athermal solvent[24,26,27] and over a wide temperature range including the Θ-point[23,24].

The transition to polydisperse block copolymer systems requires the development of the theory of grafted layers of polydisperse macromolecules. The influence of chain polydispersity on layer characteristics evidently proceeds via the effect on the inner structure of the layer. Hence, developing in this paper the theory of planar layers, we will base it on the methods and results described in ref. 24.

As an example of a layer of polydisperse chains, a layer formed by a mixture of grafted chains with degrees of polymerization N_1 and N_2 will be considered (*Figure 1*). Note that a similar problem has been considered in ref. 28. In the present paper, the range of conditions will be extended as compared to those in ref. 28 (in particular, the temperature range near the Θ-point was investigated, and layer deformation was considered). Hence, it will be possible to carry out a more complete analysis of the results and to draw several general conclusions.

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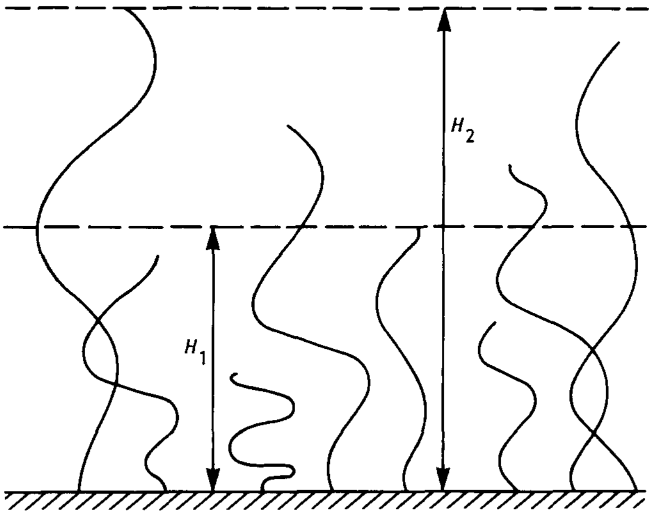

Figure 1 Planar layer of bidisperse chains

MODEL

A planar layer of chains grafted at one end onto a planar impermeable surface and immersed into a solvent at temperature T will be considered. Let the degrees of polymerization be equal to N_1 and $N_2 > N_1 \gg 1$ and let σ be the mean grafting area per chain. As before, a symmetrical chain element of length equal to chain thickness a will be chosen as a unit. Let $p = A/a \geqslant 1$ be the number of units in a stiff (Kuhn) chain segment, q_1 and $q_2 = 1 - q_1$ be the fractions of short and long chains in a layer and $\alpha = (N_2 - N_1)/N_1 > 0$ be the relative difference between chain lengths.

Let us consider different variants of structures of planar layers of bidisperse grafted chains:

(1) A free layer immersed in a good ($\tau = (T - \Theta)/\Theta \simeq 1$) or Θ ($\tau = 0$) solvent.

(2) A layer with a constant volume concentration of units $\varphi = \text{const}$ throughout the entire layer thickness. A layer containing no solvent, $\varphi = 1$, is a particular case.

(3) A deformed layer, i.e. a layer immersed into a good or a Θ-solvent and compressed by a plane parallel to the grafting plane.

In all cases it will be assumed that the condition of side overlapping of grafted chains ensuring their stretching to size $\sim N$ in the direction normal to the grafting plane is obeyed. The normal direction is singled out so that the problem is, in fact, one-dimensional, and the natural coordinate in the direction of the normal x will be counted from the grafting plane.

The following values are of interest as layer characteristics:

(a) $g_1(x')$ and $g_2(x')$ are the partial distribution functions of chain ends along the layer height.

(b) $E_1(x, x')$ and $E_2(x, x')$ are the partial functions of local stretching at a height x of the chain ending at the point x'.

(c) $\varphi_1(x)$, $\varphi_2(x)$ and $\varphi(x) = \varphi_1(x) + \varphi_2(x)$ are the partial and complete volume concentrations of units at a point x (in the case of a dense layer $\varphi(x) = \text{const}$).

(d) H_1 and H_2 are the limiting distances of the free ends of short and long chains from the grafting plane (H_1 is the height of short chain layer and H_2 is the complete height of the layer). In the case of a compressed layer, H_2 is the predetermined parameter.

THEORY

As already mentioned, grafted layers will be considered under the conditions of stretching of all chains. The elastic free energy of stretching determines to a considerable extent the complete free energy of the system. Hence, under equilibrium conditions, the chains tend to minimize their stretching. A natural consequence of this requirement in the system under consideration is the condition of non-overlapping of distribution functions of ends of short, $g_1(x')$, and long, $g_2(x')$, chains. The former should differ from zero only in the layer part adjoining the grafting plane, $0 < x' < H_1$, and the latter should differ from zero in the more distant peripheral part of the layer, $H_1 < x' < H_2$: $g_1(x') = 0$ at $x' > H_1$ and $g_2(x') = 0$ at $x' < H_1$. The value of H_1, the height of the layer of short chains, should be determined. Note that the effect of the segregation of ends of grafted chains of different lengths is completely equivalent to that of the segregation of the opposite layers of grafted chains (see refs. 10 and 23 for further details). This problem will be discussed below in the 'Discussion' section.

According to ref. 24, the free energy per unit area, a^2, is given by:

$$\Delta F = \Delta F_{\text{el},1} + \Delta F_{\text{el},2} + \Delta F_{\text{conc}} \tag{1}$$

where

$$\Delta F_{\text{el},1} = \frac{3}{2\sigma} \int_0^{H_1} g_1(x')\,\mathrm{d}x \int_0^{x'} E_1(x, x')\,\mathrm{d}x \tag{2}$$

$$\Delta F_{\text{el},2} = \frac{3}{2\sigma} \int_{H_1}^{H_2} g_2(x')\,\mathrm{d}x \int_0^{x'} E_2(x, x')\,\mathrm{d}x \tag{3}$$

are the entropy contributions of elastic chain stretching and ΔF_{conc} is the contribution of volume interactions between the units depending on their volume concentration in the layer $\varphi(x) = \varphi_1(x) + \varphi_2(x)$ where:

$$\varphi_1(x) = \frac{a^3}{\sigma} \int_x^{H_1} \frac{g_1(x')\,\mathrm{d}x'}{E_1(x, x')} \qquad x < H_1 \tag{4}$$

$$\varphi_2(x) = \frac{a^3}{\sigma} \int_{\max(x, H_1)}^{H_2} \frac{g_2(x')\,\mathrm{d}x'}{E_2(x, x')} \qquad x \lessgtr H_1 \tag{5}$$

and

$$\int_0^{H_1} g_1(x')\,\mathrm{d}x' = q_1 \tag{6}$$

$$\int_{H_1}^{H_2} g_2(x')\,\mathrm{d}x' = q_2 \tag{7}$$

Here and below all energy values are expressed in kT units. When the concentrations in the layer are not very high, $\varphi(x) \ll 1$, the density of free energy of volume interactions $f(x)a^{-3}$ may be represented in the form of a virial expansion $f(x) \approx v\varphi^2(x) + w\varphi^3(x) + \cdots$, which gives for ΔF_{conc} under the conditions of a good ($v \gg w\varphi$) and a Θ-solvent ($v \ll w\varphi$):

$$\Delta F_{\text{conc}} = \frac{1}{a} \int_0^{H_2} f(x)\,\mathrm{d}x$$

$$\approx \begin{cases} \dfrac{1}{a} \displaystyle\int_0^{H_2} v\varphi^2(x)\,\mathrm{d}x & T \gg \Theta \qquad \text{(8a)} \\ \dfrac{1}{a} \displaystyle\int_0^{H_2} w\varphi^3(x)\,\mathrm{d}x & T = \Theta \qquad \text{(8b)} \end{cases}$$

where va^3 and wa^6 are the second and third virial coefficients of unit interaction. In the case of a dense layer, $\varphi(x)=\text{const}$, ΔF_{conc} in equation (1) becomes a constant and does not affect the result of the minimization of ΔF.

Consequently, the free energy determined by equations (1)–(8) is a functional of the functions $E_i(x,x')$ and $g_i(x')$ ($i=1,2$) and contains in the general case the values of H_1 and H_2 as the unknown parameters. The minimization of this functional taking into account additional conditions:

$$\int_0^{x'} \frac{dx}{E_i(x,x')}=N_i \qquad i=1,2 \tag{9}$$

and

$$\frac{\sigma}{a^3}\int_0^{H_i} \varphi_i(x)\,dx=q_iN_i \qquad i=1,2 \tag{10}$$

or, in the case of a layer of constant density:

$$\varphi(x)=\varphi_1(x)+\varphi_2(x)=\text{const} \qquad 0\leqslant x\leqslant H_2 \tag{11}$$

determines the equilibrium characteristics of a planar layer of bidisperse chains.

In order to solve this problem, the Lagrangian method of indefinite multipliers will be used. Then the variation of the functional for the four unknown functions $E_i(x,x')$ and $g_i(x')$ ($i=1,2$) leads to Euler's system of equations. The structure of the equations and the scheme for their solution are considered in the Appendix. Here only the main results will be discussed.

RESULTS

Functions of local chain stretching

Analysis shows that in all the cases considered here the functions of local stretching of short and long chains are described by general equations:

$$E_1(x,x')=\frac{\pi}{2N_1}(x'^2-x^2)^{1/2} \qquad x\leqslant x'\leqslant H_1 \tag{12}$$

$$E_2(x,x')=\begin{cases}\dfrac{\pi}{2N_1}[u^2(x')-x^2]^{1/2} & x\leqslant H_1\leqslant x'\leqslant H_2\\[2ex] \dfrac{\pi}{2N_1}[u^2(x')-u^2(x)]^{1/2} & H_1\leqslant x\leqslant x'\leqslant H_2\end{cases} \tag{13}$$

where

$$u(x)=\frac{1}{1-\alpha^2}\{x-\alpha[x^2-(1-\alpha^2)H_1^2]^{1/2}\} \tag{14}$$

It can be seen from equation (12) that the function of local stretching of short chains at $x, x'<H_1$ is independent of α and q_1 and, hence, of the existence of long chains in the layer, i.e.

$$E_1(x,x')\equiv E_{10}(x,x') \qquad x,x'\leqslant H_1 \tag{15}$$

where $E_{10}(x,x')$ is the function of local chain stretching in a monodisperse layer containing only chains of length N_1 ($q_1=1$, $q_2=0$, subscript '0'). Hence, it is advisable to consider the layers of monodisperse chains as initial layers.

Layers of monodisperse chains

The theory of these layers under different thermodynamic conditions has been developed in refs. 24, 26 and 27. The analysis of results obtained in these papers has shown that the characteristics of free layers in a good or a Θ-solvent and those of a layer with a constant density may be described by universal relationships. In the limiting cases of an athermal ($\tau=1$) and a Θ-solvent ($\tau=0$) and a strong precipitant leading to layer compactization and the levelling-off of its density ($\tau<0$, $\varphi(x)\approx$ const), the solvent quality is contained in these equations via the exponent ν of the molecular-weight dependence of the size of free (ungrafted) chains under the corresponding thermodynamic conditions $R\sim N^\nu$. In this case we have $\nu=3/5$ and $1/2$ for a good and a Θ-solvent, respectively, and the layer of constant density corresponds to the condition of the precipitant (globular state) with $\nu=1/3$.

Universal equations for the distribution functions of chain ends $g_{10}(z)$ and of concentration profiles $\varphi_{10}(z)$ in a layer of chains of length N_1 grafted at a density $1/\sigma$ have the form[24]:

$$g_{10}(z)=2(\beta_g+1)z(1-z^2)^{\beta_g} \tag{16}$$

$$\varphi_{10}(z)=\varphi_{10}^{(m)}(1-z^2)^{\beta_\varphi} \tag{17}$$

Here $z=x/H_{10}$ is the relative coordinate along the layer height.

The limiting layer height is:

$$H_{10}=aN_1\left(K_H\frac{\sigma}{a^2}\right)^{-\beta_H} \tag{18}$$

and $\varphi_{10}^{(m)}$ is the maximum (at $z=0$) unit concentration in the layer:

$$\varphi_{10}^{(m)}=K_\varphi\frac{N_1a^3}{\sigma H_{10}} \tag{19}$$

(The theory does not consider the decrease in concentration in the near-surface layer of thickness $\sim\sigma^{1/2}$.)

The free energy of the layer (per unit volume) is given by:

$$\Delta F_{10}=N_1\left(K_F\frac{\sigma}{a^2}\right)^{-\beta_F} \tag{20}$$

The values of exponents and numerical coefficients in equations (16)–(20) are summarized in *Table 1*. It should be noted that, in the case of a layer with a constant density $\varphi(x)\equiv\varphi$, the value of ΔF_{10} in *Table 1* does not contain the contribution of volume interactions, $\Delta F_{\text{conc}}\sim N=\text{const}$.

Layers of bidisperse chains

Let us now return to the case of a layer formed by a mixture of chains of lengths N_1 and $N_2=N_1(1+\alpha)$ (their fractions are q_1 and q_2) with the average grafting density $1/\sigma$. Its characteristics will be compared to those of a monodisperse layer consisting of chains of length N_1 ($q_1=1$ and $q_2=0$) with the same grafting density, i.e. the change in the structure and characteristics of the layer when the length of the part q_2 of the chains increases from N_1 to N_2 will be considered.

As already mentioned (equation (15)), this increase in length does not affect the function of local stretching of short chains. Moreover, as follows from the Appendix, this increase does not affect the distribution function of short-chain ends so that in the range of the existence of

Table 1 Exponents and numerical coefficients in equations (16)–(20)

Expressions	Values of $\nu=3/5$	$\nu=1/2$	$\nu=1/3$
$\beta_g=\dfrac{2\nu-1}{1-\nu}$	1/2	0	−1/2
$\beta_H=\dfrac{1-\nu}{2\nu}$	1/3	1/2	1
$\beta_\varphi=\dfrac{3\nu-1}{2(1-\nu)}$	1	1/2	0
$\beta_F=\dfrac{1}{\nu}$	5/3	2	3
K_H	$\left(\dfrac{8}{\pi^2}vp\right)^{-1}$	$\left[\dfrac{4}{\pi}\left(\dfrac{wp}{2}\right)^{1/4}\right]^{-2}$	φ
K_F	$\left[\dfrac{9}{10}\dfrac{(\pi v)^{2/3}}{p^{1/3}}\right]^{-3/5}$	$\left[3\left(\dfrac{w}{2p}\right)^{1/2}\right]^{-1/2}$	$\left(\dfrac{\sqrt{8}}{\pi}\varphi\right)^{2/3}$
$K_\varphi=\dfrac{2}{\sqrt{\pi}}\dfrac{\Gamma(1/(1-\nu))}{\Gamma((1+\nu)/(2-2\nu))}$	3/2	$4/\pi$	1

this function at $z\leqslant H_1/H_{10}\equiv h_1$ we have:

$$g_1(z)=g_{10}(z) \qquad (21)$$

where $g_{10}(z)$ is determined by equation (16) and *Table 1* and z is, as before, a coordinate normal to the surface referred to the limiting height of the initial monodisperse layer H_{10} (equation (18)). Equations (16) and (21) and the normalization conditions make it possible to determine the dependence of the relative height h_1 of short chains on the composition in the bidisperse layer for which we have:

$$h_1=\frac{H_1}{H_{10}}=(1-q_2^{1/(1+\beta_g)})^{1/2}=(1-q_2^{2\beta_H})^{1/2} \qquad (22)$$

The density profile of units in the range of values $0\leqslant z\leqslant h_1$ also remains invariable:

$$\varphi(z)=\varphi_1(z)+\varphi_2(z)=\varphi_{10}(z) \qquad z\leqslant h_1 \qquad (23)$$

where φ_{10} is given by equations (17) and (19) and *Table 1*. It can be seen from the Appendix that in the range $z<h_1$ the partial values of $\varphi_1(z)$ and $\varphi_2(z)$ are also retained. For a monodisperse layer, these values have the sense of contributions to the total concentration of chains ending before and after the height h_1.

In the range $h_1\leqslant z\leqslant H_2/H_{10}\equiv h_2$ in which the ends of long chains are located (H_2 is the limiting layer height), the structure of distribution functions changes. It follows from the Appendix that:

$$\varphi(z)=\varphi_2(z)=\varphi_{10}^{(\mathrm{m})}[1-u^2(z)]^{\beta_\varphi} \qquad h_2\geqslant z\geqslant h_1 \quad (24)$$

where

$$u(z)=\frac{z-\alpha[z^2-(1-\alpha^2)h_1^2]^{1/2}}{1-\alpha^2}=\frac{z^2+h_1^2\alpha^2}{z+\alpha[z^2-(1-\alpha^2)h_1^2]^{1/2}} \qquad (25)$$

It is clear that in this external part of the layer its characteristics depend on the length and content of long chains. At $z=h_1$, $u(h_1)=h_1$ and the values of $\phi(z)$ in equations (23) and (24) coincide.

The distribution function of long-chain ends is given by:

$$g_2(z)=2(\beta_g+1)[1-u^2(z)]^{\beta_g}u(z)\frac{\mathrm{d}u(z)}{\mathrm{d}z} \qquad h_2\geqslant z\geqslant h_1 \quad (26)$$

where the values of exponents β_g are given in *Table 1*.

The total height and the free energy of the layer are given by:

$$h_2=\frac{H_2}{H_{10}}=(1+\alpha q_2^{\beta_H}) \qquad (27)$$

$$\Delta F=\Delta F_{10}(1+q_2^{\beta_F}) \qquad (28)$$

where the values of exponents are also given in *Table 1*. It can be seen that at $z=h_2$, $u(z)=1$, so that $\varphi(h_2)=g_2(h_2)=0$. These results will be discussed together with those for deformed layers.

Deformed layers of monodisperse chains

Let us consider, as in ref. 15, the deformation of monodisperse layers immersed in a solvent under conditions when the limiting layer height is restricted by the value $H'_{10}<H_{10}$, i.e. the layer is compressed compared to its size in the free state, $l_{10}=H'_{10}/H_{10}\leqslant 1$. It will be assumed that the chains of the layer also remain extended under the conditions of deformation, i.e. $H'_{10}>aN_1^\nu$. Since the calculations are very cumbersome, only the case of a layer in a good solvent will be considered here and below. It follows from the results in ref. 15 (see also ref. 29) that the layer deformation considered here leads to an increase in unit concentration along the entire layer height by a constant term:

$$\begin{aligned}\phi'_{10}(z)&=\varphi_{10}(z)+\frac{1}{l_{10}}\int_{l_{10}}^{1}\varphi_{10}(z)\,\mathrm{d}z\\&=\varphi_{10}^{(\mathrm{m})}[\tfrac{2}{3}(1/l_{10})+\tfrac{1}{3}l_{10}^2-z^2]\end{aligned} \qquad (29)$$

(here and below z is still referred to the unperturbed height of the layer).

The distribution function of chain ends also increases along the entire layer height, the change being a maximum on the layer periphery. For the case of a layer in a good solvent ($\nu=3/5$), the distribution function of chain ends in a deformed layer is given by:

$$g'_{10}(z)=z\left[3(l_{10}^2-z^2)^{1/2}+\left(\frac{1}{l_{10}}-l_{10}^2\right)\frac{1}{(l_{10}^2-z^2)^{1/2}}\right] \qquad (30)$$

The free energy of the deformed layer is described by the equation:

$$\Delta F'_{10} = \Delta F_{10} \times \tfrac{5}{9}(1/l_{10} + l_{10}^2 - \tfrac{1}{5} l_{10}^5) \qquad (31)$$

according to which $\mathrm{d}(\Delta F'_{10})/\mathrm{d}l_{10} = \mathrm{d}^2(\Delta F'_{10})/\mathrm{d}l_{10}^2 = 0$ and $\mathrm{d}^3(\Delta F'_{10})/\mathrm{d}l_{10}^3 < 0$ at $l_{10} = 1$. (It should be borne in mind that this equation refers to the case of layer compression $l_{10} \leqslant 1$ with the retention of extension of all chains.) The summand of the order of l_{10}^2 (and also that of the order of l_{10}^5 with the minus sign) in parentheses on the right-hand side of equation (31) is related to a decrease in the free energy of chain stretching with layer deformation and the summand of the order of $1/l_{10}$ (and also that of the order of l_{10}^5 with the plus sign) determine the increase in the energy of volume interactions due to increasing unit concentration in a deformed layer.

Deformed layers of bidisperse chains

Let us now consider a layer of bidisperse chains of length N_1 and $N_2 = N_1(1+\alpha)$ in a good solvent and fix its limiting height $H'_2 \leqslant H_2$ $(l_2 = H'_2/H_2 \leqslant 1)$. As in the preceding section, only the case of a layer in a good solvent will be considered, and it will be assumed as before that the chains of the layer remain extended even under the conditions of deformation. It can be seen from the preceding section that the deformation of a layer of monodisperse chains leads to its compression as a whole: layer concentration increases by a constant value throughout the layer height, equation (29).

It can be seen from the Appendix that this relationship holds for a layer of bidisperse chains:

$$\varphi'(z) = \varphi(z) + \frac{1}{h'_2}\int_{h'_2}^{h_2} \varphi(z)\,\mathrm{d}z \qquad (32)$$

where z is, as before, the coordinate normal to the surface referred to the unperturbed height of the layer of monodisperse chains $(z = x/H_{10})$, $h'_2 = H'_2/H_{10}$ and the values with and without superscripts refer to the deformed and the free layer, respectively. By using for $\varphi(z)$ equations (23) and (29), we obtain:

$$\varphi'(z) = \varphi'_1(z) + \varphi'_2(z)$$

$$= \begin{cases} \varphi_{10}^{(\mathrm{m})}[\tfrac{2}{3}(1/u(h'_2)) + \tfrac{1}{3}u^2(h'_2) - z^2] & z < h'_1 \\ \varphi_{10}^{(\mathrm{m})}[\tfrac{2}{3}(1/u(h'_2)) + \tfrac{1}{3}u^2(h'_2) - u^2(z)] & h'_1 \leqslant z \leqslant h'_2 \end{cases} \qquad (33)$$

where $h'_1 = H'_1/H_{10}$ and H'_1 are the relative and the absolute values of height of a short-chain layer, these values being smaller than the corresponding values for a free layer.

The value of h'_1 is found from the normalization condition:

$$\sigma/a^3 \int_0^{h'_1} \varphi'_1(z)\,\mathrm{d}z = q_1 N_1$$

where the expression for $\varphi'_1(z)$ is given in the Appendix.

Comparison of equations (33) and (29) shows that in the range $0 \leqslant z \leqslant h'_1$ the unit density profile of a layer of bidisperse chains compressed along the height h'_2 coincides with that of a monodisperse layer compressed up to a height $l_{10} = H'_{10}/H_{10} = u(h'_2)$.

The distribution function of short-chain ends in the range of its existence $0 \leqslant z \leqslant h'_1$ also coincides with that of the ends of chains of a monodisperse layer compressed to the value $l_{10} = u(h'_2)$:

$$g'_1(z) = z\left[3[u^2(h'_2) - z^2]^{1/2} + \left(\frac{1}{u(h'_2)} - u^2(h'_2)\right)\frac{1}{[u^2(h'_2) - z^2]^{1/2}}\right] \qquad (34)$$

(cf. equation (30)).

The distribution function of long-chain ends is given by

$$g'_2(z) = \left[3[u^2(h'_2) - u^2(z)]^{1/2} + \left(\frac{1}{u(h'_2)} - u^2(h'_2)\right)\frac{1}{[u^2(h'_2) - u^2(z)]^{1/2}}\right]u(z)\frac{\mathrm{d}u(z)}{\mathrm{d}z} \qquad (35)$$

The free energy of the deformed layer is described by the equations:

$$\Delta F' = \Delta F_{10} \times \tfrac{5}{4}\{-\tfrac{1}{5}[u^5(h'_2) + \alpha(u^2(h'_2) - (h'_2)^2)^{5/2}] + \Lambda^2 u(h'_2) + \alpha(\Lambda - h_2'^2)^2[u^2(h'_2) - (h'_2)^2]^{1/2}\} \qquad (36)$$

where

$$\Lambda = \tfrac{1}{3}[2/u(h'_2) + u^2(h'_2)] \qquad (37)$$

DISCUSSION

Two parts of a layer of bidisperse chains

The above analysis shows that in all the cases considered here, for grafted layers formed by a mixture of chains with degrees of polymerization N_1 and $N_2 > N_1$, two parts of the layer may be distinguished. The inner part is a region in which the ends of all short chains are distributed, whereas all long chains are tie chains. Short chains do not penetrate into the outer part of the layer, in which the ends of long chains are distributed. The structure of the inner part of the layer depends neither on the length nor the content of long chains (at a fixed total grafting density). Its characteristics, i.e. density profile, the mean degree of chain extension in a given layer section and distribution functions of short-chain ends, retain all the relationships obtained for the initial layer of monodisperse chains. In other words, the increase in the length of a part of the chains does not affect the structure of the inner part of the layer for which the chains of increased length are tie chains. This gives a simple relationship for describing the position of the boundary between the inner and the outer parts of the layer:

$$\int_0^{h_1} g_{10}(z)\,\mathrm{d}z = q_1 \qquad (38)$$

At this boundary, all layer characteristics undergo a break. *Figures 2* and *3* show the density profiles and distribution functions of chain ends in three types of layers of bidisperse chains ($T \gg \Theta$, $T = \Theta$ and $\varphi(z) = \mathrm{const}$). In all cases the same layer composition is considered, $q_1 = 0.6$ and $q_2 = 0.4$. With increasing q_2, the boundary between the two regions is displaced to the left according to the law determined by equation (22).

It can be seen from *Figure 3* that distribution functions of long-chain ends in the outer part of the layer are similar to those of ends in a monodisperse layer under the

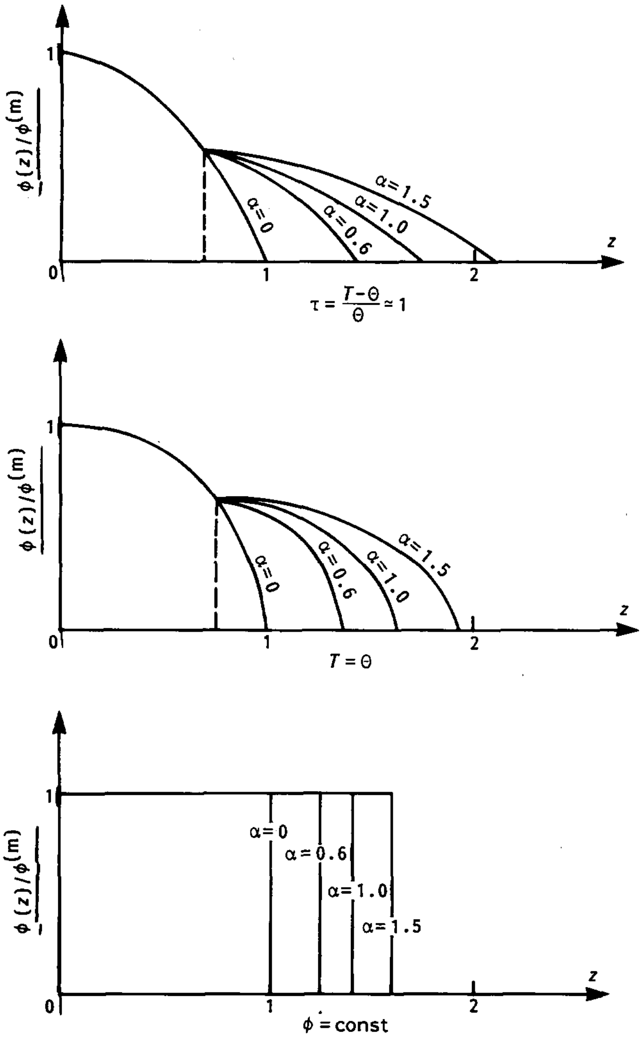

Figure 2 Density profiles of units in a layer of bidisperse chains

corresponding conditions. However, the analytical expressions differ, so that only a similarity but not complete coincidence is meant (see *Figure 4*). This difference is due to the fact that the outer part of the layer, which may be treated as a layer of chains grafted at a density q_2/σ, is a layer of polydisperse chains. With increasing α, the degree of polydispersity of chains of the outer layer decreases, and its characteristics become similar to those of a monodisperse layer of chains of length αN_1.

The conclusion about the maintenance of the structure of the inner part of the layer when part of the chains becomes longer also refers to the case of deformed layers. As already shown, each degree of deformation (compression) of a layer of bidisperse chains may be related to such a degree of deformation of the initial monodisperse layer that the character of deformation of inner regions of these layers becomes completely equivalent. This is shown in *Figure 5*.

Additivity of characteristics of a layer as a whole

In the preceding section, the structure of a layer of bidisperse chains has been considered in detail. Now the overall characteristics of the layer will be considered: the complete layer height H_2 and the free energy of the layer ΔF. As has been shown in equations (27) and (28), these characteristics are the sum of two terms. Applying equations (18) and (20) they may be written in the form:

$$H_2 = H_0(N_1, \sigma) + H_0(N_2 - N_1, \sigma/q_2) \qquad (39)$$

$$\Delta F = \Delta F_0(N_1, \sigma) + \Delta F_0(N_2 - N_1, \sigma/q_2) \qquad (40)$$

where each addend corresponds to the characteristics of layers of monodisperse chains (subscript '0'), the first addend corresponding to a layer of chains of length N_1 with an area per chain σ and the second addend to a layer of chains of length $N_2 - N_1$ with a larger area σ/q_2.

This property of overall characteristics of layers of bidisperse chains reflects the general property of additivity of these characteristics. In fact, for a layer of monodisperse chains, its height and free energy are proportional to chain length N. This relationship valid at any layer structure leads to equality of the layer height and free energy to the sum of the corresponding characteristics of sublayers formed by cutting the chains into parts ($N = \sum_i n_i$) and forming new layers by each part:

$$H_0(N, \sigma) = Na\left(K_H \frac{\sigma}{a^2}\right)^{-\beta_H} = \sum_i n_i a\left(K_H \frac{\sigma}{a^2}\right)^{-\beta_H} = \sum_i h_i(n_i, \sigma) \qquad (41)$$

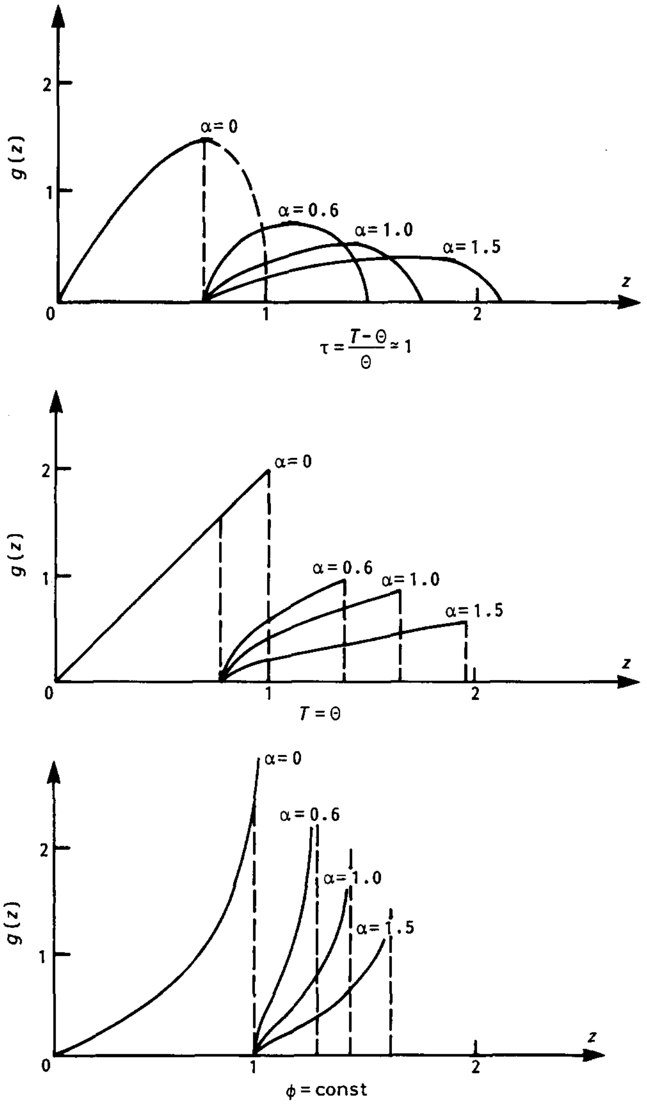

Figure 3 Distribution function of ends of short and long chains in a layer of bidisperse chains

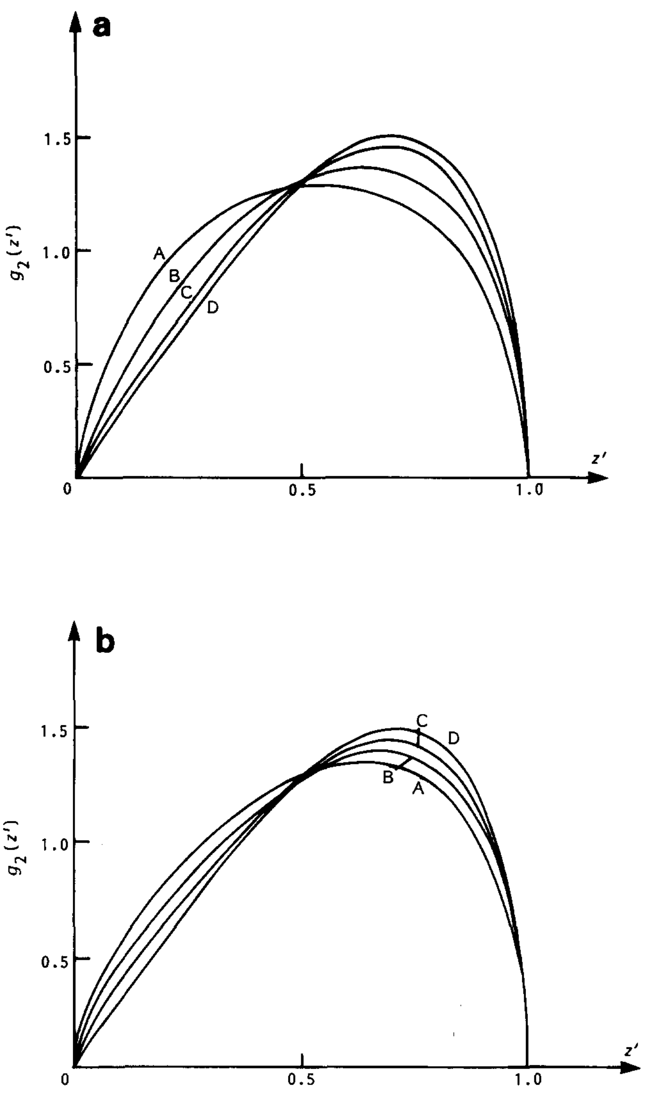

Figure 4 Distribution functions of the ends of long chains under the conditions of good solvent for the following values of the parameters: (a) $q_2=0.4$, $\alpha=0.6$ (A), 1.5 (B), 9.0 (C), ∞ (D); and (b) $\alpha=1$, $q_2=0.80$ (A), 0.95 (B), 0.99 (C), 1.00 (D)

$$\Delta F(N,\sigma)=\sum_i \Delta F(n_i,\sigma) \tag{42}$$

Figure 6 shows the density profile of the initial layer and the density profiles of successive sublayers of the same total height and with the same free energy. Note that the additivity of characteristics follows precisely from their proportionality N and, hence, is obeyed in terms of the order of N. The next terms that are not considered in this approximation (e.g. the term of the order of N^0 related to the loss in free energy of chain parts near the matrix) are not additive.

Equations (39) and (40) are a direct extension of the additivity property to the case of layers of chains of any polydispersity. Thus, for layers formed by a mixture of chains of lengths $N_1, N_2, \ldots, N_m$ in the ratio $q_1, q_2, \ldots, q_m$ at an average grafting density $1/\sigma$ per chain, we have:

$$H=a\sum_{i=1}^{m}(N_i-N_{i-1})\left(\sum_{k=i}^{m}q_k\right)^{\beta_H}\left(K_H\frac{\sigma}{a^2}\right)^{-\beta_H} \tag{43}$$

$$\Delta F=\sum_{i=1}^{m}(N_i-N_{i-1})\left(\sum_{k=i}^{m}q_k\right)^{\beta_F}\left(K_F\frac{\sigma}{a^2}\right)^{-\beta_F} \tag{44}$$

where $\sum_{i=1}^{m} q_i=1$. On passing to a continuous distribution $q(n)$ we have:

$$H=a\left(K_H\frac{\sigma}{a^2}\right)^{-\beta_H}\left[\int_{N_{\min}}^{N_{\max}}\mathrm{d}N\left(\int_N^{N_{\max}}q(n)\,\mathrm{d}n\right)^{\beta_H}+N_{\min}\right] \tag{45}$$

$$\Delta F=\left(K_F\frac{\sigma}{a^2}\right)^{-\beta_F}\left[\int_{N_{\min}}^{N_{\max}}\mathrm{d}N\left(\int_N^{N_{\max}}q(n)\,\mathrm{d}n\right)^{\beta_F}+N_{\min}\right] \tag{46}$$

where the constants K and exponents β are presented in *Table 1* and $\int_{N_{\min}}^{N_{\max}} q(n)\,\mathrm{d}n=1$. For the special cases of the athermal solvent ($\beta_H=1$, $\beta_F=5/3$) and the melt ($\beta_H=1/3$, $\beta_F=3$) the relationships (45) and (46) coincide with similar relationships of ref. 28. Note that an interesting sequence of equations (45) and (46) is the fact that the characteristics of the layer are not simple functions of the usual M_w/M_n ratio but, rather, depend on the entire structure of the distribution function $q(n)$.

Thermodynamic advantage of chain polydispersity in layers

A chain layer is, in a certain sense, a structurized system. Hence, it may seem at first sight that the most

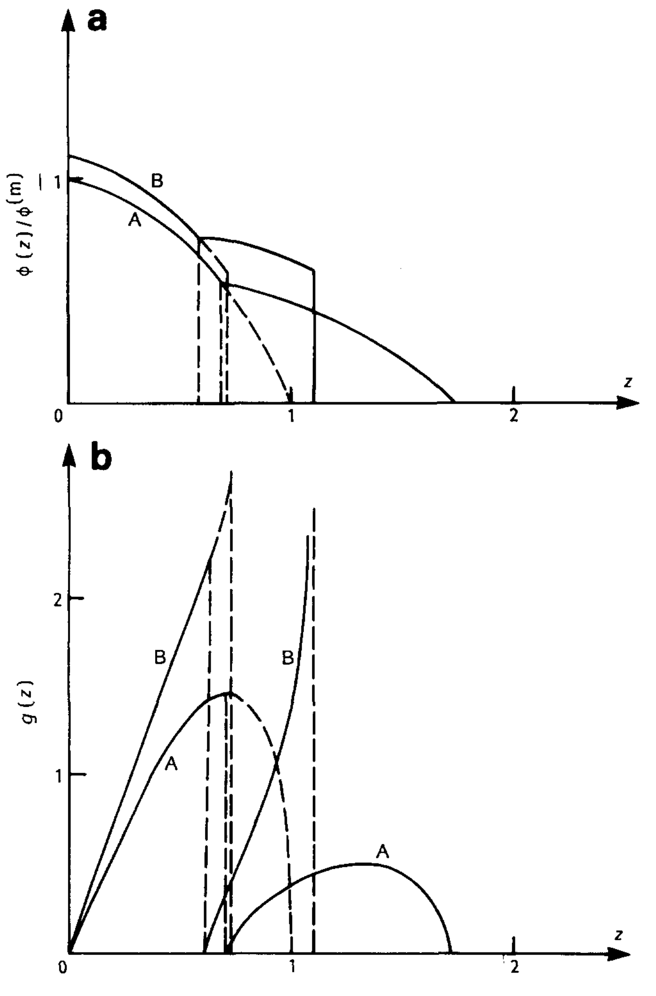

Figure 5 (a) Density profiles of units in (A) a free and (B) a compressed layer of bidisperse chains in a good solvent, $\alpha=1$. Broken curves show the density profiles of a free and a compressed monolayer in a good solvent. (b) Distribution functions of ends of short and long chains in (A) a free and (B) a compressed layer of bidisperse chains in a good solvent, $\alpha=1$. Broken curves show the distribution functions of chain ends in a free and a compressed monolayer in a good solvent

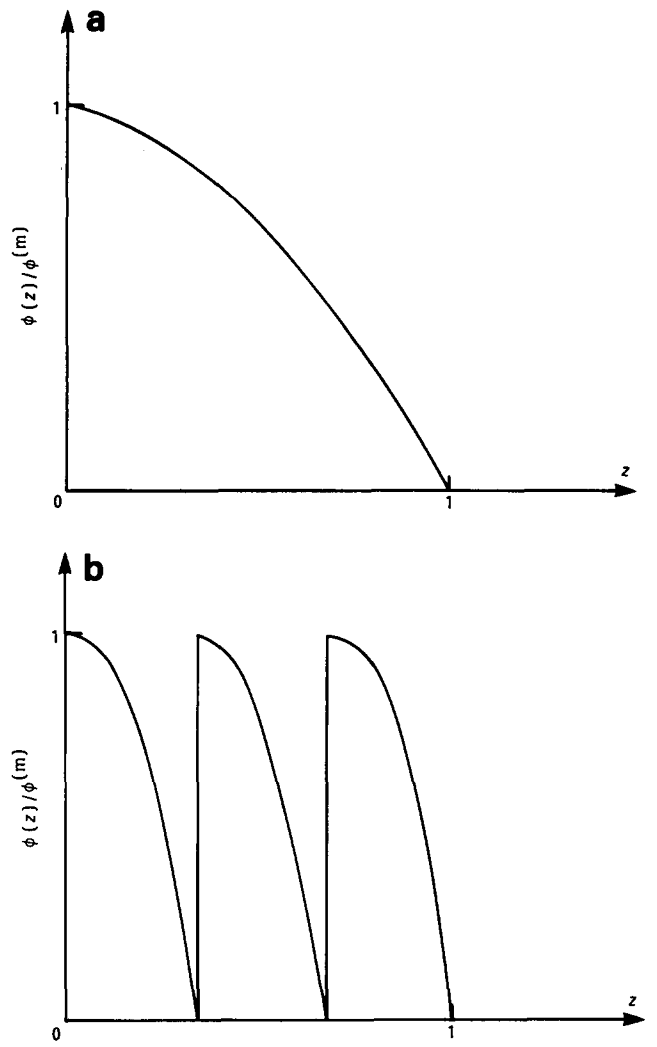

Figure 6 (a) Density profile of the initial monolayer. (b) Density profiles of sequences of sublayers

stable system is that in the case of monodisperse chains. However, it follows from the results that, in contrast, it is a mixture of chains of different lengths in layers that is the most thermodynamically stable system. Moreover, this advantage is in no way related to the small (for polymers) contribution of trivial translational entropy of mixing.

For the sake of simplicity, the free energies of a layer formed by a mixture of bidisperse chains and those of layers of monodisperse chains formed in the case of segregation of chains of different lengths will be compared (*Figure 7*). The free energy of a bidisperse layer (per unit area) is determined by equation (28), where the values of $\beta_F = 1/\nu > 1$ are given in *Table 1*, and ΔF_{10} is determined from equation (20). (It should be borne in mind that this dependence is plotted from equation (1) and does not contain the small contribution of the translational entropy of chain mixing independent of N.) For the free energy of the layer per unit surface, in the case of the segregation of chains of different lengths, we have:

$$\Delta F_s = \frac{a^2}{\sigma}\left[N_1\left(K_F\frac{\sigma_1}{a^2}\right)^{-\beta_F}\frac{\sigma_1}{a^2}q_1 + N_2\left(K_F\frac{\sigma_2}{a^2}\right)^{-\beta_F}\frac{\sigma_2}{a^2}q_2\right] \tag{47}$$

where σ_1 and σ_2 are the grafting areas per chain in segregated layers consisting of chains of lengths N_1 and N_2. In ref. 28, comparison of equations (28) and (47) was carried out under the condition $\sigma_1 = \sigma_2 = \sigma$. It has been shown for this case that $\Delta F_s > \Delta F_0$. The expression ΔF_s in equation (47) may be additionally minimized under the condition of fixation of only the mean areas per chain:

$$\sigma = q_1\sigma_1 + q_2\sigma_2 \tag{48}$$

The minimization of ΔF_s (equation (47)) for σ_1 and σ_2 with the application of equation (48) gives:

$$\begin{aligned} \sigma_1 &= \sigma\frac{1}{q_1 + q_2(1+\alpha)\nu} \\ \sigma_2 &= \sigma\frac{(1+\alpha)^\nu}{q_1 + q_2(1+\alpha)\nu} \end{aligned} \tag{49}$$

and

$$\Delta F_s = \Delta F_{10}[q_1 + q_2(1+\alpha)^\nu]^{1/\nu} \tag{50}$$

so that $\Delta F_s - \Delta F > 0$, which shows the thermodynamic advantage of mixing at any chain length and mixture composition (see also ref. 28).

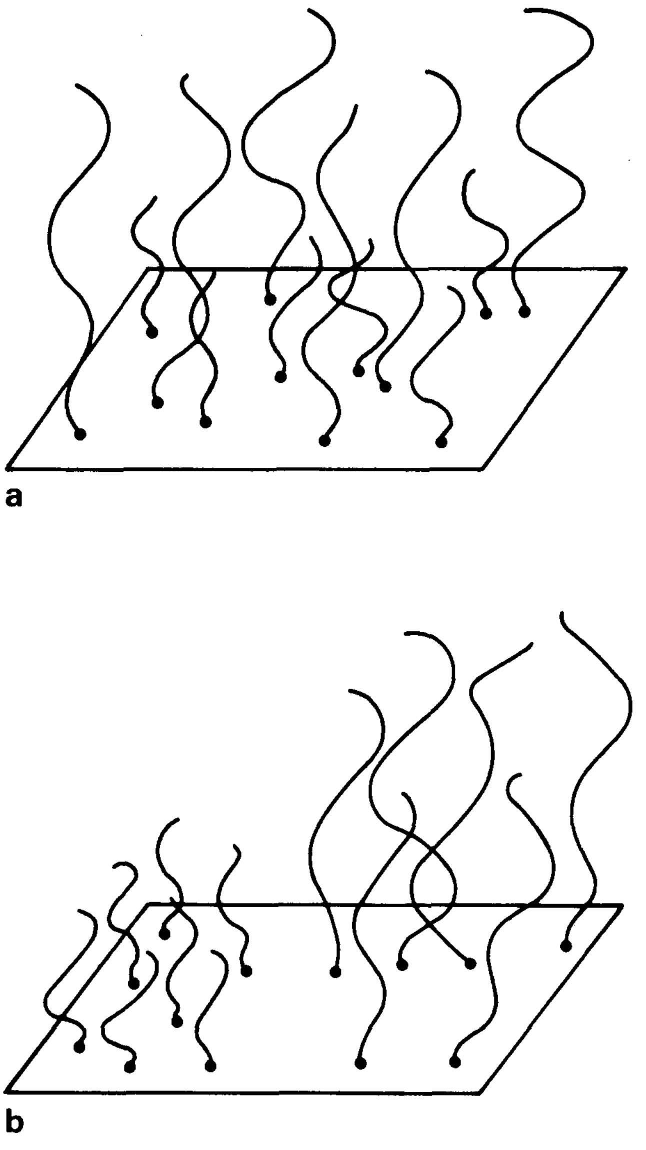

Figure 7 Two possible states of a planar layer: (a) layer with mixed short and long chains and (b) layer with segregated short and long chains

The origin of this effect is fairly clear. In segregation, both long and short chains should be relatively densely grafted onto the matrix. In a mixed layer, this density exists only in the inner part of the layer, whereas in its outer part the mean grafting density per chain is not σ but σ/q_2. Hence, the free energy of outer parts of long chains decreases considerably. Moreover, in all cases elastic contributions to ΔF decrease, and for layers in a good or a Θ solvent, the contributions of volume interactions also decrease.

Degree of segregation of chain ends

The theory of a layer of bidisperse chains developed in the present paper is based on the concept of the segregation of ends of short and long chains. The free ends of shorter chains are concentrated in the inner part of the layer adjoining the grafting plane, whereas those of longer chains are located in the outer peripheral part of the layer. This situation corresponds to the minimum of free energy (equation (1)), i.e. to the most probable state of the system. Thermal fluctuations in the system will lead to deviations from the most probable state leading, in particular, to partial mixing of ends of short and long chains. It is clear that the concept of segregation of ends is valid only when the width of the region of fluctuation mixing of ends is much smaller than the characteristic size of the layer of bidisperse chains. Let us evaluate the width of this region located near the boundary of the inner part of the layer of height H_1 containing short chains.

As already mentioned, this problem is completely equivalent to that of the determination of the width of the mixing region of ends of opposite monodisperse grafted layers considered in ref. 10. According to ref. 10, the molecular field $U(x)=\delta f(x)/\delta\varphi(x)$ will be considered. Here $f(x)$ is the density of free energy of volume interactions (see 'Theory' section) affecting the chain units. Applying the results in the Appendix we obtain:

$$U(x)=\begin{cases}\text{const}-\dfrac{3\pi^2}{8a^2pN_1^2}\,x^2, & x<H_1\\[2ex] \text{const}-\dfrac{3\pi^2}{8a^2pN_1^2}\,u^2(x), & x>H_1\end{cases} \tag{51}$$

We will find the increase in the free energy δF_1 of a short chain (in the 'outer' molecular field) when its free end arrives at a point $x'=H_1+\Delta x$. If δn is the number of units in the end part located in the range Δx, then:

$$\delta F_1 \simeq \delta n\,\Delta U \tag{52}$$

where ΔU is the characteristic value of the excessive field:

$$\Delta U(x)=\frac{3\pi^2}{8a^2pN_1^2}\left[u^2(x)-x^2\right]$$

in the scale Δx. Taking into account equations (51) and assuming that $\Delta x/H_1 \ll 1$ we obtain:

$$\Delta U \simeq \frac{H_1\,\Delta x}{N_1^2pa^2} \tag{53}$$

Since on small scales the parts of grafted chains are not stretched, the relationship between δn and Δx is determined by Gaussian statistics:

$$\Delta x^2 = pa^2\,\delta n \tag{54}$$

and from the evident condition $\delta F_1 \simeq 1$ we find the characteristic width of the region of fluctuation mixing of free ends of short and long chains:

$$\Delta x \simeq R_{\mathrm{G}1}\left(\frac{R_{\mathrm{G}1}}{H_1}\right)^{1/3} \tag{55}$$

Here $R_{\mathrm{G}1}=ap^{1/2}N_1^{1/2}$ is the Gaussian dimension of a short chain, and numerical coefficients of the order of unity have been omitted in the derivation of equation (55) for the sake of simplicity.

Hence, the condition of segregation of free ends of short and long chains is valid if two inequalities are simultaneously fulfilled:

$$\Delta x \ll H_1, \qquad \Delta x \ll H_2 - H_1 \tag{56}$$

where the dependence of H_1 on the mixture composition is determined by equation (55). It can be easily shown by using equation (55) that the stretching of short chains with respect to the Gaussian size, $R_{\mathrm{G}}/H_1 \ll 1$, ensures the fulfilment of the first inequality (56):

$$\frac{\Delta x}{H_1} \simeq \left(\frac{R_{\mathrm{G}}}{H_1}\right)^{4/3} \ll 1$$

In conclusion of this section it will be mentioned that, as can be seen from equation (55), the width of the range of overlapping of Δx is of the order of magnitude $\Delta x \sim N_1^{1/6}$, whereas the height of the inner part of the layer is $H_1 \sim N_1$. Hence, the picture of non-overlapping distribution functions of chain ends is valid in terms $\sim N$. The theory developed here and based on the assumption of chain-end segregation gives a slightly excessive value of the complete free energy of the system, however not in the main terms proportional to N. If the effect of mixing of chain ends is taken into account with the fulfilment of conditions (56), this cannot affect the main conclusions of the paper, in particular, the conclusion of the thermodynamic advantage of mixing of chains of different lengths in the layers.

CONCLUSIONS

In the present paper, the mean-field theory describing the detailed structure and properties of planar grafted layers formed by the chains of two molecular weights N_1 and N_2 is developed. Several conclusions on the structure and properties of grafted layers with arbitrary character of polydispersity of molecular weight were also drawn.

As already mentioned in the 'Introduction', the analysis of the conformational properties of grafted layers is the basis for considering a wide range of structural problems in solutions and melts of block copolymers. The aim of the papers in this series is the investigation of equilibrium characteristics of supermolecular structures formed in mixtures of block copolymers of different molecular weights, compositions and block number in both the presence and the absence of solvent. This consideration will be based on the concepts and results obtained in the present paper. In the next paper in this series, the simplest case of a mixture of diblock copolymers of different molecular weights and compositions forming a lamellar mesophase will be considered. In the following papers, the structure of lamellar mesophases formed by triblock copolymers of the ABA type and by mixtures of di- and triblock copolymers will be investigated and, subsequently, supermolecular structures of other morphologies (cylinders and spheres) and transitions between them will be analysed.

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APPENDIX 1

Minimization of the free-energy functional

The problem of finding a conventional extremum of the functional (1)–(8) with additional conditions (9)–(10) reduces to solving Euler's equations:

$$\frac{3}{2pa^2}\,g_i(x')-\frac{\lambda_i(x')}{E_i^2(x,x')}-[\mu(\varphi(x))+\lambda_{2+i}]\,\frac{g_i(x')}{E_i^2(x,x')}=0 \tag{A1.1}$$

$$\int_0^{x'}\mathrm{d}x\left\{E_i(x,x')+\frac{2pa^2}{3}\,\frac{1}{E_i(x,x')}\,[\mu(\varphi(x))+\lambda_{2+i}]\right\}=0 \tag{A1.2}$$

where

$$\mu(\varphi(x))=\frac{\delta f}{\delta\varphi(x)}=2v\varphi(x)+3w\varphi^2(x) \tag{A1.3}$$

is the chemical potential and $\lambda_i(x')$, λ_{2+i} $(i=1,2)$ are indefinite Lagrangian multipliers. Introducing the designations:

$$\frac{2pa^2}{3}\,\frac{\lambda_i(x')}{g_i(x')}\equiv\psi_1^{(i)}(x'),$$
$$\frac{2pa^2}{3}\,[\mu(\varphi(x))+\lambda_{2+i}]\equiv-\psi_2^{(i)}(x) \tag{A1.4}$$

it is possible to rewrite equations (A1.1) in the form:

$$E_i(x,x')=[\psi_1^{(i)}(x')-\psi_2^{(i)}(x)]^{1/2} \tag{A1.5}$$

Since the chain is not extended at the free end ($E_i(x,x')=0$, $i=1,2$), it follows that $\psi_1^{(i)}=\psi_2^{(i)}=\psi^{(i)}$ and the functions $E_i(x,x')$ should be given by:

$$E_i(x,x')=[\psi^{(i)}(x')-\psi^{(i)}(x)]^{1/2} \tag{A1.6}$$

The substitution of equation (A1.6) into equation (9), $i=1$, gives an integral equation for the function $\psi^{(1)}(x)$. The solution of this equation is given by:

$$\psi^{(1)}(x)=\frac{\pi^2}{4N_1^2}\,x^2 \tag{A1.7}$$

The substitution of this equation into equation (A1.6) gives:

$$E_1(x,x')=\frac{\pi}{2N_1}\,(x'^2-x^2)^{1/2} \tag{A1.8}$$

Further calculations depend on whether the case of a good or a Θ solvent is considered, i.e. on whether only the first (at $v\gg w\varphi>0$) or the second (at $v\sim\tau\ll w\varphi$) term is retained in equation (A1.3) for the chemical potential. Let us deal in greater detail with all calculations for the case of a good solvent.

The density profile of units in a layer $\varphi(x)$ may be found from equation (A1.4), $i=1$, taking into account equation (A1.7):

$$\varphi(x)=-\frac{3\pi^2}{16vpa^2N_1^2}\,x^2+\Lambda_1,\qquad x<H_1 \tag{A1.9}$$

where

$$\Lambda_1=-\lambda_3/(2v)$$

Now the substitution of equation (A1.9) for $\varphi(x)$ into equation (A1.4), $i=2$, gives the type of function $\psi^{(2)}(x)$ at $x<H_1$:

$$\psi^{(2)}(x)=\frac{\pi^2}{4N_1^2}\,x^2\times\Lambda_3,\qquad x<H_1 \tag{A1.10}$$

where

$$\Lambda_3=\tfrac{2}{3}pa^2(\lambda_3-\lambda_4)$$

The substitution of equations (A1.6) and (A1.10) into equation (9), $i=2$, gives an integral equation for the function $\psi^{(2)}(x)$ at $x>H_1$. The solution of this equation is given by:

$$\begin{aligned}\psi^{(2)}(x)&=\frac{\pi^2}{4N_1^2}\,\frac{1}{(1-\alpha^2)^2}\,\{x-\alpha[x^2-(1-\alpha^2)H_1^2]^{1/2}\}^2\\&=\frac{\pi^2}{4N_1^2}\,u^2(x),\qquad x>H_1\end{aligned} \tag{A1.11}$$

The final expressions for the function $E_2(x,x')$ and $\varphi(x)$ with the aid of the known function $u(x)$ are written in the following form:

$$E_2(x,x')=\frac{\pi}{2N_1}\begin{cases}[u^2(x')-x^2]^{1/2}, & x<H_1\\ [u^2(x')-u^2(x)]^{1/2}, & x>H_1\end{cases}\tag{A1.12}$$

$$\varphi(x)=-\frac{3\pi^2}{16va^2pN_1^2}u^2(x)+\Lambda_2,\qquad x>H_1\tag{A1.13}$$

where

$$\Lambda_2=-\lambda_4/(2v)$$

Equations (A1.8) and (A1.12) taking into account expressions (A1.4), (A1.7) and (A1.11) also satisfy equations (A1.2).

The condition of continuity of $\varphi(x)$ at the point H_1 and equation (A1.11) yield the equality $\Lambda_1=\Lambda_2$, and equations (A1.9) and (A1.13) rearrange to give:

$$\varphi(x)=\frac{3\pi^2}{16vpa^2N_1^2}\begin{cases}\Lambda-x^2, & x<H_1\\ \Lambda-u^2(x), & x>H_1\end{cases}\tag{A1.14}$$

The constant Λ in equation (A1.14) may be found from the fact that $\varphi(x)$ becomes zero at the end of the layer, i.e. $\varphi(x=H_2)=0$, and the expression for $\varphi(x)$ becomes:

$$\varphi(z)=\begin{cases}\varphi_{10}^{(m)}(1-z^2), & z<h_1=H_1/H_{10}\\ \varphi_{10}^{(m)}[1-u^2(z)], & z>h_1\end{cases}\tag{A1.15}$$

where $z=x/H_{10}$ is the coordinate normal to the surface referred to the limiting value of the monodisperse layer.

Taking into account that at $x>H_1$ we have $\varphi(x)=\varphi_2(x)$ the expressions (A1.15) and (A1.12) for functions $\varphi(x)$ and $E_2(x,x')$ will be substituted into equation (5), $x>H_1$, and an integral equation for the function $g_2(x')$ will be obtained.

The solution of this equation is given by:

$$g_2(z)=3[1-u^2(z)]^{1/2}u(z)\frac{\mathrm{d}u(z)}{\mathrm{d}z}\tag{A1.16}$$

Substitution of this equation into equation (5), $x<H_1$, and the application of equation (A1.12) to the function $E_2(x,x')$ give the form of the density profile of short and long chains. In the coordinates $z=x/H_{10}$ these functions have the following form:

$$\varphi_1(z)=\varphi_{10}^{(m)}\frac{2}{\pi}\left[(h_1^2-z^2)^{1/2}(1-h_1^2)^{1/2}+(1-z^2)\arctan\left(\frac{h_1^2-z^2}{1-h_1^2}\right)^{1/2}\right],\qquad z>h_1\tag{A1.17}$$

$$\varphi_2(z)=\begin{cases}\varphi(z)-\varphi_1(z), & z<h_1\\ \varphi(z), & z>h_1\end{cases}\tag{A1.18}$$

where $\varphi_{10}^{(m)}$ is the maximum concentration of units in a monolayer described by equation (19).

In order to calculate distribution functions of short-chain ends $g_1(z')$, it is possible to use equation (4), substituting into it equations (A1.8) and (A.17) for $E_1(x,x')$ and $\varphi_1(x)$ and regarding it as an integral equation for $g_1(x')$.

The solution of this equation is given by:

$$g_1(z)=3z(1-z^2)^{1/2}=g_{10}(z)\tag{A1.19}$$

where $z=x/H_{10}$; $g_{10}(z)$ is the distribution function of chain ends in a monolayer.

Two conditions will be used for the determination of the values of $h_1=H_1/H_{10}$ and $h_2=H_2/H_{10}$ (and, hence, for the total layer height H_2 and the height of a short-chain layer H_1): equation (10) and the condition of normalization of the function $g_2(z)$ (equation (7)). The final expressions have the following form:

$$h_1=H_1/H_{10}=(1-q_2^{2/3})^{1/2}\tag{A1.20}$$

$$h_2=H_2/H_{10}=1+\alpha q_2^{1/3}\tag{A1.21}$$

where q_2 is the fraction of long chains, $\alpha=(N_2-N_1)/N_1$, H_1 is the height of a short-chain layer, H_2 is the total height of a bidisperse layer and H_{10} is the height of a monodisperse layer.

The free energy of the bidisperse layer (per unit area) may be found from equation (1) and is given by:

$$\Delta F=\Delta F_{10}(1+q_2^{5/3})\tag{A1.22}$$

where ΔF_{10} is the free energy of the monodisperse layer.

In the case of a Θ solvent with $\mu(\varphi(x))=3w\varphi^2(x)$ all calculations are completely analogous to those reported above. In addition to the results presented in the text, only the density profiles of units of short and long chains will be given:

$$\varphi_1(z)=\varphi_{10}^{(m)}(h_1^2-z^2)^{1/2},\qquad z<h_1\tag{A1.23}$$

$$\varphi_2(z)=\begin{cases}\varphi(z)-\varphi_1(z), & z<h_1\\ \varphi(z), & z>h_1\end{cases}\tag{A1.24}$$

In the case of layers that do not contain the solvent ($\varphi=\text{const}$), the value of ΔF_{conc} in equation (1) becomes a constant and does not affect the result of minimization of ΔF. However, additional condition (11) is used.

The main results obtained in this case are presented in the text. Here only the density profiles of units of short and long chains will be reported:

$$\varphi_2(z)=\frac{1}{2}+\frac{1}{\pi}\arcsin\left(\frac{1-2h_1^2+z^2}{1-z^2}\right),\qquad z<h_1\tag{A1.25}$$

$$\varphi_1(z)=\varphi(z)-\varphi_2(z),\qquad z<h_1\tag{A1.26}$$

APPENDIX 2

Structure of a deformed bidisperse layer

In this Appendix, the deformation of a planar layer consisting of chains of two lengths, N_1 and $N_2=N_1(1+\alpha)$, and immersed in a good solvent will be considered in detail. This deformation reduces to layer compression to a certain height $H'_2<H_2$. The general formalism for a deformed polydisperse layer was considered in ref. 28.

In this case equations (1)–(8) for the free energy with additional conditions (9) and (10) remain valid, and the structure of Euler's equations does not change. Hence, the expressions for the functions of local stretching $E_1(x,x')$ and $E_2(x,x')$, (A1.8) and (A1.12), and equation (A1.14) for unit density profile in a layer obtained in Appendix 1 also remain valid.

As before, equations (4) and (5) in combination with equations (A1.8) and (A1.12) for the functions $E_1(x,x')$ and $E_2(x,x')$ make it possible to find the unknown characteristics of the compressed layer, which in the relative coordinates $z=x/H_{10}$ are given by the following.

Distribution function of long-chain ends:

$$g_2(z)=\left(3[u^2(h'_2)-u^2(z)]^{1/2}+\frac{\frac{3}{2}[\Lambda-u^2(h'_2)]}{[u^2(h'_2)-u^2(z)]^{1/2}}\right)u(z)\frac{\mathrm{d}u(z)}{\mathrm{d}z}\tag{A2.1}$$

Density profile of long- and short-chain units:

$$\varphi_2(z)=\varphi(z)-\varphi_1(z), \qquad z<h'_1 \tag{A2.2}$$

$$\varphi_1(z)=\varphi_{10}^{(\mathrm{m})}\frac{2}{\pi}\left[\left\{(h_1'^2-z^2)[u^2(h'_2)-h_1'^2]\right\}^{1/2} + (\Lambda-z^2)\arctan\left(\frac{h_1'^2-z^2}{u^2(h'_2)-h_1'^2}\right)^{1/2}\right] \tag{A2.3}$$

Distribution function of short-chain ends:

$$g_1(z)=z\left(3[u^2(h'_2)-z^2]^{1/2}+\frac{\frac{3}{2}[\Lambda-u^2(h'_2)]}{[u^2(h'_2)-z^2]^{1/2}}\right) \tag{A2.4}$$

where $\varphi_{10}^{(\mathrm{m})}$ is the maximum concentration of units of the unperturbed monodisperse layer.

The unknown values $h'_1=H'_1/H_{10}$ and Λ may be found by using equations (7) and (10). Bearing in mind equation (25) for $u(z)$ we obtain the equation for the value of Λ:

$$\Lambda=\tfrac{1}{3}[2/u(h'_2)+u^2(h'_2)] \tag{A2.5}$$

and the equation with respect to the value of ξ that will be determined as follows $\xi=[h_2'^2-(1-\alpha^2)h_1'^2]^{1/2}$, where $h'_2=H'_2/H_{10}$ is the given height of the bidisperse layer and $h'_1=H'_1/H_{10}$ is the unknown height of a short-chain layer referred to the unperturbed height of the monodisperse layer:

$$(\alpha\xi-h'_2)(h_2'^2-\xi^2)(\xi-\alpha h'_2) = (1-\alpha^2)^2[(\alpha+q_2)h'_2+(1+\alpha q_2)\xi] \tag{A2.6}$$

Solving equation (A2.6) numerically for the variable ξ, it is possible to find the value of h'_1 for any given values of α, q_2 and h'_2.

The free energy of a bidisperse layer compressed to the height H'_2 is written with the aid of the values of Λ and $u(h'_2)$ determined by equations (A2.5) and (25) and is given by:

$$\Delta F=\Delta F_{10}\times\tfrac{5}{4}\{-\tfrac{1}{5}[u^5(h'_2)+\alpha(u^2(h'_2)-h_2'^2)^{5/2}] + \Lambda^2u(h'_2)+\alpha(\Lambda-h_2'^2)^2[u^2(h'_2)-h_2'^2]^{1/2}\} \tag{A2.7}$$

where ΔF_{10} is the free energy of an unperturbed monodisperse layer.