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Polymer Science U.S.S.R. Vol. 31, No. 1, pp. 205-216, 1989
Printed in Poland

0032-3950/89 \$10.00+.00
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STRUCTURE AND CONFORMATIONAL TRANSITIONS IN GRAFTED POLYMER CHAIN LAYERS. A NEW THEORY*

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(Received 17 August 1987)

A theory that has been developed as an average field approximation describes the structure and conformations of chains consisting of long semirigid polymer chains grafted to an impermeable plane surface. The chains are immersed in a solvent and under the dense grafting conditions there is a marked degree of overlapping of individual chains. Analytical expressions have been derived to describe the density profile for units in the layer, the distribution of chain ends along the layer height and the distribution of local elongation in particular chains. The conformational transition due to collapse of the layer when the temperature falls (deterioration of the solvent quality) has been investigated. In contradistinction to a coil-globule transition occurring in an isolated macromolecule the transition studied is not a true thermodynamic phase transition.

AMONG recent achievements in the field of statistical polymer physics is the progress made in describing the structure of semidilute solutions of linear and branched macromolecules, as well as the structure of layers of polymer chains immersed in a solvent

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and grafted at one end to matrices differing morphologically. It was found that a scaling method may be successfully used to describe systems of this type.

Scaling theory with regard to its application to chain layers grafted to an impermeable plane surface was developed in papers [1-5]. In so doing the layer was viewed as a whole and was characterized by the average height \bar{H} of chain ends or by the average concentration of units in the layer. The layer structure and chain conformations in the layer remained broadly speaking, outside the scope of the analysis. In view of this, asymptotic exponential relations linking \bar{H} to layer parameters were derived: the parameters were the degree of polymerization $N \gg 1$ of chains forming the layer, the surface area σ pertaining to a single chain and the relative temperature $\tau = \frac{T - \theta}{T} \geq 0$, characterizing the quality of the solvent and the rigidity of the chains p .

It was found that with a dense degree of grafting resulting in marked overlapping of individual chains there are strong volume interactions in the layer such that the chains are stretched in the direction normal to the matrix to the extent of their contour length ($\bar{H} \sim N$), irrespective of the solvent quality [1-5]. This fact was illustrated by a blob pattern in which the layer was represented by a set of blobs of uniform size $\xi = \xi(\sigma)$ (which is equivalent to an assumption that the layer is a homogeneous one), and each chain in the layer is fully extended in the normal direction by a succession of blobs [6]. Researchers came gradually to the conclusion that this pattern reflects the actual layer structure: there is thus a constant number of units in the layer and all the chains in the layer are uniformly stretched the same way.

However, in recently published theoretical papers [7-9] numerical methods were used by authors for structural analysis of grafted chain layers. It was shown that the number of units in the layer decreases monotonically with the increase in distance from the surface, and moreover the different chains in the layer were stretched unevenly and non-uniformly.

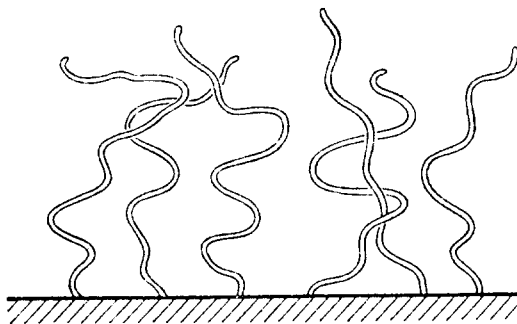


FIG. 1. Layer of polymer chains grafted to a plane surface.

Our aim in the present work was to develop a strictly analytical theory taking account of the concentration distribution of units and chain ends in the layer and providing a basis for a correct description of the structure and conformations of individual chains in the layer, as well as facilitating analysis of structural transitions accompanying a

collapse of the layer when the solvent quality deteriorates. Theoretical analysis of the relevant conformational transitions in systems of this type is essential if one is to determine the flocculation mechanism [10] as well as the temperature-controlled permeability mechanism for membranes modified with a graft copolymer [11], and other factors.

The model and the method used. Let us consider polymer chain layers where the chains with $N \gg 1$ units are grafted at one end to an impermeable plane surface, with a density of $1/\sigma$ such as would ensure a marked overlapping of polymer coils ($\sigma \ll R^2$, where R is the characteristic length of an isolated chain, and σ is the surface area pertaining to a single chain). The chains were immersed in a solvent at temperature T , and $\tau \equiv \frac{T - \theta}{T} \geq 0$ (Fig. 1). The chain unit selected for study was a chain section whose length was equal to the chain thickness a , and the volume of the latter being $V_0 \sim a^3$; the segmental asymmetry $p = l/a \geq 1$, where l is the length of the Kuhn segment ($p = 1$ for a flexible chain and $p > 1$ for a semirigid one; $N/p \gg 1$).

The equilibrium structure of the layer is obtained from the condition for its minimum free energy. The conformational free energy ΔF for chains in a layer of thickness H

$$\Delta F = \Delta F_{el} + \Delta F_{conc} \quad (1)$$

includes the contributions made by elastic stretching of the chains (ΔF_{el}) and by volume interactions (ΔF_{conc}). Calculating for a single chain in the layer we have

$$\Delta F_{conc} = \frac{\sigma}{a^3} \int_0^H f[\varphi(x)] dx, \quad (2)$$

where $f[\varphi]/a^3$ is the free energy density for volume interactions of units in the layer, $\varphi(x)$ is the dimensionless concentration (the volume fraction) of units at a point x (x being the coordinate in the direction that is normal to the surface). Here and later in the paper energy values are all expressed in kT units. To find the elongation entropy ($-\Delta F_{el}$) we use a Gaussian free energy approximation δF_{el} for the local elongation when the ends in a chain section containing δn units is elongated by a distance of δx

$$\delta F_{el} = \frac{3}{1pa^2} \frac{\delta x^2}{\delta n}$$

Changing over now to a continual limit, the elongation free energy for the chain as a whole is expressed in the form of the integral

$$\Delta F_{el}(x') = \frac{3}{2pa^2} \int_0^{x'} E(x, x') dx,$$

where x' is the height of a free chain end over the plane and the function $E(x, x') = dx/dn$ characterizes the local elongation of the chain at a point x . The physical significance

of function $E(x, x')$ is quite simple: it defines the degree of elastic force $f = \frac{3}{pa^2} E(x, x')$ that is acting in an elongated chain at a height of $x \leq x'$.

To allow for the possibility of nonuniform elongation of chains in the layer we introduce a distribution function for free chain ends $g(x')$ according to layer height. Now $g(x')dx'$ is the fraction of chains whose ends are located in a layer of thickness dx' at a height x' from the surface ($\int_0^H g(x') dx' = 1$). To express the entropy contribution to the free energy of the layer, calculating for one chain, we have

$$\Delta F_{el} = \int_0^H \Delta F_{el}(x') g(x') dx' = \frac{3}{2pa^2} \int_0^H g(x') dx' \int_0^{x'} E(x, x') dx \quad (3)$$

Approximation (3) for the elongation entropy was proposed in paper [12] in an analysis of the structure of densely packed domains in block copolymer systems: the approximation assumes that there will be a marked elongation of chains in the direction normal to the surface.

Equilibrium characteristics of the layer are obtainable from the condition of a minimal free energy ΔF defined by equations (1)–(3) as a functional of $E(x, x')$ and $g(x')$ allowing for additional normalization conditions

$$\int_0^{x'} \frac{dx}{E(x, x')} = N \quad (4)$$

$$\frac{\sigma}{a^3} \int_0^H \varphi(x) dx = N, \quad (5)$$

where the dimensionless concentration (volume fraction) of units $\varphi(x)$ is related to functions $E(x, x')$ and $g(x')$ by the formula

$$\varphi(x) = \frac{a^3}{\sigma} \int_x^H \frac{g(x') dx'}{E(x, x')} \quad (6)$$

This variational problem calls for solution of a set of Euler equations for functions $E(x, x')$ and $g(x')$

$$\frac{3}{2pa^2} g(x') - \frac{1}{E^2(x, x')} \{ \mu [\varphi(x)] g(x') - \lambda_1(x') - \lambda_2 g(x') \} = 0 \quad (7)$$

$$\int_0^{x'} dx \left\{ E(x, x') + \frac{2pa^2}{3E(x, x')} (\lambda_2 + \mu [\varphi(x)]) \right\} = 0, \quad (8)$$

where $\mu[\varphi(x)] = \delta f[\varphi]/\delta \varphi(x)$ is the chemical potential, and $\lambda_1(x')$ and λ_2 are indeterminate Lagrangian factors. Introducing the notation

$$\frac{2pa^2}{3}\lambda_1(x')/g(x') \equiv \psi_1(x'), \quad \frac{2pa^2}{3}\{\lambda_2 + \mu[\varphi(x)]\} \equiv -\psi_2(x), \quad (9)$$

equation (7) may now be expressed as $E^2(x, x') = \psi_1(x') - \psi_2(x)$; moreover from the condition of disappearance of local elongation at the free end of the chain we have $\psi_1 = \psi_2 = \psi$. Looking upon relation (4) as an integral equation in relation to an unknown function ψ , we obtain

$$\psi(x) = \frac{\pi^2}{4N^2} x^2 \quad (10)$$

Now the final expression for $E(x, x')$ may be written as

$$E(x, x') = \frac{\pi}{2N} \sqrt{x'^2 - x^2} \quad (11)$$

It is apparent that, allowing for relations (9) and (10), expression (11) satisfies equation (8) as well. This means that each polymer chain in the layer is elongated most of all close to the surface (where $x=0$); as the distance from the surface increases, the local elongation decreases monotonically, becoming zero at the free end of the chain. Let us now consider the universal character of the function $E(x, x')$ for local elongation distribution according to height; it is not a function of the type of free energy density for volume interactions $f[\varphi(x)]$, the explicit form of $E(x, x')$ is determined solely by the Gaussian character of local elongation of the chain.

To determine the density profile for units in the layer $\varphi(x)$ and the distribution function for chain ends according to height $g(x')$ it is necessary that one should know the explicit form of the relation of the chemical potential $\mu(\varphi)$ to the concentration φ . Provided that the degree of grafting is not too dense, ($\sigma/a^2 \gg 1$) we may use a virial expansion for the density of free energy of volume interactions

$$f[\varphi(x)] \simeq v\varphi^2(x) + w\varphi^3(x) + \dots, \quad (12)$$

where $v \sim \tau$ and w are dimensionless second and third virial coefficients for interaction of the units. Now, using equations (9), (10) and (12) we obtain the density profile for units in the layer

$$\varphi(x) = \frac{v}{3w} [\sqrt{1 + \kappa^2(\lambda - x^2)} - 1], \quad (13)$$

where $\lambda = -\lambda_2 \frac{8a^2 N^2 p}{3\pi^2}$ and $\kappa^2 = \frac{9\pi^2 w}{8v^2 a^2 N^2 p}$. The value of the indeterminate multiplier λ included in formula (13) is obtainable from the normalization condition (5); substituting expression (13) into relation (5) we obtain a transcendental equation for λ at

a fixed value of H

$$\frac{Na^3}{\sigma H} = \frac{v}{3w} \left[\frac{1}{2} \sqrt{1 + \kappa^2(\lambda - H^2)} - 1 \right] + \frac{1 + \kappa^2 \lambda}{2\kappa^2} \frac{\pi}{\sqrt{8wp} aNH} \arcsin \sqrt{\frac{\kappa^2 H^2}{1 + \kappa^2 \lambda}} \quad (14)$$

To calculate the $g(x')$ function we use formula (6) as an integral equation in respect to $g(x')$. To solve equation (6) while allowing for expressions (11) and (13) we have

$$g(x') = \frac{x' \sigma}{Na^3 3w} \left\{ \frac{\sqrt{1 + \kappa^2(\lambda - H^2)} - 1}{\sqrt{H^2 - x'^2}} + \frac{\kappa}{2} \left[\frac{\pi}{2} + \arcsin \frac{2H^2 - x'^2 - \kappa^{-2} - \lambda}{\lambda + \kappa^{-2} - x'^2} \right] \right\} \quad (15)$$

Expressions (11) and (13)–(15) were derived from the condition of a free energy minimum for the layer with a fixed H (i.e. for a layer positioned in a slit of width H), and from these expressions we obtain the equilibrium value of the conformational free energy $\Delta F(H)$ for the layer in a slit of a fixed width. The condition $(\partial \Delta F(H) / \partial H)_{H=H_0} = 0$ is equivalent to the condition for disappearance of pressure on the upper plane, and together with equation (14) it determines the equilibrium value H_0 of the free layer height and the corresponding value of the indeterminate multiplier $\lambda = \lambda_0$

$$\lambda_0 = \begin{cases} H_0^2, & v \geq 0 \\ H_0^2 - \frac{2}{3} \frac{v^2}{w} \frac{a^2 N^2 p}{\pi^2}, & v < 0 \end{cases} \quad (16)$$

Substituting into equation (14) we obtain a closed equation giving the free layer height H_0 as a function of its parameters N, σ, v and w , and putting $\lambda = \lambda_0$ and $H = H_0$ in expressions (13) and (15), we obtain the density profile and the distribution function for chain ends in a free layer. It should be noted that, as is evident from relations (13) and (16), when $v \geq 0$, parameter λ_0 may also be determined from the condition $\varphi(x = H_0) = 0$. In other words, according to relations (13) and (16), when $v \geq 0$ the density of units at the end of the layer is continually transformed to zero, and when $v < 0$ there is a jump amounting to the value of $|v|/2w$ in the density of the units.

Let us now consider in some detail how the characteristics of the layer will change with a change in temperature (in the solvent quality).

The layer height. Equations (14), (16) for the full layer height H_0 may conveniently be put in the form of an equation for the swelling coefficient for the layer α in respect to its dimensions at the θ point (when $v = 0$)

$$\alpha \equiv H_0(v) / H_0(v = 0), \quad (17)$$

where

$$H_0(v = 0) = \frac{2}{\pi} (8wp)^{1/4} \left(\frac{\sigma}{a^2} \right)^{-1/2} Na, \quad (18)$$

Introducing two auxiliary dimensionless parameters

$$\beta = vp^{1/4} w^{-3/4} (\sigma/a^2)^{1/2} \quad (19)$$

$$\delta = 3 \times 2^{1/4} \alpha / \beta, \quad (20)$$

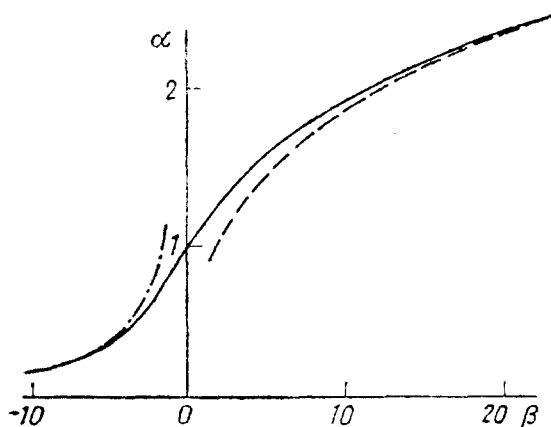


FIG. 2

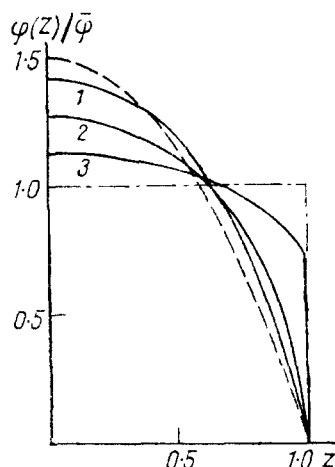


FIG. 3

FIG. 2. Swelling coefficient for layer relative to θ -dimensions α vs. parameter $\beta = vp^{1/4}w^{-3/4}\left(\frac{\sigma}{a^2}\right)^{1/2}$.

Here and in Figs. 3 and 4 explanations are to be found in the text.

FIG. 3. Density profile for units in the layer on the cited coordinates ($\phi/\bar{\phi}$, $z=x/H_0$) for a good solvent $\alpha=1.3$ (1), for a θ -solvent $\alpha=1$ (2) and for a poor solvent $\alpha=0.68$ (3).

we may express equations (14) and (16) in the form

$$\frac{9\pi}{\sqrt{2}} \frac{1}{\beta^2} = \begin{cases} -\delta + (1+\delta^2) \arcsin \sqrt{\frac{\delta^2}{1+\delta^2}}, & \beta \geq 0 \\ -\frac{5}{2}\delta + \left(\frac{1}{4} + \delta^2\right) \arcsin \sqrt{\frac{4\delta^2}{1+4\delta^2}}, & \beta < 0 \end{cases} \quad (21)$$

It can be seen from relations (20) and (21) that the swelling coefficient α is a function solely of parameter $\beta \propto v$, and does not depend on N . This means that the layer height $H_0 \propto N$, irrespective of v . Figure 2 shows the universal dependence of $\alpha(\beta)$ calculated by equation (21). It is seen that a fall in temperature (reduction in β) leads to a monotonic decrease in the layer height. The fractured line and the fractured-dotted one show the high- and low-temperature asymptotes for the $\alpha(\beta)$ function. The asymptotes were obtained from equation (21) with $\beta \rightarrow \pm \infty$

$$\alpha \approx \begin{cases} (\pi/2^{9/4})^{1/3} \beta^{1/3}, & \beta \gg 1 \\ (\pi/2^{3/4}) |\beta|^{-1}, & \beta < 0, |\beta| \gg 1 \end{cases} \quad (22)$$

These correspond to the following asymptotes for the layer height:

$$H_0 \approx \begin{cases} \left(\frac{8}{\pi^2}\right)^{1/3} (vp)^{1/3} \left(\frac{\sigma}{a^2}\right)^{-1/2} Na, & \beta \gg 1 \\ \frac{2w}{|v|} \frac{Na^3}{\sigma}, & \beta < 0, |\beta| \gg 1 \end{cases} \quad (23)$$

The swelling coefficient for the layer α is a universal function of β , so irrespective of N the dependence of α on $v \sim \tau$ will be described by a smooth curve. It follows that the conformational transition due to collapse of the layer when the temperature falls is not a phase transition. It should be noted that in the area where $\beta < 0$ the validity of equations (22), (23) is limited by the condition $\varphi(x) \ll 1$, which allows a virial expansion of (12), as well as by the condition of elongation of the chains relative to the Gaussian dimensions.

The density profile for units in the layer. The density profile for units in a free layer is described by relations (13) and (16). Allowing for calculations of expressions (17)–(20) it may be represented in the form

$$\frac{\varphi(z)}{\bar{\varphi}} = \begin{cases} \frac{4}{\pi} \frac{\alpha^2}{\delta} [\sqrt{1 + \delta^2(1 - z^2)} - 1], & \beta \geq 0 \\ \frac{4}{\pi} \frac{\alpha^2}{|\delta|} \left[\sqrt{\frac{1}{4} + \delta^2(1 - z^2)} + 1 \right], & \beta < 0, \end{cases} \quad (24)$$

where a relative coordinate $z = x/H_0$ has been introduced as well as the mean density of units in the layer $\bar{\varphi} = Na^3/\sigma H_0$. Using the asymptotes of (22) for $\alpha(\beta)$ we readily obtain from expression (24) asymptotic forms for the density profile in the high- and low-temperature regions, and also at the θ -point.

$$\varphi(z) \simeq \begin{cases} \frac{3}{2} \bar{\varphi}_+ (1 - z^2), & \beta \gg 1 \\ \frac{4}{\pi} \bar{\varphi}_\theta (1 - z^2)^{1/2}, & \beta = 0 \\ \bar{\varphi}_-, & \beta < 0, |\beta| \gg 1, \end{cases} \quad \begin{matrix} (25a) \\ (25b) \\ (25c) \end{matrix}$$

where the asymptotic values of the mean density in the layer

$$\begin{aligned} \bar{\varphi}_+ &= \frac{3}{4} \pi^{2/3} (vp)^{-1/3} (\sigma/a^2)^{-2/3} \\ \bar{\varphi}_\theta &= \left(\frac{2}{wp} \right)^{1/4} (\sigma/a^2)^{-1/2} \\ \bar{\varphi}_- &= |v|/2w \end{aligned} \quad (26)$$

Thus it appears that a free plane layer of grafted chains, at any values of $N \gg 1$, is heterogeneous as a whole: using the given coordinates $\left(\frac{\varphi}{\bar{\varphi}}, z = \frac{x}{H} \right)$ the density profile is described by a universal monotonically diminishing function, which depends, apart from z , solely on parameter β . The degree of polymerization N in this case plays the role merely of a scale factor. Figure 3 shows plots of $\varphi/\bar{\varphi}$ vs. z based on equations (21) and (24) for cases of a good solvent ($\alpha = 1.3$, curve 1), a θ -solvent ($\alpha = 1$, curve 2) and a poor solvent ($\alpha = 0.68$, curve 3). The fractured line and the fractured dotted line show the corresponding high- and low-temperature asymptotes (25a) and (25c). It is

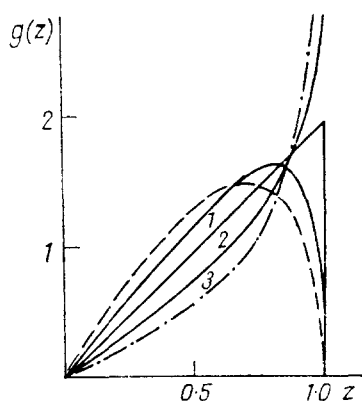


FIG. 4

FIG. 4. Distribution function for chain ends in the layer $g(z)$ (on the cited coordinates) for a good solvent $\alpha=1.3$ (1), a θ -solvent $\alpha=1$ (2), and a poor solvent $\alpha=0.68$ (3).

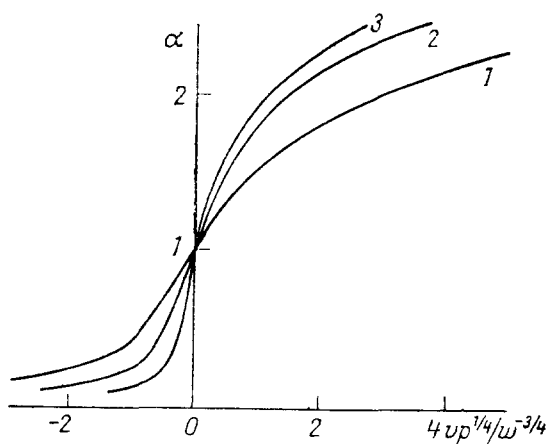


FIG. 5

FIG. 5. Swelling coefficient for the layer relative to θ -dimensions of α vs., $vp^{1/4}w^{-3/4}\tau$ with grafting density $\sigma/a^2=16$ (1), 64 (2) and 100 (3).

evident from Fig. 3 that a temperature fall giving rise to collapse of the layer as a whole is accompanied by a density redistribution for units in the layer.

In the high-temperature region ($\beta \gg 1$) the density profile is parabola-shaped in line with equation (25a). As the temperature falls (as the solvent quality deteriorates), the layer as a whole comes under pressure, and the mean density of the units increases. At the same time there is a preferential compaction of the outer (looser) part of the layer, and the density diminution on its periphery becomes more marked. With $\beta \geq 0$ the density of units at the end of the layer abruptly returns to zero, and the derivative $(\partial\varphi/\partial x)_{x=H_0}$ decreases with decreasing β , and returns to $-\infty$ at the point ($\beta=0$). Below the θ -point (with $\beta < 0$) the density of units at the layer boundary (when $x=H_0$) abruptly returns to zero; moreover the magnitude of the jump in $|v|/2w$ coincides in a volume approximation with the density of an isolated globule [13, 14] (it coincides with the equilibrium density of the precipitated polymer). At the low temperature limit $\beta \rightarrow -\infty$ the density profile tends to the gel-like form shown in Fig. 3 by the fractured-dotted line in accordance with equation (25a).

Distribution of chain ends. The distribution function for free chain ends in the layer may be obtained by substituting equation (16) into formula (15): in the case of the cited variables we have

$$g(z) = \begin{cases} \alpha^2 z \left[1 + \frac{2}{\pi} \arcsin \frac{1-z^2-\delta^2}{1-z^2+\delta^2} \right], & \beta > 0 \\ 2z, & \beta = 0 \\ \alpha^2 z \left[1 + \frac{2}{\pi} \arcsin \frac{4(1-z^2)-\delta^2}{4(1-z^2)+\delta^2} - \frac{6\delta}{\pi\sqrt{1-z^2}} \right], & \beta < 0 \end{cases} \quad (27)$$

Figure 4 shows the $g(z)$ plots calculated by formula (27), the values of β being the same as for the density profiles in Fig. 4. The fractured line and the fractured-dotted line in Fig. 4 show the asymptotic distribution functions $g_{\pm}(z)$ corresponding to the high- and low-temperature limits in formula (27)

$$g(z) \simeq \begin{cases} g_+(z) \equiv 3z\sqrt{1-z^2}, & \beta \gg 1 \\ g_-(z) \equiv z/\sqrt{1-z^2}, & \beta < 0, |\beta| \gg 1 \end{cases} \quad (28)$$

Thus it appears that a fall in temperature (deterioration in the solvent quality) is accompanied by a change in the distribution of chain ends in the layer on account of a preferential decrease in stretching for the most stretched chains.

The investigations carried out in the present instance have enabled us to give a much stricter and more detailed description of the structure of grafted chain layers compared with that achieved in earlier work [1-5]. The method used in the present case is a variant of the mean field approximation which is valid for semirigid chains under conditions where $\frac{v}{\phi p^2} \ll 1$ [15, 16]. Moreover the general pattern of the layer structure and relations between its integral characteristics and the principal parameters ought to hold even where $\frac{v}{\phi p^3} > 1$ (the scaling temperature range) [4].

The most interesting and theoretically significant result of this investigation is the fact that on the basis of strict analytical theory it has been shown that a plane layer formed by however large a number of long chains is invariably heterogeneous as a whole: the density profile of units in the layer is described by a monotonically decreasing function, and the characteristic scale of the density reduction is a function of the total layer height; the chains in the layer are elongated unevenly and to varying extents, and the distribution of chain ends occurs within the limits of the entire layer. Functions describing the density profile and the distribution of chain ends are universal functions into which the degree of polymerization enters merely as a scale factor.

Thus it appears that the layer structure differs markedly from the former blob pattern in which it was assumed that the layer is homogeneous as a whole and that a reduction in the number (and distribution) of chain ends occurs solely in the vicinity of the end of the layer on a scale of the order of ξ which is not a function of N .

These conclusions are fully in agreement with the results of numerical analysis of the structure of grafted chains reported in papers [7-9]. Moreover equations for the density profile $\phi(z)$ and for the distribution of chain ends $g(z)$ derived in [8, 9] for the case of a good solvent are very satisfactorily approximated by expressions (16) and (18).

There is good agreement all the way up to relatively high grafting densities $\frac{a^2}{\sigma} \propto 0.1$ [17].

In addition, all the asymptotic exponential equations for integral characteristics of the layer — the total (or average) height and the average number of units in the layer — agree with expressions previously derived in papers [1-5] on the basis of a simple

scaling analysis. The equation in [14] relating the number of units in the layer to the coordinate is not an exponential one but is of a weaker type, and the layer could be called homogeneous in a scaling approximation. This means that it is justifiable to use the scaling method described in papers [1-5] to analyze the mean (integral) layer characteristics.

In particular the conclusion drawn in paper [5] remains valid, i.e. in regard to the universal character of the equation relation the swelling coefficient of the layer to parameter $\beta = \nu p^{1/4} w^{-3/4} \left(\frac{\sigma}{a^2} \right)^{1/2}$ whereby one may deduce that the transition due to collapse of the layer is of a nonphase nature (the dependence of $\alpha(\tau)$ is described by a smooth curve irrespective of the magnitude of N , and similarly the width of the transition interval $\Delta\tau \sim \left(\frac{a^2}{\sigma} \right)^{1/2} w^{3/4} p^{-1/4}$ corresponding to a variation in α of $\Delta\alpha \sim 1$ is likewise not a function of N , but increases with increasing grafting density (Fig. 5) and increasing chain flexibility). The nonphase character of the transition is due to powerful interchain interactions which in the case of dense grafting and a plane surface make chains in the layer effectively one-dimensional [5]. With a diminution of the grafting density the layer disintegrates into noninteracting grafted chains and the collapse of each of these takes place as a second-order phase transition [13, 14].

It is also clear from the results of this investigation that collapse of the layer as a whole is accompanied by a reorganization of its structure: there is a leveling out (equalization) of the density profile for units within the layer and a more drastic decay of density for those on the boundary of the layer (Fig. 3). This structural reorganization takes place by means of a redistribution of chain ends: there is a preferential decrease in the drawing of those chains whose ends are situated on the periphery of the layer.

The authors wish to thank T. M. Birshtein, A. M. Skvortsov and L. I. Klushin for their discussion of this paper.

Translated by R. J. A. HENDRY

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Polymer Science U.S.S.R. Vol. 31, No. 1, pp. 216-219, 1989
 Printed in Poland

0032-3950/89 \$10.00+ .00
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TRYPSIN MACROMONOMER AND ITS COPOLYMERIZATION WITH HYDROPHILIC MONOMERS*

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Trypsin macromonomer, an enzyme derivative whose molecule contains one C=C bond, has been synthesized. Radical copolymerization of this macromonomer with acrylamide has been investigated and the effective copolymerization constant for acrylamide has been determined. Properties of trypsin-acrylamide copolymers of various compositions and differing MW have been evaluated.

MACROMONOMERS form a new group of polymerizable substances, and whatever the origin (natural or synthetic) of these polymer molecules their composition contains functional groups that enter into polymerization reactions [1, 2]. Among methods used to prepare macromonomers containing physiologically active substances is the process of inserting the unsaturated C=C bond into their macromolecules via reactions of acylation of free amino-groups by chlorides of unsaturated carboxylic acids [3].

Earlier papers of ours [4, 5] show that reactions of radical polymerization of these macromonomers containing physiologically active substances of various types are theo-

* *Vysokomol. soyed.* **A31**: No. 1, 195-197, 1989.