$- 8) + \ldots$ and $B = 2(n-5)(n-6) + 3(n-6)(n-7) + 4(n-7)(n-8) + \ldots$.

Discussion of Equation 1

Let us call $\langle r_{n-2}{}^2\rangle_{\text{bound}}$ the mean end-to-end distance of the population of configurations of chain $n-2$ obtained by removing the two segments of a primary contact of the configurations of the chain n and $\langle r_{n-2}{}^2\rangle_{\text{free}}$ the mean end-to-end distance of the total number C_{n-2} of configurations of the chain $n-2$. When in eq 1 we replace $\langle r_{n-2}{}^2\rangle_{\text{bound}}$ by $\langle r_{n-2}{}^2\rangle_{\text{free}}$ we make a good approximation, which rapidly becomes better as n increases. This allows us to determine rather good values of $\langle r_n{}^2\rangle_0$ since γ is known. These values can be calculated by eq 2 and 3. For numerical application, one has to remember that the terms $n - i$ can never be applied if they are negative. For $i > n$, the term disappears.

In the literature,[4] we can find values of $\langle r_n{}^2\rangle$ obtained by many authors, using exact enumeration. These values, considered as accurate up to $n = 15$, are given in Table I. They have been obtained for simple cubic lattice chains. These values allowed us to test the validity of our relations 2 and 3. The results given by these equations are practically the same as the values of Table I, from $n = 2$ to 15.

We now give some examples of numerical applications of eq 2 and 3: (1) For $n = 2$ (eq 2)

$$E_2{}^0 = \frac{6(n-1)}{5n} - \frac{6}{5}\frac{1}{(n-1)^2}\frac{1}{n} = 0$$

$$\gamma = 0; \qquad \langle r_2{}^2\rangle = \langle r_2{}^2\rangle_0 = 2^0 = 1$$

(2) For $n = 3$ (eq 3)

$$E_3{}^0 = \frac{6(n-1)}{5n} - \frac{1}{4}\frac{1}{n^4} - \frac{1}{25}\frac{1}{n-1}\frac{1}{n^6} = 0.79688615$$

For $n = 3$, there are no configurations presenting first contacts between nearby segments, then $\gamma = 1$ and $\langle r_3{}^2\rangle = \langle r_3{}^2\rangle_0$. (3) For $n = 5$, by eq 3

$$E_5{}^0 = \frac{6(n-1)}{5n} + (n-3)\left[\frac{3}{10n} + \frac{1}{n(n-1)}\right] + \frac{1}{n^3}\left[n + 2 + \frac{1}{n} + \frac{3}{2}\frac{1}{n^2} + \frac{7}{4}\frac{1}{n^3} + \frac{11}{6}\frac{1}{n^4} + \ldots + \frac{35}{18}\frac{1}{n^{10}}\right]^{-1} - \frac{1}{4}\frac{1}{n^4} - \frac{1}{25}\frac{1}{n-1}\frac{1}{n^6} = 1.18069861$$

$$A = 0; \qquad B = 0$$

Then $\langle r_5{}^2\rangle_0 = 5^{1.18069861} = 6.68764045$

$$[N]_5{}^0 = 534 \text{ and } C_5 = 726; \qquad \gamma = 0.73553719$$

Therefore by eq 1

$$\langle r_5{}^2\rangle = \gamma\langle r_5{}^2\rangle_0 + (1-\gamma)\langle r_3{}^2\rangle = 5.55371909$$

For $n = 15$

$$A = (n-4)(n-6) + 2(n-5)(n-7) + 3(n-6)(n-8) + 4(n-7)(n-9) + 5(n-8)(n-10) + 6(n-9)(n-11) + 7(n-10)(n-12) + 8(n-11)(n-13) + 9(n-12)(n-14) = 1.155$$

$$B = 2(n-5)(n-6) + 3(n-6)(n-7) + 4(n-7)(n-8) + 5(n-8)(n-9) + 6(n-9)(n-10) + 7(n-10)(n-11) + 8(n-11)(n-12) + 9(n-12)(n-13) + 10(n-13)(n-14) = 1.320$$

$$E_{15}{}^0 = \frac{6(n-1)}{5n} + (n-3)\Bigg[\frac{3}{10n} + \Bigg[1/[(n-1) + (n-7) + (n-13)]\Bigg[n + A\left\{\frac{1}{n} + \frac{1}{n^3} + \frac{1}{n^5} + \frac{1}{n^7}\right\}\Bigg]\Bigg]\Bigg] + \Bigg\{\Bigg[(n-4)\frac{1}{n^3} + (n-8)\frac{1}{n^5} + (n-12)\frac{1}{n^7}\Bigg]\Big/\Bigg[n + 2 + \frac{1}{n} + \frac{3}{2}\frac{1}{n^2} + \frac{7}{4}\frac{1}{n^3} + \frac{11}{6}\frac{1}{n^4} + \frac{15}{8}\frac{1}{n^5} + \frac{19}{10}\frac{1}{n^6}\Bigg]\Bigg\} - \frac{1}{4}\frac{1}{n^4} - \frac{1}{25}\frac{1 + B[(n-7) + (n-14)]}{n-1}\frac{1}{n^6} = 1.36559806$$

Then $\langle r_{15}{}^2\rangle_0 = 15^{1.36559806} = 40.37085448$. In a preceding article,[3] we showed how to calculate $[N]_{15}{}^{x=0}$. We found $[N]_{15}{}^{x=0} = 984\,003\,000$. The value of C_{15} considered as accurate is $C_{15} = 4\,468\,921\,678$. Then $\gamma = 0.22018851$ and $\langle r_{13}{}^2\rangle = 20.952845$. Hence $\langle r_{15}{}^2\rangle = \gamma\langle r_{15}{}^2\rangle_0 + (1-\gamma)\langle r_{13}{}^2\rangle = 25.22846758$.

References and Notes

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Theory of Adsorption of Macromolecules. 1. The Desorption–Adsorption Transition Point

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ABSTRACT: The general theory of adsorption of a single long ideal polymer chain on the surface is developed. The basic equation for the adsorption–desorption phase transition point is derived. In the phase transition point the grand partition functions of sequences of units adsorbed on the surface or on the thread are shown to be equal to 1. The equations connecting the critical energy of adsorption with the conformational partition functions of units on the surface and in volume are obtained. In order to show the generality of the derived equations, they are applied to determination of the critical adsorption energies for a number of model chains considered previously elsewhere. The developed theory may be used as a base for the creation of the quantitative theory of adsorption of macromolecules (as far as the determination of the phase transition point is concerned).

I. Introduction

The process of adsorption of macromolecules is of considerable interest both with respect to its practical use and to theoretical aspects as an example of conformational transition. A single ideal polymer chain adsorbed on a homogeneous (and usually flat) surface is the simplest

0024-9297/79/2212-0715$01.00/0

initial model in the theory of adsorption. Theoretical treatment of this model can be found in quite a number of papers.[1-15]

The results are the following: (1) One of the two distinct states is found to be in equilibrium depending on the adsorption strength: molecules free in solution and molecules adsorbed. (2) There is a well-defined threshold in adsorption strength below which no adsorption takes place. (3) The desorption–adsorption transition of a chain from free space (solution) to a flat surface occurs at the threshold adsorption energy and provides a second-order phase transition.

Nevertheless, the problem of the desorption–adsorption conformational transition cannot be regarded as completely solved even in this simplest case, since quantitative results were obtained only for rather specific model systems, i.e., the lattice random chains walking on the specific lattices.

It is obvious that the development of the quantitative molecular theory of adsorption first of all requires the development of the general phenomenological theory containing some thermodynamic parameters which can be estimated for real systems, at least in principle.

This series of papers is devoted to deriving the general theory of the desorption–adsorption conformational transition in a single polymer chain. In the present paper, we discuss the dependence of the transition point on the thermodynamic and conformational properties of a long ideal chain. (The self-excluded volume of the chain is ignored.)

We shall first present in sections II and III a simple version of the starting stages of the theory. Then by exploiting some results of random-walk statistics we obtain the basic equation for the transition point. This central part of our paper is presented in section IV. The results are described in some detail in section V and applied to several model systems in section VI.

II. The Chain Partition Function

To derive the chain partition function, we use the standard techniques of the grand ensemble (the method of generating functions).[16,17] Consider the grand ensemble, i.e., the ensemble of single chains of every degree of polymerization N. The fixed parameter is the chemical potential μ (all energetic quantities are expressed in kT units) or its associated exponent

$$\lambda = \exp(-\mu) \tag{1}$$

A polymer chain capable of connecting with some adsorbing surface may be either entirely in a free space (in solution) or be connected with the surface. Because of this the grand partition function includes two items: one describing an entirely free chain

$$\Xi'(\lambda) = \Xi_V(\lambda) \tag{2}$$

and the other describing a chain connected with a surface

$$\Xi''(\lambda) = \frac{(\Xi_T(\lambda) + 1)^2 \Xi_S(\lambda)}{1 - \Xi_L(\lambda)\Xi_S(\lambda)} \tag{3}$$

They are composed of the grand partition functions for the free chain $\Xi_v(\lambda)$, the chain ends (tails) $\Xi_T(\lambda)$, the adsorbed sequences $\Xi_S(\lambda)$, and the loops $\Xi_L(\lambda)$. Equation 3 is obtained by summation over all possible numbers of the adsorbed sequences separated by loops in an adsorbed chain (taking into consideration the presence or absence of tails dangling in free space, Figure 1).

The grand partition function is the generating function

$$\Xi(\lambda) = \sum_{N=1}^{\infty} \frac{Z(N)}{\lambda^N} \tag{4}$$

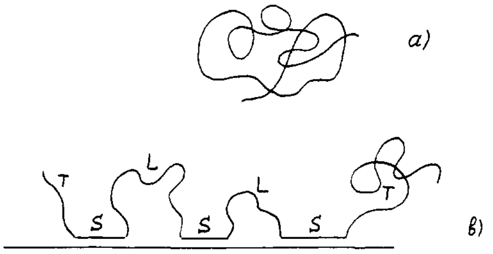

Figure 1. Free (a) and adsorbed (b) chains: T = tail, L = loop, S = adsorbed segment.

for the canonical partition function $Z(N)$ of a chain with a fixed polymerization index. At $N \to \infty$ one can write

$$Z(N) = \lambda_0^N = \exp(-\mu_0 N) \tag{5}$$

where μ_0 is a chemical potential (or free energy) of a monomer unit. From eq 4 and 5 it is easy to obtain the well-known result that λ_0 (the partition function per monomer unit) is the largest root of the equation

$$\Xi^{-1}(\lambda) = 0 \tag{6}$$

(see ref 16 and 17).

From eq 6 (taking account of eq 2 and 3) it may be seen that in our case λ_0 is a maximum among the largest roots of the following equations (cf. ref 3 and 5a)

$$\Xi_L(\lambda)\Xi_S(\lambda) = 1 \tag{7}$$

$$\Xi_V^{-1}(\lambda) = 0 \tag{8}$$

$$\Xi_T^{-1}(\lambda) = 0 \tag{9}$$

$$\Xi_S^{-1}(\lambda) = 0 \tag{10}$$

In order to avoid any misunderstanding, it should be emphasized that eq 7–10 are independent and give the number of alternative solutions. Equation 8 describes a *free chain in solution*, eq 9 describes a chain as a tail, and eq 10 describes a chain wholly in contact with the surface. In contrast, the root of eq 7 characterizes the partition function for a partially adsorbed chain containing both adsorbed segments and loops.

III. The Adsorption–Desorption Phase Transition

Let us consider the possible behavior of a macromolecule when a certain external parameter X changes (e.g., the effective adsorption strength). Now suppose that in some range of X the largest root of one of eq 7–10 is maximum and in another range the maximum is that of another equation. This means that the change in X leads to *the transition between these two equilibrium states.* This condition is *necessary* for the *real thermodynamic transition*, i.e., for the *phase transition* according to the classification of Ehrenfest (the derivative of some order of the free energy shows a discontinuity in the transition point). We should recall that for the cooperative conformational helix–coil transition in a single-stranded polypeptide chain, a similar condition is not satisfied; i.e., the maximum root is always that of an equation similar to eq 7. The helix–coil transition in a single-stranded chain is not a transition in the thermodynamic sense. Such behavior is typical for the one-dimensional Ising model with short-range interactions. The phase nature of adsorption–desorption transition as well as helix–coil transition in double stranded DNA results from the long-range forces of entropic origin operating in loops.

Equations 7–10 refer to four different states of a polymer chain. The state of the partially adsorbed chain (eq 7) is composed of microstates characterized by different numbers and lengths of adsorbed segments and loops. Statistical weights of microstates depend on X, so that the average properties of the chain change with X. The state with all chain units attached to the surface is one of the microstates of the partially adsorbed chain. As the spectrum of states given by eq 7 includes the state of the completely adsorbed chain (eq 10), the partition function given by eq 7 is always greater than that of eq 10.

We may come to this conclusion by a more formal treatment. Indeed, $\Xi_S(\lambda)$ is a diminishing function of λ (see eq 20). So the value of λ satisfying eq 10, $\Xi_S(\lambda) \to \infty$, is smaller than that satisfying eq 7, $\Xi_S(\lambda) = \Xi_L^{-1}(\lambda) < \infty$. Hence eq 7 is unsuitable to give a true phase and may be excluded from consideration. This refers also to eq 9, on the condition that the chain–surface interaction results from the short-range forces operating only near contact points (i.e., there is no weakly diminishing surface field, e.g., electrostatic, which interacts with long chain tail as a whole; see ref 18 and 19). In fact, the number of conformations of the tail attached to the surface is always less than the number of those of a free chain in solution. Thus, the partition function of the chain tail (the largest root of eq 9) cannot exceed the partition function of a free chain (the largest root of eq 8). Consequently, eq 9 may be excluded from consideration.

Hence, the problem of adsorption reduces to the estimation of the maximum among the two largest roots of eq 7 and 8 describing two different states of a chain. It is evident that the partition functions for these states change in different ways with the external conditions. For instance, partition function of a free chain does not depend on the adsorption energy, while that of the partially adsorbed chain grows rapidly with this energy.

Now the general qualitative picture of the macromolecule behavior may be drawn out and this picture of course agrees with that outlined in the Introduction. In the region of small adsorption energies, the macromolecule is in solution and its thermodynamic properties do not depend on the presence of the surface. When the adsorption energy grows up to some threshold value, the macromolecule undergoes a phase transition into a partially adsorbed state. Further increase of the energy is accompanied by the growth of a fraction of the adsorbed units, and the chain asymptotically approaches to the completely adsorbed state.

IV. The Phase Transition Point

Let the value of the external parameter $X = X_c$ (it will be further called "critical value") determine the position of the transition point when the largest roots of eq 7 and 8 coincide. Use this condition to obtain the critical value X_c.

Consider eq 8. The grand partition function of a free chain may be, formally speaking, a function of the external conditions X so that the largest root λ_{0V} of eq 8 is a function of X: $\lambda_{0V} = \lambda_{0V}(X)$. In accordance with eq 5, the partition function of a free chain of N units in solution is

$$Z_V(N,X) = \lambda_{0V}^{N}(X) \tag{11}$$

For $X = X_C$ the value λ_{0V} satisfies likewise eq 7. Thus, substitution of λ_{0V} in eq 7 gives us the basic equation to determine X_C (cf. ref 3, 5a, and 11).

$$\Xi_L(X_c,\lambda_{0V}(X_C))\Xi_S(\lambda_{0V}(X_C),X_C) = 1 \tag{12}$$

(In eq 12 the direct dependence of the grand partition functions of loops and adsorbed segments on the external condition is taken into account.)

Equation 12 can be simplified. Consider the grand partition function of loops (cf. eq 4)

$$\Xi_L(\lambda,X) = \sum_{N=1}^{\infty} \frac{Z_L(N,X)}{\lambda^N(X)} \tag{13}$$

Here $Z_L(N,X)$ is the partition function of a loop of N units (N loop). For convenience, all effects at the beginning of a loop (in particular, the probability of starting from the surface) may be attributed to the preceding adsorbed segment. (We treat the details in Section V.) Then the partition function of an N loop may be written as follows

$$Z_L(N,X) = Z_V(N,X)W(N,X) \tag{14}$$

The partition function of an N chain in solution $Z_V(N,X)$ gives the total number of states of a free N chain. $W(N,X) = Z_L(N,X)/Z_V(N,X)$ characterizes a fraction of these states in an N loop and is the probability for a free chain starting off the surface to return to it just at the N-th step. A quantity identical with the probability of the first return $W(N,X)$ is considered in the problem of the diffusion of particles in space in the presence of the adsorbing surface.[20] In this case $W(N)$ is the probability for a particle to be adsorbed on the surface after the N-th step diffusion (or after the diffusion during $t \sim N$ period of time) under the condition that the initial position of this particle was near the surface.

The precise form of the function $W(N,X)$ is determined by the dimension and shape of the surface, the conditions of walking in space, the chain stiffness, etc. However, calculation of Ξ_L at $\lambda = \lambda_{0V}$ requires less information than the thorough form of this function. Indeed, substituting eq 14 in eq 13 at $\lambda = \lambda_{0V}$ and taking into account eq 11 we have

$$\Xi_L(\lambda_{0V},X) = \sum_{N=1}^{\infty} \frac{Z_v(N,X)}{\lambda_{0v}^{N}(X)} W(N,X) = \sum_{N=1}^{\infty} W(N,X) \tag{15}$$

The right-hand sum has a simple physical sense. From the determination of the terms of eq 15 one may see that their sum is the *total probability* for an infinite chain with the first monomer on the surface *to return* on this starting surface after random walks in solution (or the probability for a particle starting from the surface and diffusing in space to be adsorbed on this surface).

To obtain the probability of return to the adsorbing surface, one may use the solution of the Pōlya random-walk problem.[21] As was shown in ref 21, the probability of at least one return to any previously visited lattice point is exactly 1, when the lattices are of one or two dimensions. It is easy to see that the return to a point for a one-dimensional walker is equivalent to the return to an infinite plane (two-dimensional surface) for the three-dimensional walker of interest. Similarly, the return to a point for a two-dimensional walker is equivalent to the return to a line (one-dimensional surface) for a three-dimensional walker.

From this it follows that at the transition point ($\lambda = \lambda_{0V}$) the long polymer chain connected at some point with a one- or two-dimensional adsorbing surface and started off this surface always returns to it, making up a loop. Hence

$$\Xi_L(\lambda_{0V},X) = \sum_{N=1}^{\infty} W(N,X) = 1 \tag{16}$$

Substituting eq 16 in eq 12 one can see that the grand partition function of the adsorbed sequence is also equal to 1 at the transition point. Thus, the basic equation for the phase transition point becomes a simple form

$$\Xi_S(\lambda_{0V}(X_C),X_C) = 1 \tag{17}$$

Now, in order to find the phase transition point X_C from eq 17 it is enough to construct the grand partition function

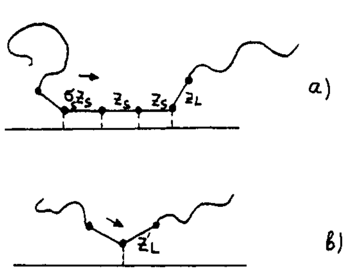

Figure 2. (a) Adsorbed segment of $N = 4$ units. Dashed lines represent four contacts with the surface. $\sigma_S z_S$, z_S, and z_L are the conformational partition functions for the first, next, and first starting-off units, respectively. The partition function of the segment is $Z_S(4) = \sigma_S z_S^3 z_L e^{-4\epsilon}$. (b) Point contact, i.e., adsorbed segment of $N = 1$ units. z'_L is the partition function of the starting-off unit for the point contact; the partition function of the segment is $Z_S(1) = z'_L e^{-\epsilon}$.

of the adsorbed sequences, using the partition function λ_{0V} of a free chain unit.

Equations 16 and 17 are valid for long Gaussian polymer chains with any short-range restrictions operating along a chain, as statistics of walking is unaffected by such restrictions. These restrictions may include restricted internal rotation, a chain stiffness, cooperative interactions along the chain (H bonds, for instance), and so on. The absence of long-range interactions, resulting from excluded volume effects, is necessary; i.e., eq 17 is valid if the Θ conditions are approached for a free chain in solution, as well as for a connected chain on the surface.

In deriving eq 17 we considered the adsorbed surface in the form of an infinite plane or a line. It is easy to see that the probability of return retains its value equal to 1 for adsorbed surfaces of any form being infinitely long (i.e., long enough compared to the chain length) at least in one dimension. As the considered probability cannot exceed 1 it retains this value also at closing the two-dimensional surface. Thus, eq 17 is the basic equation for the transition point in the process of polymer adsorption on a line (with cross-dimensions being about the chain unit size), on a plane, on a two-dimensional surface of any form, between two plates, in pores of any form, etc.

The adsorption on the point adsorbent displays some peculiarities, as the probability κ of return to any given point is not equal to 1 for three-dimensional lattice walks.[21] Its value is the function of lattice structures; for random walks on different cubic lattices $\kappa = 0.25$–0.35.[21] Now from eq 12 and 15 we obtain the basic equation in the form

$$\Xi_S(\lambda_{0V}(X_C),X_C) = \frac{1}{\kappa} \tag{18}$$

where κ is the additional parameter depending on the properties of the system under study.

Below we shall treat in detail eq 17 for the general case of adsorption on infinite long surfaces. The point adsorption requires a special examination.

V. The Grand Partition Function of the Adsorbed Segment and the Phase Transition Point

Consider an adsorbed segment of N units (Figure 2), i.e, a segment with N bonds with the surface. Each pair of consecutive bonds restricts the conformations of a unit (monomer) between these two bonds. Hence, $(N - 1)$ units lie on the surface and the last N-th monomer starts off it, beginning a loop. Therefore, the statistical weight of the withdrawal off the surface is included in the partition function of the segment adsorbed. Only in this case may the grand partition function of the loop be treated as the probability of the first return to the surface (see preceding paragraph).

Consider now the simplest case when all monomers in adsorbed segments are identical thermodynamically. Now the partition function of a segment of any number of units ($N \geq 1$) is

$$Z_S(N) = z_S^{N-1} z_L e^{-N\epsilon} \tag{19}$$

where z_S is the conformational partition function of a unit (monomer) lying on the surface, z_L is that of the monomer starting off the surface (Figure 2), and $-\epsilon$ is the adsorption energy of the monomer. This "energy" is the effective difference quantity determined by the change of energy when a monomer drops on the surface and the solvent is displaced off it. The displaced molecules mix with other molecules of the solvent and this may produce a rearrangement of the solvent. These processes contribute $-\epsilon$, which turns out to be a free energy difference (the difference between the conformational free energy of a chain unit in solution and on the surface is taken into consideration independently and is not included in $-\epsilon$).

The grand partition function of the segments adsorbed is

$$\Xi_S(\lambda) = \sum_{N=1}^{\infty} \frac{Z_S(N)}{\lambda^N} \tag{20}$$

Substituting λ in eq 20 by the partition function of a free chain unit $\lambda_{0V} = z_V$

$$Z_V(N) = \lambda_{0V}^N = z_V^N \tag{21}$$

one can obtain the value of Ξ_S at the critical point. Using eq 17 and 19–21, the equation for the phase transition point can be obtained as

$$\left[e^{\epsilon} - \frac{z_S + z_L}{z_V}\right]_C = 0 \tag{22}$$

or

$$\left[e^{\epsilon} - \left(1 - \frac{z_f}{z_V}\right)\right]_C = 0 \tag{22'}$$

where $z_f/z_V = 1 - (z_S + z_L)/z_V$ is the fraction of monomer conformations forbidden by the presence of the surface. As can be seen from eq 22 and 22′, the adsorption energy for each unit in the transition point precisely compensates the restrictions introduced by the presence of the surface.

In real systems (and even in model ones, see below) the end effects in the adsorbed segments may be present, and monomers lying on the surface may differ in their thermodynamic characteristics. We consider the end effects extending only to one unit. Now the partition function of the adsorbed segment of $N \geq 2$ units can be written as

$$Z_S(N) = \sigma_S z_S^{N-1} z_L e^{-N\epsilon} \tag{23}$$

and for a specific case of the point contact $N = 1$ (Figure 2) we have

$$Z_S(N = 1) = z'_L e^{-\epsilon} \tag{24}$$

Here $\sigma_S z_S$ is the partition function of the first unit in a segment adsorbed and z'_L is that of a unit started off the surface after the point contact.

Substituting eq 23 and 24 in eq 20, summing, and using eq 17 and 21, we obtain the equation for the phase transition point

$$\left[e^{2\epsilon} - \frac{z_S + z'_L}{z_V} e^{\epsilon} + \frac{z_S z'_L - \sigma_S z_S z_L}{z_V^2}\right]_C = 0 \tag{25}$$

which includes eq 22 (at $\sigma_S = 1$, and $z'_L = z_L$) as a particular case.

Comparing eq 25 and 22 one can easily see that the end effects extending to one unit in a segment adsorbed lead to the equation of the second order in the unknown $\exp(\epsilon)$. With the use of this scheme one can derive an analogous equation, taking into account the more lengthy end effects. This will lead to the increase of the order of the equation. But there are minimal end effects for the most interesting cases, and as a rule eq 25 is quite general for the determination of the phase transition point.

Equation 25 connects a number of parameters characterizing the system in the phase transition point. Defined by the way the problem is stated, any of these parameters may be treated as a variable external parameter X which induces the desorption–adsorption phase transition. In this case eq 25 gives the dependence of the value of this parameter in the transition point X_C on the fixed characteristics of the system. The adsorption strength $-\epsilon$ is often taken as an external parameter. The change of this quantity in experiment can be induced by the change of temperature, solvent, etc. (It must be recalled that ϵ is expressed in kT units.) The influence of the external conditions on the conformational partition functions of units in solution and on the surface is also possible (when $z_v = z_v(X)$, $z_S = z_S(X)$, etc.).

Equation 25 provides the opportunity to create the molecular theory of adsorption (as far as the determination of the position of the adsorption–desorption phase transition is concerned) for real macromolecules. This requires the conformational parameters to be calculated by methods of molecular physics. In this paper we treat, however, a more simple problem. Equation 25 will be applied to a number of models which have been treated previously in the theoretical references 4, 14, 15, 22, and 23. It should be emphasized that in the cited papers there is a separate treating of each model, based on the calculation of the number of chain conformations on different lattices.

VI. The Phase Transition Point in the Simplest Models

Considering the energy of adsorption as an external parameter and using eq 25, we obtain the equation for the critical energy of adsorption ϵ_C, i.e., energy at which a model chain undergoes the adsorption–desorption phase transition. Examine now the adsorption on the infinite flat surface (paragraphs 1, 2a–d, and 4 below).

(1) Random Walks on the Lattice.[4a] As can be easily seen, in this case the characteristics of the end and middle units in an adsorbed segment coincide; i.e., eq 25 reduces to eq 22 and 22′. Now z_V and z_S are the coordination numbers of the space and plane lattices, respectively, z_L is the number of ways by which a unit can leave the surface, and z_f is a number of the monomer conformations forbidden by the presence of the surface. We have, obviously, $z_L = z_f = (z_v - z_S)/2$, and then eq 22 gives

$$e^{\epsilon_C} = \frac{z_v + z_S}{2z_V} \tag{26}$$

in accordance with ref 4a.

2. Stiff Chains on Simple Cubic Lattice (scl) in Space and on Square Lattice on the Surface.[14,15] Following ref 14 and 15, consider several slightly different models: (a) For the six-choice scl, the statistical weight of the step forward is g and those of the steps backward and sideways are 1; each attachment to the surface results in a gain of energy $-\epsilon$ (model II from ref 15). Now the values of parameters are (Figure 3) $z_V = g + 5$, $z_S = g + 3$, $\sigma_S z_S = 4$, $z_L = z'_L = 1$, and from eq 25 one can obtain

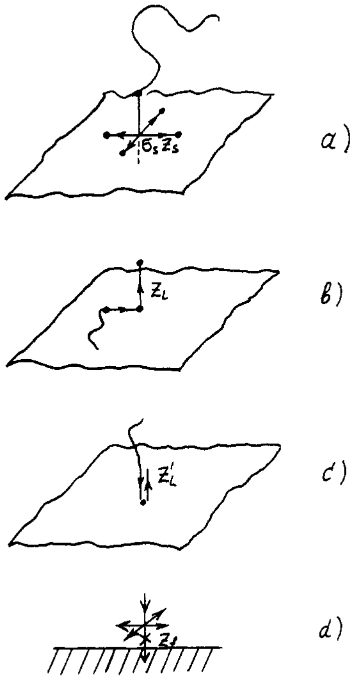

Figure 3. Chains on the cubic lattice near the surface. The first steps in the segment adsorbed (a) and at the point starting off the surface (b) are always connected with a sideways bend of chain. There are four possibilities for the first step and 1 for the start off, i.e., $\sigma_S z_S = 4$, $z_L = 1$. (c) The point contact is connected with the step backward. Therefore, $z'_L = 1$ on the six-choice scl (case 2a in text) and $z'_L = 0$ on the five-choice scl with the step backward forbidden (case 2b in text). (d) Plane and thread forbid one step marked by cross, $z_f = 1$.

$$e^{\epsilon_C} = \frac{g + 4 + [(g + 2)^2 + 16]^{1/2}}{2(g + 5)} \tag{27}$$

in accordance with ref 15. In the particular case $g = 1$ (unrestricted random walks) we have $\exp(\epsilon_C) = {}^5/_6$ in accordance with eq 26.

(b) An example of a five-choice scl is one meeting conditions 2a, the step backward being forbidden (model 1 from ref 15). This restriction eliminates the point contact (Figure 3), i.e., $z'_L = 0$. Other parameters are $z_V = g + 4$, $z_S = g + 2$, $\sigma_S z_S = 4$, $z_L = 1$; eq 25 gives

$$e^{\epsilon_C} = \frac{g + 2 + [(g + 2)^2 + 16]^{1/2}}{2(g + 4)} \tag{28}$$

in accord with ref 15. In the particular case where $g = 0$ (random walks on the scl, the bond angle being $\pi/2$), one obtains $\exp(\epsilon_C) = (1 + 5^{1/2})/4$ (cf. ref 4).

(c) Model 2b but with the energy of an adsorbed strand of N-monomers (N lattice points) is $-(N - 1)\epsilon$[14] (see also model 1* in ref 15). Diminishing the number of active contacts in a segment adsorbed by unity can be taken into account if $\sigma_S z_S$ is displaced by $\sigma_S z_S / e^{-\epsilon}$, other parameters being equal to those in 2b. In accord with ref 14 and 15, we have

$$e^{\epsilon_C} = \frac{g^2 + 6g + 12}{(4 + g)^2} \tag{29}$$

(d) In order to describe the stiff chain, a simple model was suggested:[15] a chain with virtual steps. For this model the basic equation for the transition point appears to be the first order in $\exp(\epsilon_C)$. From this it follows that the

$(\mathrm{h,c})^{\kappa}$ $\kappa = 1, 2, \ldots$
$(\mathrm{h,c})^{\kappa}\mathrm{h}$ $\kappa = 0, 1, 2, \ldots$
$\mathrm{c}(\mathrm{h,c})^{\kappa}$ $\kappa = 0, 1, 2, \ldots$
$\mathrm{c}(\mathrm{h,c})^{\kappa}\mathrm{h}$ $\kappa = 0, 1, 2, \ldots$

Figure 4. Possible secondary structures of a lengthy adsorbed segment (the number of units not less than 2). c and h are coil and helical segments, respectively. The bonding energy of the first unit is always $-\epsilon^{c}$, the partition function of the starting-off unit is always z_{L}, and the partition function for the point contact is $Z_{S}(1) = e^{-\epsilon^{c}}(z_{L}/z_{v})$ and may be included in Figure 4 as $(\mathrm{h,c})^{\kappa}$ at $\kappa = 0$. Summing up the geometrical progression, we obtain eq 33.

principal assumption in this model is the neglect of the end effects in the segments adsorbed. Therefore we assume $\sigma_{S} = 1$ and $z'_{L} = z_{L}$ even though these conditions are valid strictly only for random walks. The other parameters for the stiff chains on the six-choice lattice are $z_{f} = 1$ and $z_{V} = g + 5$; eq 22 gives

$$e^{\epsilon_{C}} = (g + 4)/(g + 5) \qquad (30)$$

in accordance with ref 15. The strict description of the analogous lattice chain gives $\sigma_{S} < 1$ (see paragraph 2a); therefore, a simple model overstates the conformational contribution to the partition function of the adsorbed segment. This leads to the shift of the phase transition to smaller adsorption energy. With the stiffness increasing, the lengths of the adsorbed segments increase, the end effects contributions decrease, and the results obtained by a simple model become closer to the strict ones (cf. ref 15).

(3) Adsorption on a Thread. Now apply eq 25 to the adsorption on the one-dimensional thread. Following ref 4b, consider unrestricted random walks on the lattice (an impenetrable thread is a linear strand of consecutive points) when eq 25 reduces to eq 22 and 22′. Equation 22 shows that the critical adsorption energy is determined by the fraction of the conformations forbidden by the presence of the surface. Unrestricted random walks on the scl give $z_{f}/z_{V} = {}^{1}/_{6}$, the adsorbing surface being a plane or a line (Figure 3). This fact explains the conclusion derived from direct calculations[4b] that $\exp(\epsilon_{C}) = {}^{5}/_{6}$ for adsorption both on a plane and a line (note that $z_{S} = 2$, $z_{L} = 3$ for a line and $z_{S} = 4$, $z_{L} = 1$ for a plane).

(4) Adsorption of a Polypeptide Chain. Finally, in order to demonstrate the generality of the approach, apply our method to the sufficiently complicated system and consider a model of the adsorbed polypeptide chain with secondary structure. Adsorption of such a chain composed of helical and coiled segments has been considered elsewhere.[22,23] The helix and coil contents in a free chain (determined by the Zimm–Bragg parameters s and σ) were calculated with the use of the well-known formulas of the theory of the helix–coil transition. The partition function of the partially adsorbed chain was described by the model with virtual steps (see above paragraph 2d); i.e., as it has been pointed out, end effects were ignored in the segment adsorbed. For the model with virtual steps on the scl, direct calculations give the equation for the critical point:[22,23]

$$[(\lambda - e^{-\epsilon^{c}-\tilde{\epsilon})})(\lambda - se^{-\epsilon^{h}}) - \sigma s e^{-(\epsilon^{c}-\tilde{\epsilon})-\epsilon^{h}}]_{C} = 0 \qquad (31)$$

where λ is the partition function of the free chain unit and satisfies the equation

$$(\lambda - 1)(\lambda - s) - \sigma \mathrm{s} = 0 \qquad (32)$$

and $\tilde{\epsilon}$ is the critical adsorption energy of the pure coil chain determined from eq 22 or 26. In eq 31 the adsorption energies of the coiled and helical units $-\epsilon^{c}$ and $-\epsilon^{h}$ are supposed to be different.

Let us show that eq 31 may be derived directly from the results of this paper. Using eq 17 and taking into account that each unit of the adsorbed segment may be in a coiled (c) or helical (h) state, one can obtain the grand partition function of an adsorbed segment (Figure 4)

$$\Xi_{S} = e^{-\epsilon^{c}}\frac{z_{L}/z_{V}}{\lambda}(1 + \Xi_{S}^{(c)})\frac{1}{1 - \Xi_{S}^{(h)}\Xi_{S}^{(c)}}(1 + \Xi_{S}^{(h)}) \qquad (33)$$

Here we summed on all possible secondary structures of the adsorbed segment and

$$\Xi_{S}^{(c)} = \sum_{N=1}^{\infty}\left(\frac{z_{S}}{z_{V}}\right)^{N}\frac{e^{-N\epsilon^{c}}}{\lambda^{N}} = \frac{(z_{S}/z_{V})e^{-\epsilon^{c}}}{\lambda - \dfrac{z_{S}}{z_{V}}e^{-\epsilon^{c}}} \qquad (34)$$

and

$$\Xi_{S}^{(h)} = \sum_{N=1}^{\infty}\frac{\sigma s^{N}}{\lambda^{N}}e^{-N\epsilon^{h}} = \frac{\sigma s e^{-\epsilon^{h}}}{\lambda - se^{-\epsilon^{h}}} \qquad (35)$$

are the grand partition functions of the pure coiled and pure helical segments on the surface; z_{V}, z_{S}, and z_{L} are, as before, the numbers of states of a unit in solvent and on the surface and the number of ways to leave the surface, respectively, but they refer only to units in the coiled states. In eq 34 the factor z_{S}/z_{V} is stipulated by the change of the number of states of the coil unit on adsorption. The surface does not affect the number of states of a unit in the stiff helical segment.

Substituting eq 34 and 35 into eq 33 and equating the right-hand side of eq 33 to unity (in accord with eq 17), one can obtain the next equation for the transition

$$\left[\left(\lambda - \frac{z_{S} + z_{L}}{z_{v}}e^{-\epsilon^{c}}\right)(\lambda - se^{-\epsilon^{h}}) - \sigma s\frac{z_{S} + z_{L}}{z_{V}}e^{-\epsilon^{c}-\epsilon^{h}}\right]_{c} = 0 \qquad (36)$$

where $\lambda = \lambda_{0V}$ satisfies also eq 32. Under the conditions given by eq 22, eq 36 reduces to eq 31.

Conclusion

We believe that the results given in the last section demonstrate the great generality of the basic equation for the adsorption–desorption transition point developed in this paper. The results also show the possibility of using the basic equation to determine the critical adsorption energy in sufficiently complicated cases.

The character of the desorption–adsorption phase transition will be considered in the next paper.

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Mechanical Properties of Racemic Poly(α-methyl-α-n-propyl-β-propiolactone)

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ABSTRACT: Stress–relaxation and dynamic mechanical behavior of the racemic homopolymer of α-methyl-α-n-propyl-β-propiolactone (PMPPL) have been investigated. Using Ferry's reduction method, experimental shift factors that satisfactorily agree with the WLF equation in the transition region were determined. The apparent activation energy of the sample is temperature dependent, and it passes through a maximum near the glass-transition temperature whose value has been found to be 270 ± 2 K. The relaxation spectrum was calculated according to the first approximation method proposed by Schwarzl and Staverman. The slope of its wedge portion is equal to –0.28, which is the type of value often found for a semicrystalline polymer. In addition to the β transition region, a second transition zone is revealed at low temperatures by the dynamic mechanical measurements. This transition is probably due to the mobility of the propyl side group of the polymer or to a restricted motion of its main chain. Dynamic mechanical measurements were also conducted on a second PMPPL sample which is optically active. The tan δ, E', and E'' curves of the latter sample are very similar to those of the racemic polymer. These results seem to indicate that the mechanical properties are not much influenced by the change of structure of the polymer brought up by the optical activity, except for small changes which can be associated to the difference in the degree of crystallinity between the two samples.

Poly(pivalolactone) [$(CH_2C(CH_3)_2COO)_n$; PPL] has been shown to be an interesting polymer since it can be produced in the form of fibers having high melting points.[1–4] It has however several undesirable properties which are related to a crystal–crystal transition occurring upon stretching.[2,3,5] In order to avoid this problem, several studies have been devoted to the preparation of copolymers of PPL with a comonomer of lower degree of crystallinity. In particular, poly(α-methyl-α-n-propyl-β-propiolactone) [$(CH_2C(CH_3)(CH_2CH_2CH_3)COO)_n$; PMPPL] has been used.[6,7] Some attempts have also been made to prepare graft copolymers of PMPPL on elastomers.[8] In such materials, PMPPL does not present the crystal–crystal phase transition which occurs in the homopolymer,[9] similar to the PPL case. In order to explain the mechanical properties of such materials, it is necessary to determine first the mechanical properties of the PMPPL homopolymer.

It is then the purpose of the present paper to study the linear viscoelastic behavior of PMPPL homopolymer in order to obtain its rheological functions and also to determine its glass-transition temperature, T_g. This goal will be achieved by using the stress–relaxation measurements as well as dynamic mechanical methods.

Since a PMPPL sample showing optical activity was also available,[10] the dynamic mechanical measurements were conducted on this second sample as well.

Experimental Section

Two samples were used in this study. The racemic PMPPL, hereafter called PMPPL-R, was prepared using standard anionic polymerization procedures and a tetrahexylammonium benzoate initiator. It did not present any specific rotation when run in chloroform, at a 0.4% concentration, at 25 °C, and using a wavelength of 546 nm. Its molecular weight was found to be 88 000 by osmometry. The optically active PMPPL, hereafter called PMPPL-OA, was prepared using a 1–1 mixture of diethylzinc–(R)-(–)-3,3-dimethyl-1,2-butanediol "stereoelective" initiator. It gave a value of specific rotation of –0.6 in the same conditions as those used for the PMPPL-R sample. Its molecular weight was 26 000. These two samples were respectively samples No. 7 and 3 of a previous publication.[10]

Both polymers were cast into thin films by pouring their chloroform solutions in a crystallizing pan, followed by gradual evaporation at room temperature. The resulting films were dried at 318 K in a vacuum oven for 24 h. They were annealed at 335 K during 16 h and then used. Under these conditions, both polymers are semicrystalline and are found by X-ray diffraction in the α form, which is characterized by a 2_1 helical conformation of the chains.[9] DSC measurements yielded an enthalpy of fusion of 8.2 and 12.6 $J \cdot g^{-1}$ for PMPPL-R and PMPPL-OA, respectively. Even if the enthalpy of fusion of pure PMPPL crystal is not known, such a value certainly corresponds to a low degree of crystallinity probably of the order of 10%.[10] Melting points, T_m, of 366 and 375 K were determined for PMPPL-R and PMPPL-OA, respectively. These specimens reach ultimate elongations of about 750%. The strains at yield point are respectively 17 and 15% for the racemic and the optically active polymer. All these measurements indicate a significant increase in the degree of crystallinity of the optically active polymer as compared to the racemic one.

Relaxation measurements were carried out at different temperatures on an Instron tester (table Model 1130) which we used as a relaxometer. Before each measurement, the sample specimen was preconditioned at zero strain in the jaws of the relaxometer, at least 1 h at the desired temperature. All series of measurements were performed starting from the highest measuring temperature. It was found that under these conditions, the relaxation curves were reproducible. This result indicates that there is no change in the structure of the sample due to heat treatment. No dependence of the viscoelastic properties on relative humidity was noticed.

The linear viscoelastic theory implies no permanent change in microstructure, which could occur with deformation and cause a permanent hysteresis on repeated loading. To ascertain that

0024-9297/79/2212-0721$01.00/0