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# Conformations of Polymers Attached to an Interface

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ABSTRACT: We discuss the conformations and the concentration profiles for long, flexible chains ($N$ monomers per chain) grafted at one end on a solid surface (fraction of surface sites grafted $\sigma$). The chains are immersed either in a pure (good) solvent or in a solution of the same polymer ($P$ monomers per mobile chain, volume fraction $\phi$). It is assumed that the polymer does *not* adsorb on the wall surface. The zone occupied by the grafted chain may contain a large fraction of mobile P chains: we call this a mixed case (M), as opposed to the unmixed case (UM). Also the chains may be stretched (S) or unstretched (US). The combination of these two criteria gives four possible regimes. Using scaling laws, we locate the domains of existence of these four regimes in terms of the variables $\sigma$ and $\phi$. High $\sigma$ values may be hard to reach by grafting but could be obtained with block copolymers at an interface between two immiscible solvents.

## I. Introduction

Polymers grafted onto solid walls can be useful for many physicochemical applications:[1] wetting, adhesion,[2] chromatography,[3] colloid stabilization,[4] and biocompatibility[5] are typical examples. In the present paper, we discuss theoretically some conformation problems for grafted, flexible polymers immersed in *good* solvents. The situation which we have in mind is described on Figure 1: here, a set of linear chains (with $N$ monomers per chain) is attached to a wall and immersed in a liquid which may be either a pure solvent or, more generally, a solution of the same polymer (with $P$ monomers per chain). We assume that all chains are *uncharged*: this eliminates some important practical situations but is logical in view of the difficulties found in understanding polyelectrolyte conformations in solution. We also assume *no adsorption*: the chains are not attracted to the wall. The opposite case can be treated and has in fact been discussed in some limits[6] but is obscured by the increase in number of relevant parameters.

A global Flory–Huggins theory for the selective properties of a set of grafted chains with respect to solvent mixtures has recently been constructed.[7] Our aim here is somewhat different:

(a) We are mainly concerned with conformational properties and with spatial distributions.

(b) We wish to cover situations where the fraction $\sigma$ of grafted sites on the solid surface is large (up to unity). Of course, these situations are not easy to achieve on a solid wall. But they may be reached with *monolayers of block copolymers* at an interface between two solvents.

(c) We allow for a liquid phase which contains mobile polymer chains (P chains), but we restrict our attention to P chains which are *chemically identical* with the N chains. This excludes a number of interesting chromatographic effects[7] but preserves some important physical questions: (i) the concentration (or volume fraction $\phi$) of the mobile chains can be used to modify the properties of the grafted layer; (ii) the limit of a dense polymer melt ($\phi \to 1$) which is included here is of interest for certain applications, such as incompatible polymer mixtures doped by block copolymer additives.[8]

Clearly, the statistical problem raised by these rather complex interfaces is very delicate. However, it is possible to delineate the main *qualitative* features by comparatively simple arguments based on scaling laws.[9] We do this here in one limit, namely, when the system is athermal ($\chi = 0$ in the Flory–Huggins[10] notation). Also we restrict our attention to mobile chains which have lengths comparable to (or smaller than) that of the grafted chain ($P \lesssim N$).

There are three successive steps in our discussion. The case of grafted chains plus *pure solvent* is treated in section II. Here, most of the relevant scaling laws have already been constructed by Alexander:[6] we add only a few novel features, such as the concentration profile close to the wall. In section III, we discuss the opposite limit of a grafted wall in contact with a polymer melt. Of particular interest here is the progressive expulsion of the mobile chains from the grafted film when the graft density $\sigma$ increases. Finally in section IV we deal with semidilute solutions: here we find that the regime of section II is prevalent when $\phi < \sigma^{2/3}$. In the opposite limit ($\phi > \sigma^{2/3}$) there are still two different possibilities, one with penetration of the grafted layer by the P chains and one without penetration.

The main conclusions are summarized in Figure 2, showing the different regimes which we expect for any given $\phi$ and $\sigma$. It should be immediately pointed out that the boundaries between successive regimes are not sharp: they correspond in reality to smooth crossovers.

## II. Grafted Chains plus Good Solvent

**A. Separate Coils.** The limit of low $\sigma$ is particularly simple (Figure 3): each chain occupies roughly a half-sphere with a radius comparable to the Flory radius for a coil in a good solvent[10]

$$R_F = N^{3/5}a \tag{II.1}$$

where $a$ is a monomer size ($a$ is the mesh size in the lattice model of Figure 1). Here, the different coils do not overlap: thus we must have $\sigma a^{-2} R_F^2 < 1$ or

$$\sigma < N^{-6/5} \tag{II.2}$$

Let us now discuss the *average* profile $\phi(z)$ for a random distribution of grafting points on the wall. We call $z$ the

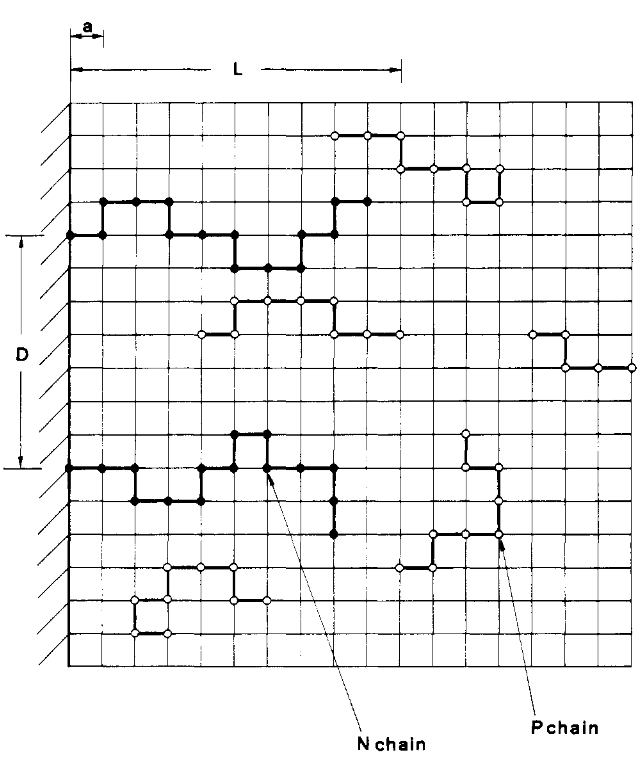

**Figure 1.** Lattice model for grafted chains ($N$ monomers per chain) and mobile chains ($P$ monomers per chain) in an athermal solvent. On this picture $N = 15$ and $P = 9$. In the text we are concerned with larger values ($N \gtrsim 10^3$ and $P \gtrsim 10^2$).

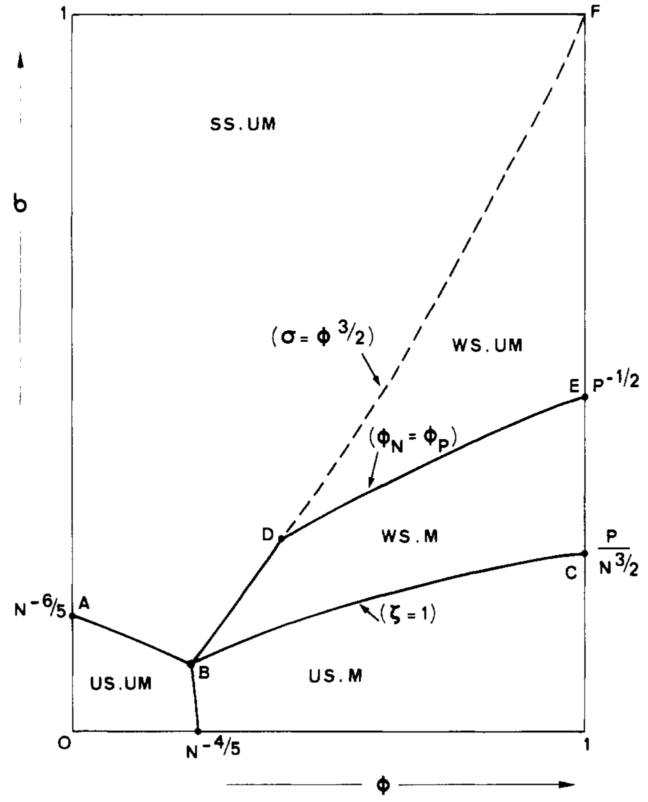

**Figure 2.** Various regimes for the grafted layer (density of graft points $\sigma$ (in dimensionless units)) in the presence of a solution of P chains (volume fraction of P chains in the bulk $\phi$). Symbols: S = stretched, SS = strongly stretched, WS = weakly stretched, US = unstretched, M = mixed (penetrated by the P chains), UM = unmixed. The figure is drawn for the case $N^{1/2} < P < N$ and is only qualitative.

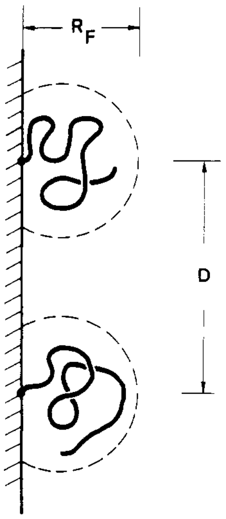

**Figure 3.** Low density of grafted points ($\sigma \to 0$) and pure solvent.

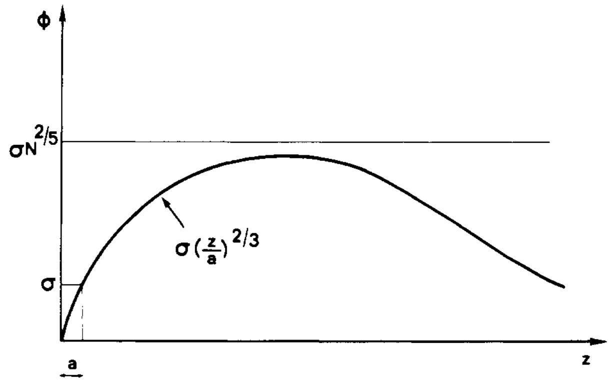

**Figure 4.** Average concentration profile for the situation of Figure 3.

distance to the wall and focus our attention on the interval $a \ll z \ll R_F$. At the upper limit ($z \sim R_F$) we expect a concentration equal to the concentration inside a single coil ($N/R_F^3$) times the fraction of wall area occupied by coils ($\sigma/a^2)R_F^2$. Thus

$$\phi(z = R_F) \simeq N\sigma a/R_F = \sigma N^{2/5} \qquad \text{(II.3)}$$

At the lower limit ($z \sim a$) we should return to the fraction of grafted points $\sigma$. Interpolating between these two ends by a power law

$$\phi(z) = \sigma(z/a)^m \qquad \text{(II.4)}$$

(with an unknown exponent $m$) and imposing the condition (II.3), we arrive at

$$\sigma(R_F/a)^m = \sigma N^{2/5}$$

$$m = \tfrac{2}{3} \qquad \text{(II.5)}$$

The resulting profile is very different from what we know for solutions of mobile chains.[11] Our conclusions for the profile are summarized in Figure 4. Note that for $z > R_F$ the concentration drops out very fast.

**B. Overlapping Coils.** This is the most interesting regime. It is obtained when $D < R_F$ or $\sigma > N^{-6/5}$. The general physical picture for this case (shown on Figure 5) is due to Alexander.[6] He has shown that the fundamental distance $D$ of the problem is the average distance between grafted sites on the surface. In terms of the grafting fraction $\sigma$, we may define $D$ through

$$D = a\sigma^{-1/2} \qquad \text{(II.6)}$$

A grafted chain may be subdivided into "blobs" of linear size $D$, each of them containing a number $g_D$ of monomers. Since at small scales ($r < D$) the correlations are dominated

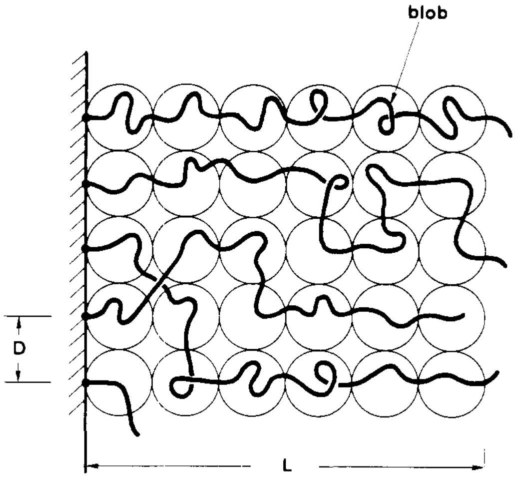

**Figure 5.** Strongly stretched situation for a grafted layer in a good solvent. The chains are mainly stretched along the normal to the wall.

by excluded-volume effects, the relation between $g_D$ and $D$ is of the form (similar to II.1)

$$a g_D^{3/5} = D \tag{II.7}$$

It is immediately seen that when $D \ll R_F$ (overlapping regime), we have $g_D \ll N$. In the region occupied by the grafted chains, the blobs act as hard spheres and fill space densely. Thus the polymer concentration is

$$a^{-3}\phi_N \simeq g_D/D^3 \tag{II.8}$$

Inserting (II.6) and (II.7) into (II.8) we get

$$\phi_N \simeq \sigma^{2/3} \tag{II.9}$$

The thickness $L$ of the grafted layer is then immediately derived: the volume per grafted chain is $LD^2$ and this contains $N$ monomers. Thus

$$\phi_N a^{-3} = N/(LD^2) = N/(La^2\sigma^{-1})$$

$$L \simeq N a \sigma^{1/3} \tag{II.10}$$

Note that $L$ is proportional to the molecular weight. This corresponds to a regime of *stretched chains* (S).

It is also possible to write this thickness in the form

$$L \simeq (N/g_D)D \tag{II.11}$$

showing that the chain is mainly a linear string of blobs stretched along the normal to the wall. There is, however, a random-walk component parallel to the wall plane: as shown on Figure 5, each chain is expected to show a (root mean square) spread along these directions of magnitude

$$\Delta x \simeq (N/g_D)^{1/2} D \tag{II.12}$$

In this stretched regime the concentration profile is essentially flat, except for two adjustment regions at the end (Figure 6). The profile near the wall is still given by eq II.4 and II.5 but this equation applies only in an interval $a < z < D$. For $z > D$ we recover the concentration $\sigma^{2/3}$ of eq II.9.

To summarize, we find two extreme regimes, one unstretched and one stretched, depending of the graft density $\sigma$. In both regimes the concentration profile is predicted to show a depletion layer near the wall, although each chain must reach the wall.

## III. Grafted Chains plus Polymer Melt

We now consider a less familiar case where the grafted chains (N chains) are in contact with a pure polymeric liquid (P chains). Thus at any distance $z$ from the wall we have to define two volume fractions $\phi_N$ and $\phi_P$, with $\phi_N + \phi_P = 1$.

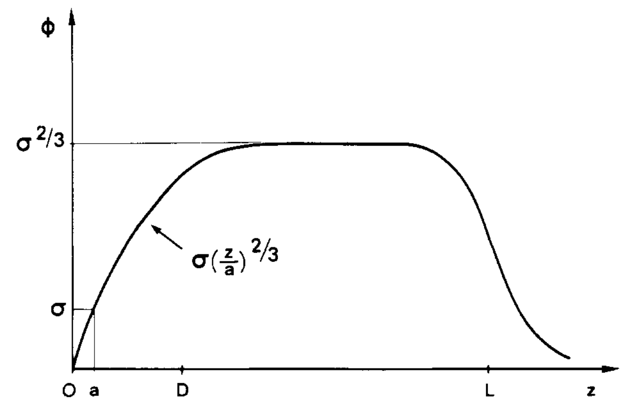

**Figure 6.** Concentration profile for a grafted layer immersed in a good solvent in the overlapping regime.

**A. Low-Density Limit.** Here, the N chains do not overlap. One major difference with section II is that the N chains, being immersed in a sea of P chains, are *ideal* (provided that $P > N^{1/2}$).[9,10] For such a case, it is possible to construct the concentration profiles exactly. We shall not, however, insist on these technical points. The central fact is that each chain occupies a region of linear dimension $R_0 = N^{1/2}a$. The grafted chain concentration scales like

$$\phi_N(z) = \sigma z/a$$

$$a < z < R_0 \tag{III.1}$$

and reaches a maximum of order $\sigma N^{1/2}$ at $R_0$. This is correct since it corresponds to $N$ monomers distributed in a region of volume $D^2R_0$.

The limit of validity of this regime is defined by $\sigma a^{-2} R_0^2 < 1$ or

$$\sigma < N^{-1} \tag{III.2}$$

Thus the density $\phi_N$ is always small ($<N^{-1/2}$). This is an important check of our starting assumption: mobile chains can screen out the interactions between the grafted chains only if $\phi_P$ dominates over $\phi_N$.

We conclude that when eq III.2 holds, the grafted chains are mixed with the mobile chains and are unstretched (symbol US.M).

**B. Onset of Stretching.** If we increase the density $\sigma$ of grafted points beyond the limit (III.2), the grafted coils begin to overlap, and this may lead to stretching. However, as we shall see, there is an intermediate domain where the chains overlap but where their interactions are still negligible: thus, up to a certain value $\sigma_1$ we still retain a grafted layer of thickness $R_0$. For $\sigma > \sigma_1$ the chains do stretch. Later, when we reach a second crossover region ($\sigma = \sigma_2$), the mobile chains are progressively expelled from the grafted layer.

The threshold $\sigma_1$ can be obtained from a consideration of the $\zeta$ parameter used in perturbation calculations of excluded-volume effects.[13] Essentially $\zeta$ measures the average repulsion energy inside one chain divided by the thermal unit $kT$. In our case the monomers have a "bare" excluded volume $v = a^3$ and a "screened" excluded volume $\tilde{v} = a^3P^{-1}$. (For a detailed discussion of screening by long chains, see ref 14 and 9.) The $\zeta$ parameter is then of order

$$\zeta = N\phi_N a^{-3}(a^3P^{-1}) \tag{III.3}$$

corresponding to $N$ monomers, each of them feeling a repulsive potential proportional to the concentration ($\phi_N a^{-3}$) and to $\tilde{v}kT$. We estimate (III.3) by assuming that the chains are ideal and spread over a thickness $R_0$. This corresponds to $a^{-3}\phi_N = N/(D^2R_0)$ and gives

$$\zeta = \sigma N^{3/2}P^{-1} \tag{III.4}$$

We conclude that whenever $\sigma$ is smaller than

$$\sigma_1 = PN^{-3/2} \tag{III.5}$$

the $\zeta$ parameter is small, the interactions are weak, and the ideal-chain assumption is correct. But when $\sigma > \sigma_1$ the chain must stretch.

**C. Expulsion of the Mobile Chains.** The calculations based on a $\zeta$ parameter are essentially limited to dilute N coils ($\phi_N \ll 1$). We shall now write down a slightly more general analysis, allowing for arbitrary values of $\phi_N$ and $\phi_P = 1 - \phi_N$. Our calculation here is extremely rough: it does not reach the scaling accuracy of the Alexander argument in section II but is based rather on a Flory type of self-consistency.

The starting point is a form of the free energy (per N chain) containing two physical contributions: (a) an entropy of mixing between P chains and N chains, which tends to swell the grafted chains, and (b) elastic terms for the grafted chains, which limit the swelling.

The usual expression for the entropy of mixing per lattice site in the Flory–Huggins scheme is $-\Delta S_{\text{mix}} = (1/N)\phi_N \ln \phi_N + (1/P)\phi_P \ln \phi_P$. However, for grafted N chains, we must drop out the first term, which is normally associated with translational freedom. Thus we shall write the corresponding free energy per grafted chain, $F_{\text{mix}}$, in the form

$$\frac{F_{\text{mix}}}{kT} = \frac{LD^2}{a^3}\,\frac{1}{P}\phi_P \ln \phi_P \tag{III.6}$$

where $L$ is the thickness of the grafted layer (and is yet unknown) and $LD^2$ is the volume per grafted chain ($LD^2/a^3$ being the corresponding number of lattice sites).

To this we must add an elastic energy, which we take in the simplest form

$$\frac{F_{\text{el}}}{kT} = \frac{3}{2}\left(\frac{L^2}{R_0^2} + \frac{R_0^2}{L^2}\right) \tag{III.7}$$

The first term (dominant at large elongations) corresponds to ideal-chain behavior under stretch, while the second term gives the correct ideal-chain behavior under compression[15] (except for numerical coefficients). The whole expression is not perfect, but comparing with other known situations, we are led to hope that the inaccuracies in (III.6) and (III.7) cancel out to some extent.[9] Because of these difficulties, we shall omit all coefficients such as the factor $^3/_2$ in eq III.7.

We must now minimize the sum $F_{\text{mix}} + F_{\text{el}}$, keeping in mind the constraints

$$\phi_N = 1 - \phi_P = Na^3/(LD^2) \tag{III.8}$$

The result, expressed in terms of $\phi_N$, has the form

$$kP\sigma^2[1 - (\phi_N{}^2/N\sigma^2)^2] = \phi_N \ln (1 - \phi_N) + \phi_N{}^2 \tag{III.9}$$

where $k$ is a coefficient of order unity. The condition (III.9) is qualitatively displayed in Figure 7 as a plot of $\phi_N$ vs. $P\sigma^2$. There are three regions in the curve.

(a) When $\sigma < \sigma_1$ ($\sigma_1$ being defined in eq III.5), the relation reduces to $\phi_N{}^2 = N\sigma^2$ and this simply corresponds to $L \simeq R_0$, i.e., to unstretched chains.

(b) When $\sigma_1 < \sigma < \sigma_2$, where

$$\sigma_2 = P^{-1/2} \tag{III.10}$$

it is possible to expand the right-hand side of eq III.9 in powers of $\phi_N$; then the leading term (of order $\phi_N{}^3$) dominates. Physically this means that we have $L \gg R_0$ but still $\phi_N \ll 1$. We associate this with the symbol S.M.

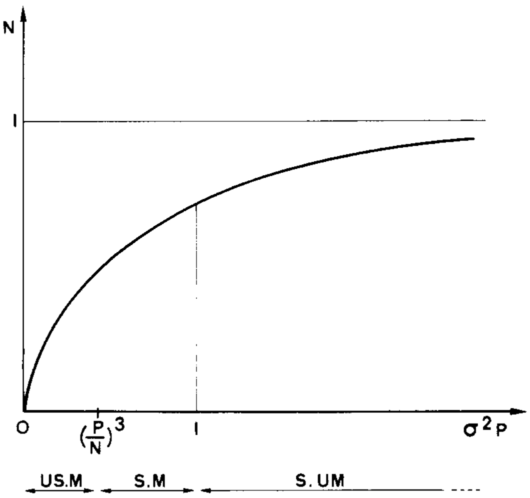

**Figure 7.** Relation between the grafted chain concentration ($\phi_N$) and the density of grafted points ($\sigma$) for a grafted layer in contact with a polymer melt (mobile chains of $P$ monomers per chain, with $P < N$) (qualitative plot).

(c) When $\sigma \gtrsim \sigma_2$, $\phi_N$ and $\phi_P$ become comparable: we find a progressive expulsion of the P chains, and we reach a regime UM.S. Ultimately for $\sigma \rightarrow 1$ the N chains are completely stretched and segregated from the melt.

It is of importance to note that

$$\sigma_1/\sigma_2 = (P/N)^{3/2} \leq 1 \tag{III.11}$$

Thus when all chains become equal in length, the intermediate regime b becomes evanescent. For $P > N$ we cannot use the simple form (III.6) of the mixing entropy: the P chains are too large, and a more detailed spatial calculation would be required.

## IV. Semidilute Solutions

Let us start from the pure-solvent case of section II, assuming that the chains *do overlap* and build up a certain swollen layer. We now add mobile chains to this solvent, imposing a polymer volume fraction $\phi_P = \phi$ far from the wall. What happens to the grafted layer? Two regimes are clearly present, depending on the ratio $\phi/\phi_{N0}$, where $\phi_{N0} = \sigma^{2/3}$ was the concentration inside the grafted layer for the pure-solvent case (eq II.9).

**A. Low Concentration of Mobile Chains. Strongly Stretched Regime.** Here the layer is still essentially described by the analysis of section II. The layer thickness $L$ is large and is given by eq II.10. The overall concentration profile does not differ much from Figure 6 (except for the presence of a small nonzero value at $z > L$).

We shall briefly discuss the *partition* of the mobile chains between the bulk solution and the layer. This can be calculated in detail by the propagator methods of Edwards,[16] adjusted for a case where blobs of size $D$ are the basic unit. We give here a rough, but simplified calculation. Physically (for $P < N$) there are two regions of importance: one inner region, where standard partition arguments apply, and one outer region, where the chains penetrate partially (see Figure 8).

**1. Outer Penetration Layer.** Consider first the case of one mobile chain which has *partially* entered in the layer, $\nu$ monomers being inside and $P - \nu$ outside. Scaling theorems tell us that the work $W_\nu$ required to bring it from the low-$\phi$ solution outside to this situation is essentially $kT$ per blob[9]

$$W_\nu = (\nu/g_D)kT \tag{IV.1}$$

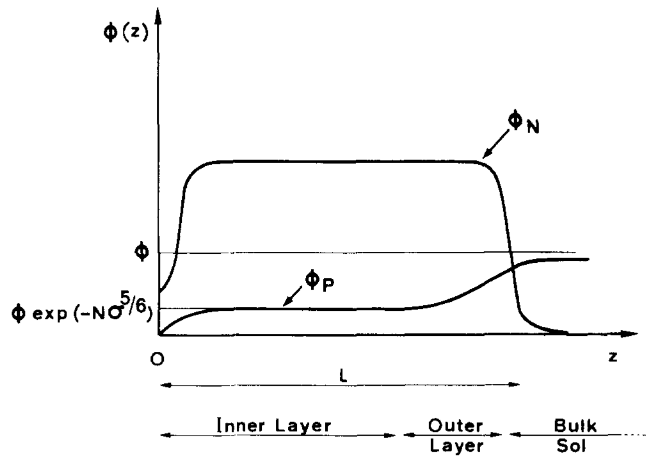

**Figure 8.** Concentration profiles in the strongly stretched regime.

(Note that there is no important contribution to $W_\nu$ originating on the other side by extraction from the bulk solution, since $\phi \ll \phi_{N0}$.) Omitting all prefactors, we write

$$\frac{\phi_P(z)}{\phi} \simeq \sum_{\nu=1}^{P} \exp\left(-\frac{W_\nu}{kT}\right) H\left[(L-z)^2 \Big/ \frac{\nu}{g_D} D^2\right] \qquad \text{(IV.2)}$$

The function $H(u)$ must be unity when $u$ is small, i.e., when a random walk of $\nu$ blobs can reach point $z$. But $H(u)$ must be zero for the opposite case. It is natural (and in fact correct) to assume that $H(u) = \exp(-u)$. Then we can compute (IV.2) by saddle-point integration and find that the leading contributions come from

$$\nu/g_D = (L - z)/D \qquad \text{(IV.3)}$$

giving

$$\phi_P(z)/\phi \simeq \exp[-(L - z)/D] \qquad \text{(IV.4)}$$

The result (IV.4) is meaningful only when $\nu < P$ or, equivalently, in a certain outer layer

$$L - z < P/g_D = aP\sigma^{1/3} \qquad \text{(IV.5)}$$

Note that the thickness of the outer layer is *linear in P*: in this layer the mobile chains are stretched as much as the grafted chains.

**2. Inner Region.** When the inequality IV.5 is reversed, our eq IV.2 ceases to be valid: penetration occurs through mobile chains which are entirely immersed in the grafted layer; for these chains $\nu = P$ and there is no factor equivalent to $H(0)$. Thus we arrive at

$$\phi_P = \phi \exp(-N/g_D) \simeq \phi \exp(-N\sigma^{5/6})$$

This is the type of result which is discussed in ref 7.

**B. Transition from Strong Stretching to Weak Stretching.** Let us now assume that the bulk polymer concentration $\phi$ is larger than the threshold $\sigma^{2/3}$. We shall see that this leads to a *decrease* of the layer thickness $L$: we expect a (progressive) transition from strong stretching to weak stretching.

There are, in fact, two possible schemes for this process, and both of them can be physically obtained. We discuss them successively below.

**1. Mobile Chain Dominance (Figure 9a).** In this scheme, we reach a situation where the N chains are still a minority component, with $\phi_N \ll \phi_P$ in the grafted layer. Then $\phi_P$ is not very different from the bulk concentration $\phi$. We say that, in this regime, the mobile chains are *dominant*. They impose, in particular, the blob size: this becomes equal to the correlation length $\xi$ associated with the overall semidilute solution

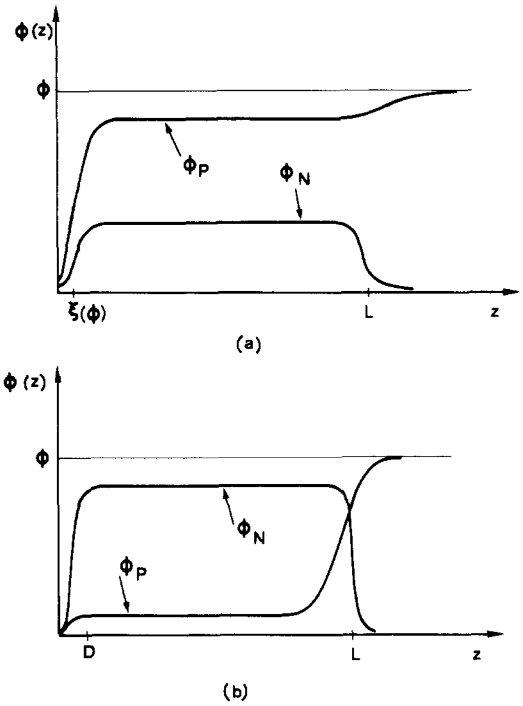

**Figure 9.** Two regimes of weak stretching: (a) mobile chain dominance $\phi_P \gg \phi_N$; (b) grafted chain dominance $\phi_P \ll \phi_N$.

$$\xi = a\phi^{-3/4} \qquad \text{(IV.6)}$$

The corresponding number of monomers per blob is

$$g = \phi^{-5/4} \qquad \text{(IV.7)}$$

For all properties which involve scales larger than the blob size, we can transpose immediately our discussion of section III for melts, treating the solution as a *melt of nonoverlapping blobs*.[9] For instance, the $\zeta$ parameter of eq III.3 becomes

$$\zeta = \left(\frac{N}{g}\right)^2 \frac{\xi^3 g}{P} \frac{1}{D^2 R(\phi)} \qquad \text{(IV.8)}$$

where $N/g$ is the number of blobs per grafted chain, $\xi^3$ is the bare excluded volume per blob, and $g/P$ is the *screening factor*. (For a different discussion of these factors, see ref 12.) Finally $R(\phi)$ is the ideal size for a string of $N/g$ blobs, each of size $\xi$

$$R^2(\phi) = (N/g)\xi^2 \qquad \text{(IV.9)}$$

It is essential to appreciate the difference introduced here by screening effects: for $\phi < \sigma^{2/3}$ we had an unscreened repulsion between blobs of size $D$, leading to very strong stretching. But for $\phi > \sigma^{2/3}$ (and if we are in a case of mobile chain dominance) the P chains penetrate in the grafted layer and screen out the interactions between the N chains: then the thickness of the grafted layer is significantly reduced.

Let us first write down the $\zeta$ parameter explicitly. Inserting (IV.6), (IV.7), and (IV.9) into (IV.8), we arrive at

$$\zeta = \sigma N^{3/2} P^{-1} \phi^{-7/8} \qquad \text{(IV.10)}$$

The condition $\zeta = 1$ corresponds to a crossover between unstretched and stretched chains. This defines a certain line BC in the $(\phi, \sigma)$ plane of Figure 2

$$\sigma = \phi^{7/8} P N^{-3/2} \qquad \text{(IV.11)}$$

Note that for $\phi = 1$ this agrees, as it should, with the corresponding result of section III.

Let us now assume that we are in the region $\zeta > 1$ (always maintaining our assumptions $\phi > \sigma^{2/3}$ and $\phi_P \gg \phi_N$) and compute the thickness $L$ in this weakly stretched regime. The starting point is a free energy per chain, $F$, with the qualitative form

$$\frac{F}{kT} \simeq \frac{L^2}{R^2(\phi)} + \left(\frac{N}{g}\right)^2 \frac{\xi^3 g}{P} \frac{1}{LD^2} \qquad \text{(IV.12)}$$

After optimization with respect to $L$ this gives

$$L \simeq \xi \frac{N}{g} \left(\frac{\xi}{D}\right)^{2/3} \left(\frac{g}{P}\right)^{1/3} \qquad \text{(IV.13)}$$

$$= \sigma^{1/3} N P^{-1/3} \phi^{-5/12} \qquad \text{(IV.14)}$$

Note that this value does *not* cross over to eq II.10 when $\phi = \sigma^{2/3}$. The screening effect (described by $P^{-1/3}$ in eq IV.14) disappears when we return to the regime of section IV.1.

Let us now discuss the internal self-consistency of our approach. We assumed $\phi \simeq \phi_P \gg \phi_N$, but we can now compute the concentration due to grafted chains $\phi_N$ inside the grafted layer from eq IV.14. The result is

$$\phi_N = \sigma^{2/3}(P/g)^{1/3} = \sigma^{2/3} P^{1/3} \phi^{5/12} \qquad \text{(IV.15)}$$

Our assumption of mobile chain dominance is correct only when $\phi_N \ll \phi$ or

$$\sigma < P^{-1/2} \phi^{7/8} \qquad \text{(IV.16)}$$

This defines the line DE in Figure 2. Our next task is to find out what happens for $\sigma$ values above this line.

**2. Grafted Chain Dominance (Figure 9b).** The second scheme, which can also be realized when $\phi > \sigma^{2/3}$, corresponds to $\phi_N \gg \phi_P$, i.e., to an unmixed (UM) situation.

This automatically implies

$$\phi_N = \phi \qquad \text{(IV.17)}$$

The argument is the following: in the bulk solution each P chain sees a certain repulsive potential due to the other P chains, which we call $\mu_{rep}(\phi)$. Scaling imposes

$$\mu_{rep}(\phi) = kTPg^{-1} \simeq kTP\phi^{5/4} \qquad \text{(IV.18)}$$

in the semidilute region, but we shall not need this precise form here. In the grafted layer, if the P chains are dilute, each of them sees a repulsive potential which is due only to the N chains and is the same function $\mu_{rep}(\phi_N)$. The equilibrium condition for the P chains then requires

$$\mu_{rep}(\phi) = \mu_{rep}(\phi_N) \qquad \text{(IV.19)}$$

and this leads to (IV.17).

In this situation, we can easily find out the thickness $L$ of the grafted layer: we must have $LD^2\phi_N = N$ and, using eq IV.17, this gives

$$L = \sigma N \phi^{-1} \qquad \text{(IV.20)}$$

If we compare this form to eq IV.14, we see that the two predictions coincide when $\sigma = P^{-1/2}\phi^{7/8}$, in agreement with our definition (IV.16) of the crossover line DE (Figure 2). We conclude that above the line DE the second scheme is indeed realized: we have a weakly stretched, unmixed situation (WS.UM). One final remark concerns the crossover SS.UM $\leftrightarrow$ WS.UM on the line $\sigma = \phi^{3/2}$. If we compare eq IV.19 and II.10, we find that there is also a smooth crossover for $L(\sigma, \phi)$ on this boundary.

Thus the behavior of the grafted layer thickness—when we increase $\phi$ beyond the line $\phi = \sigma^{2/3}$—is very different in the two schemes. In the first scheme (line portion BD) we expect a rather abrupt collapse of the grafted layer. In the second scheme (line portion DF) the contraction is more gradual.

## V. Conclusions

How can we test the simple ideas which have been presented above?

(1) For the pure-solvent limit, the thickness $L$ of the grafted layer can be measured by hydrodynamic techniques[17] (investigating either the permeability of fine pores or the mobility of small spheres with a grafted surface). The main laws to be checked here are the linear dependence of $L$ on molecular weight in the overlapping regime and the $\sigma^{1/3}$ dependence on graft density (eq II.10). It may be difficult to achieve $\sigma$ values well beyond the overlap criterion ($\sigma > N^{-6/5}$): rather than bringing polymer chains to the surface and attaching them there, it may be preferable to synthesize them in situ, from an initiator site on the surface. Another approach employs a liquid interface, with amphiphilic block copolymers anchored at the interface, instead of a solid wall: here, each half of a diblock spreads in its preferred solvent and plays the role of a grafted chain. Our discussion may be useful in discussing the *detergent properties of block copolymers*.

(2) When some solute P chains are added, it is of interest to study their penetration in the grafted layer. One parameter that can be obtained by ellipsometry,[18] the local refraction index

$$n(z) = n_s + n_1[\phi_P(z) + \phi_N(z)] = n_s + n_1\phi(z) \qquad \text{(V.1)}$$

measures only the global polymer concentration $\phi(z)$. A more sophisticated method would be based on neutron diffraction.[19] Using deuterated N chains, for instance, one can first (in principle) determine $\phi_N$. Then deuterating the solvent, one obtains from a second experiment an independent combination of $\phi_N$ and $\phi_P$. However, this requires large samples with a sizable surface-to-volume ratio and is clearly not an easy experiment.

(3) For the case of polymer melts, deuteration would again by very helpful. Another method would imply a slight generalization of our model: if the N chains and P chains are chemically different but compatible (as is known for a few favorable cases), our analysis should remain meaningful. Using two optical wavelengths, one could then, in principle, measure both $\phi_N$ and $\phi_P$ by ellipsometry.

Of course, in all these situations, we can also think of *local studies* by EPR, NMR, fluorescence, etc.[20] However, the interpretation of the resulting data is much more complex and is sometimes complicated by special effects due to the "label" molecule itself.

The essential conclusion is derived from Figure 2: in view of the many states predicted here it is absolutely necessary to start from a relatively *simple model system*; then there is hope for reaching a clear-cut classification and a good physicochemical picture for all states, provided that the parameters $\sigma$, $N$, $P$, and $\phi$ are varied systematically. On the other hand, all more delicate effects related to poor solvents, adsorption, etc. will probably not be understood fully before the end of this first step.

We particularly need model systems with *long chains* ($N \gtrsim 100$). Most practical systems have $N < 20$ (either in chromatography or for conventional detergents). However, a fundamental understanding of the amphiphilic properties of detergents is still lacking: the chains are too long to be analyzed by fully detailed molecular models, but at the same time they are too short to display the general scaling laws discussed here. What is needed is a systematic effort based on block copolymers.

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# Ring–Chain Equilibrium of Macrocyclic Formals[1]

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ABSTRACT: Equilibrium polymerizations of 1,3,6-trioxacyclooctane (TOC), 1,3,6,9-tetraoxacycloundecane (11-CF-4), 1,3,6,9,12-pentaoxacyclotetradecane (14-CF-5), and 1,3,6,9,12,15-hexaoxacycloheptadecane (17-CF-6) were studied in dichloromethane by using boron trifluoride ethyl etherate ($BF_3 \cdot OEt_2$) as a catalyst. Thermodynamic parameters of the polymerization of these macrocyclic formals and their oligomers were evaluated from the dependence of their equilibrium concentrations on polymerization temperature. Although the enthalpy changes for polymerization, $\Delta H_p$, are observed to be finite even for the 34-membered ring (dimer of 17-CF-6), those for the cyclic oligomers having rings with more than 40 members are virtually equal to 0. The polymerizability of these macrocyclic oligomers is controlled only by the entropy term. The molar cyclization equilibrium constant decreases in proportion to the −2.5 power of the ring size $x$, in accordance with the Jacobson–Stockmayer theory, when $\Delta H_p$ is negligibly small.

The polymerizability of cyclic monomers has been extensively investigated for the cyclics having rings with less than 10 members, but little attention has been devoted to macrocyclics. The recent development of GPC has made it posible to isolate, identify, and quantify high molecular weight compounds, and formation of cyclic oligomers has become a matter of increasing interest, particularly in the field of cationic polymerization of heterocyclic monomers.

We investigated the polymerization behavior of macrocyclic formals having ether oxygens along with acetal oxygens and found that the cationic polymerization of these monomers was accompanied by the formation of considerable amounts of cyclic oligomers,[2-5] a fact which seems very interesting from a thermodynamic point of view. Recently, we reported[6] that the polymerization of 17-CF-6 could be described essentially as a thermodynamically controlled ring–chain equilibrium system and suggested that its dimer (34-membered ring) might have some ring strain because a negative enthalpy value (−0.76 kcal/mol) was determined from a plot of Dainton's equation. In order to clarify the nature of the ring-opening polymerizability of these macrocyclic formals, we have carried out an investigation on the thermodynamics of the cationic polymerizations of TOC, 11-CF-4, 14-CF-5, and 17-CF-6 by $BF_3 \cdot OEt_2$.

## Experimental Section

**Materials.** TOC, 11-CF-4, 14-CF-5, and 17-CF-6 were prepared from the corresponding glycols and paraformaldehyde according to the method described in the literature.[2,5] These formals were purified by fractional distillation over lithium aluminum hydride. They were redistilled from lithium aluminum hydride under a nitrogen atomosphere just before use: TOC, bp 66.0 °C (50 mm); 11-CF-4, bp 60.0 °C (0.5 mm); 14-CF-5, bp 98 °C (1.8 mm); 17-CF-6, bp 127 °C (0.1 mm). These monomers proved to be pure (>99.98%) by gas chromatography. Commercial dichloromethane was refluxed over phosphorus pentoxide and fractionally distilled under a nitrogen atmosphere. Commercial *n*-decane and *n*-tetradecane were used as internal standards in gas chromatography.

**Polymerization and Depolymerization Products.** Under a nitrogen atmosphere the dichloromethane solutions of a monomer, an internal standard, and an initiator were mixed in a 30-mL volumetric flask to which was attached a three-way stopcock, and the flask was immediately immersed in a thermostated bath. At specified intervals, a small portion of the reaction mixture was taken out with a syringe through the

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