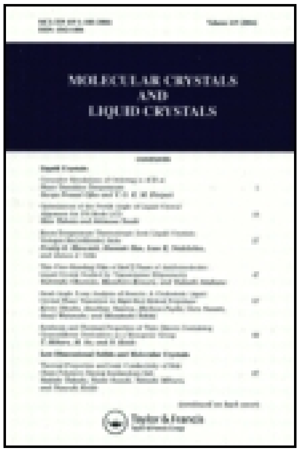

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Polymers at Interfaces

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POLYMERS AT INTERFACES

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Abstract Basics ideas on the behavior of polymer solutions near solid surfaces is given. A review of the various theories describing the distribution of monomers in the interfacial layer is developped. The various experimental techniques available to characterize the polymer distribution at the interface are described, together with a comparison of the data to the theoretical predictions. Some theoretical and experimental results on mixtures of polymers and liquid crystals, in solutions and at interfaces, are recalled.

INTRODUCTION

Polymer molecules, owing to their large extension exhibit very particular properties in bulk or at solid/liquid interfaces. This later case has lead to interesting technological developments in various fields, such as lubrication, adhesion, and colloid stabilization. Before going into the description of the adsorbed polymer, I shall recall some properties of bulk polymer solutions.

A polymer molecule is made of a succession of N identical units of length a : the monomers. The discussion will be restrict to linear and flexible chains. The later assumption means that each unit can rotate freely around its end bonds.

The structure of a chain depends on the solvent and also on the concentration of polymer molecules in the solution. We will restrict our description to the case of polymer chains in "good solvent". This situation occurs when the monomer-solvent interactions are favorised. The monomers are thus preferentially surrounded by solvent molecules and avoid the other monomers. If the concentration of polymer is small, the chains do not interact and they can be seen as swollen coils with a radius of gyration[1] R_G (fig. 1a) :

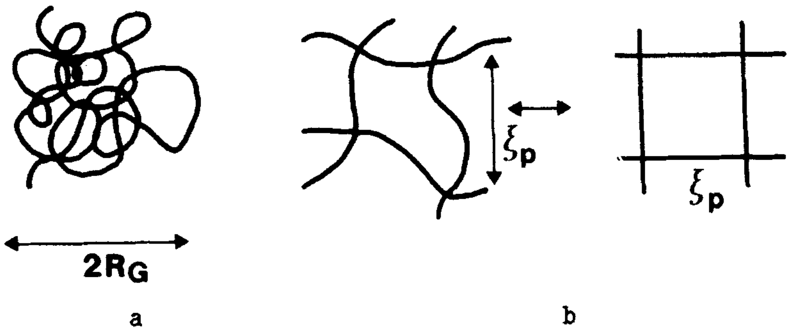


FIGURE 1. Structure of polymer chains in bulk solutions. a) Polymer coil of size R_G in dilute solution; b) semi-dilute polymer solution (volume fraction $\phi_b > \phi^*$) idealized as a "grid" with the same mesh size $\xi(\phi_b)$.

$$R_G = aN^{3/5} \quad (1)$$

Above a critical volume fraction of polymer ϕ^* equal to Na^3/R_G^3 the chains overlap, this is the so-called semi-dilute regime. The characteristic length is now the distance between entanglements ξ_p (fig. 1b) :

$$\xi_p = a\phi_b^{-3/4} \quad (2)$$

where ϕ_b is the volume fraction of polymer in the solution. The number of monomers g in one subunit of size ξ_p is:

$$g = \phi_b^{-5/4} \tag{3}$$

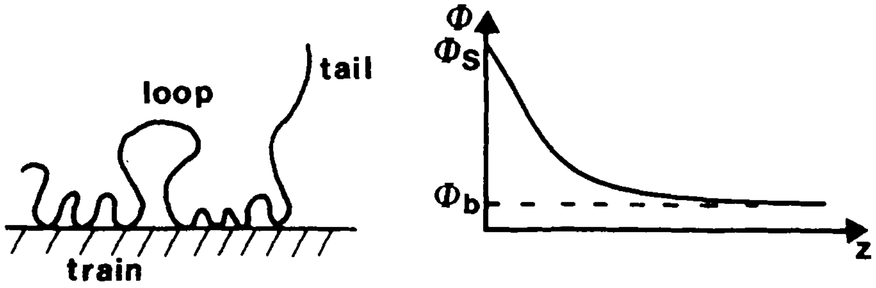
Typically N is of the order of 10-10000,a ≅ 3A° and ξ_p in the range 0 - 100 A°. g and ξ_p will be useful to understand the structure of the adsorbed layer.

POLYMERS SOLUTIONS AND SOLIL SURFACES

ADSORPTION VERSUS DEPLETION

When a polymer chain in solution comes into contact with a solid surface two cases are possible :

1) If the polymer monomers prefer some particular sites of the surface to the solvent molecules, the chains will adsorb on the surface. The gain in free energy per adsorbed monomer is of the order of kT, and the adsorbtion is said "strong".



a b

FIGURE 2. Multichain adsorption from a good solvent : a) qualitative aspect of the diffuse layer ; b) concentration profile $\phi(z)$.

The structure of the adsorbed molecules at high coverage density is described in terms of tails, loops and trains (fig. 2a), and the polymer distribution $\phi(z)$ has the general shape given in fig. 2b.

2) If the surface prefers the solvent to the polymer, the chains will avoid the surface, leading to a depletion layer at the interface (fig. 3). Depletion is not common, and generally occurs in charged systems, when the surface and the monomers are of opposite sign.

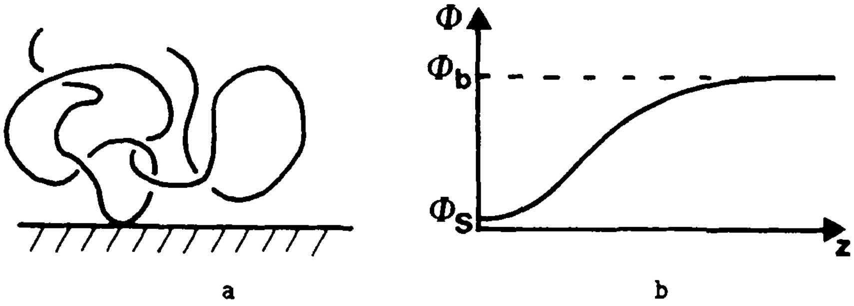


FIGURE 3. Depletion layer near a repulsive wall : a) qualitative aspect of the interfacial layer ; b) concentration profile $\phi(z)$.

For adsorption and depletion, the thickness of the interfacial layer will be that of the characteristic length of the solution, i.e. R_G for dilute solutions or ξ_p for semi-dilute solutions.

MODES OF ADSORPTION

Physisorption (or Adsorption)

In the case of neutral polymers the attractive forces can be van der Waals forces or hydrogene bonds[2,3], this is the usual adsorption process.

Grafting

If the polymer does not attach spontaneously to the surface, one can chemically attach the chains by one end to the surface (fig. 4). In good solvent conditions the monomers will repell each other and the grafting reaction leads to "mushrooms" at low grafting density or "brushes" at high grafting density.An example is the grafting of polystyrene (PS) on hydrophobic silica spheres.[4]

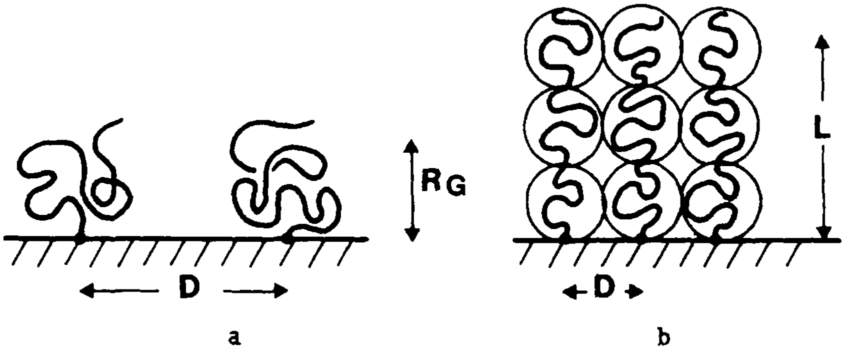


FIGURE 4. Two types of grafted surfaces : a) low grafting density. The distance between heads D is larger than the radius of gyration R_G ("mushroom" regime) ; b) high grafting density $D < R_G$ ("brush" regime).

Diblock Copolymers

A diblock copolymer is made of a chain A linked to a chain B. If for a given solid/solvent couple, A is insoluble and spontaneously adsorbs on the solid, while B is in good solvent and does not adsorb, A precipitates on the surface while B builds up an external brush (fig. 5). An example is the case of a chain where A is polystyrene (PS) and B is polyvinylpyridine (PVP) in water facing a mica surface.[5]

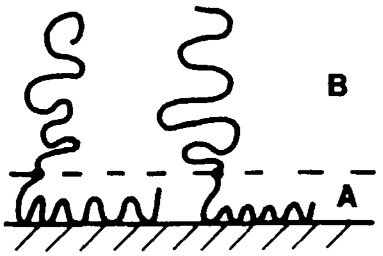


FIGURE 5. Attached diblock copolymers AB : A precipitates against the wall while B protrudes towards the solution.

THEORETICAL DESCRIPTION OF THE ADSORBED LAYER

The problem of describing the distribution of monomers in the adsorbed layers has been tackled by two different approaches : mean-field and scaling.

MEAN FIELD THEORIES

In the mean-field analysis a polymer chain experiences an average potential composed of a short-range part due to the wall, and a long-range repulsive part proportional to the concentration profile $\phi(z)$. Such a problem can be treated analytically and one gets analytical expressions for $\phi(z)$ of the form :[6-8]

$$\phi(z) \sim \phi_b \, \mathrm{cotanh}^2 \, ((z + a)/\xi_{MF}) \qquad (4)$$

with ξ_{MF} is the mean-field distance between entanglements in semi-dilute solutions. Another approach is to use mean-field assumptions and to inscribe the polymer chains on a lattice adjacent to the adsorbing wall,[9,10] the lattice sites being either occupied by a segment or a solvent molecule. The recent Scheutjens and Fleer[10] calculations give a detailed description of the adsorbed layer with quantitative informations on the trains, the loops and the tails.

SCALING ANALYSIS

Adsorbed Chains

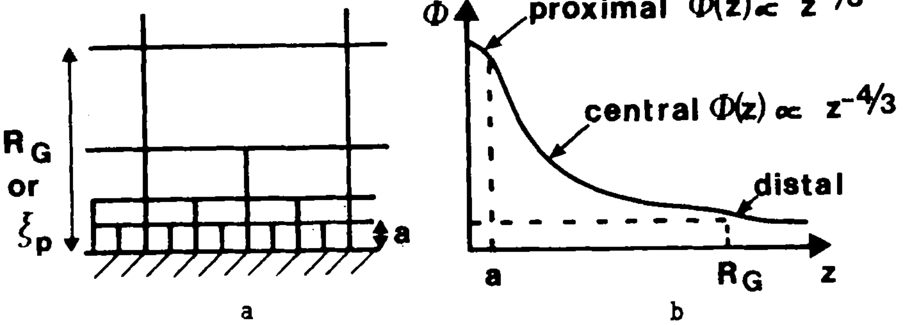


FIGURE 6. Structure of the adsorbed layer. a) the "self-similar grid", at any distance z from the wall, the local mesh size is equal to z. b) the concentration profile, $\phi(z)$, with the three regions : 1) proximal (very sensitive to the details of interactions) ; 2) central (self-similar) ; 3) distal (controlled by a few loops and tails).

Due to the low concentration of polymer in the adsorbed layer, there exist large fluctuations not taken into account in the mean-field theories. This has lead to the development

of the scaling law analysis[1] which treats the fluctuations and the correlations in a more rigorous way. The keypoint is that the adsorbed layer is considered as a semi-dilute solution. Thus the layer is described as a self-similar structure where at any distance z from the wall, the local mesh size $\xi_p(z)$ is equal to z (fig. 6). This assumption gives the structure of the profile.[11]
In the case of good solvents $\phi(z)$ is derived as :

$$\xi_p(\phi(z)) = z \tag{5}$$

using Eq. (3) we get:

$$\xi_p(z) \sim (a/z)^{4/3} \tag{6}$$

The self-similar structure is no longer valid at very small z and at very large z. In the case of strong adsorption the lower limit is the monomer size (Zmin = a). For an adsorbed layer facing a dilute solution, the upper limit is the size of a chain ($Z\text{max} = R_G = N^{3/5}$). If the adsorbed layer is facing a semi-dilute solution Zmax is equal to the characteristic length of the solution $\xi_p(\phi_b)$. Due to the large number N of monomer units, the self-similar description is meaningful. In the proximal region, $0 < z < a$, $\phi(z)$ is of the form :[12]

$$\phi(z) \sim (a/z)^{1/3} \tag{7}$$

For $z > R_G$ (or $z > \xi_p(\phi_b)$), extends the distal region where $\phi(z)$ relaxes exponentially to the bulk concentration ϕ_b.

End Grafted Chains

Following the same basic ingredients as those used for normal adsorption, Alexander[13] and de Gennes,[14] described the profile of a grafted layer when the chains do not adsorb on the surface. If the grafting level is low, the chains adsorb like separate "mushrooms", each of size R_G (fig. 4a). At high grafting density the adsorbed layer is described as a "brush" of length L. The crucial parameter of the system is the distance D between attachment points. In the central part of the layer the concentration is uniform (fig.4b), $\bar{\phi}$, and the mesh size is equal to D.

$$\xi(\bar{\phi}) = D \tag{8}$$

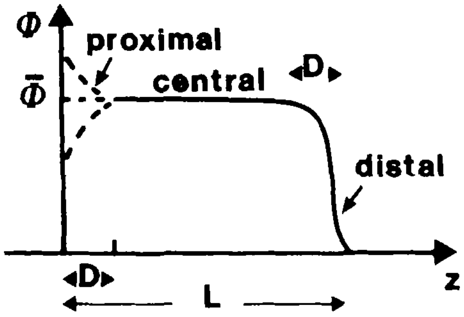


FIGURE 7. Theoretical concentration profile inside an end grafted layer. In the central region the concentration is uniform. In the proximal region the profile depends on the details of the monomer-wall interactions.

As shown in fig. 4b, the chains in the brush are stretched out and can be described as a sequence of subunits of size D containing g monomers each, with:

$$g = \phi^{-5/4} = (D/a)^{5/3} \qquad (9)$$

The overall thickness of the layer is then :

$$L = (N/g)D = Na(a/D)^{2/3} \qquad (10)$$

This ideal situation, $D \ll R_G$ is experimentally hard to achieve. Recent experiments with diblock copolymers[5] tend to support the above description.

More General Situations

The above description of adsorbed layers and brushes assumed a good solvent and no additives.

1) If we decrease the quality of the solvent, the structures tend to become more compact. Klein and Pincus[15] have made some computations for adsorbed layers.

2) In the case of brushes if we add some free polymer (chemically identical to the grafted chains), the layer tends also to shrink.[14] One basic source of shrinkage is a "screening effect" : the free polymers screen out the repulsive interactions between monomers from the brush.

EXPERIMENTAL TECHNIQUES AND RESULTS

Determination of the exact concentration profile is on the way as we shall see later, but nevertheless a lot of data on macroscopic observables are already available.

SURFACE EXCESS AND ADSORBTION ISOTHERMS

The surface excess Γ can be seen as the zeroth moment of the adsorbed polymer distribution :

$$\Gamma = \int_0^\infty (\phi(z)dz)/a^3 \qquad (11)$$

Γ is expressed either in monomers/m2 or g/m2. A classical technique to determine Γ is the analysis of the supernatant solution after incubation of the polymer solution with the solid surface. To ensure enough sensitivity the solid surface needs to have a large adsorbing surface. The resulting isotherm of adsorption has the shape given in fig. 8 :

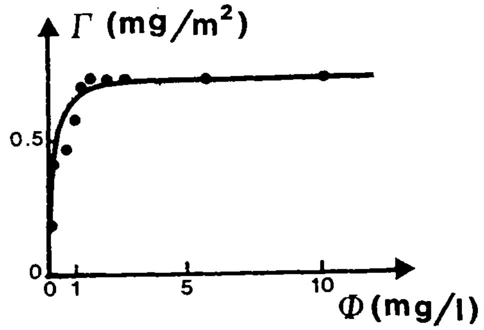


FIGURE 8.Adsorption isotherm of polyacrylamide (Mw = 1.2 x 10^6) on modified silica spheres from Pefferkorn et al..[16]

The general result is that in the plateau region the surface excess is of the order of a few mg/m2, equivalent to about one monolayer of monomer. The experimental data are in good agreement with the theoretical predictions. Furthermore an interesting result is that for large chains, the surface excess is roughly independent of the molecular weight as predicted from Eq. (6)

$$\Gamma \sim (1/a^2) \qquad (12)$$

HYDRODYNAMIC THICKNESS

A flow of solvent near an adsorbed layer is highly perturbed even by a few tails or loops. The theory predicts that the hydrodynamic thickness e_H should be comparable to the coil size R_G. e_H is measured either by measuring the self-diffusion of small particles covered with polymer[17] or by monitoring the reduction of the flow of solvent through polymer coated capillaries.[18] The experimental data on polystyrene spheres covered with polyethylenoxide (PEO) in water[19] support Eq. (15), although other data[17] on the same system give $e_H - N^{0.8}$.

ELLIPSOMETRIC THICKNESS

A flat bare surface reflects light of all polarizations. However for incident light polarized in the plane of incidence, for a special incidence (the Brewster angle), there is no reflected intensity. This cancellation disappears as soon as the surface is covered by an adsorbed layer with a different optical index than that of the bare surface. The reflected intensity is related to the surface excess. A detailed study shows that ellipsometric measurements give the first moment z of the profile.[20] From Eq. (6) the ellipsometric thickness e_l is thus :

$$e_l \sim aN^{2/5} \tag{13}$$

The results of Kawaguchi et al.[21] support this theoretical prediction.

FORCES MEASUREMENTS

Recent advances in the determination of forces between plates separated by very small distances (10 A° < h < 104 A°) by Israelashvili[22] have opened new possibilities for the measurement of the extension of the adsorbed layer. J. Klein and coworkers[23-25] have performed experiments with polyethylenoxide adsorbed on mica surfaces in water at room temperature. They observed that in reversible conditions the forces between the plates are repulsive at all measurable distances, and shows up at a distance of about 4 R_g More recently M. Tirrell et al.[5] have performed force measurements on diblock copolymer (PS + PVP), investigating the thickness of the brush. Their results tend to support the "self-similar" structure.

NEUTRON SCATTERING TECHNIQUES

The small angle neutron scattering technique has been used to investigate the profile $\phi(z)$ of the adsorbed layer.[26,27] In these experiments the polymer chains were not long enough to reach the domain where scaling laws are applicable, and the data fit pretty well the Scheutjens and Fleer model.[28] Recent experiments performed by Auvray and Cotton[29] with bigger molecules (PDMS, Mw = 265000 on silica) are in agreement with the "self-similar" picture of the adsorbed layer.

FLUORESCENCE TECHNIQUE

Combining the spatial resolution of the optical evanescent waves and the sensitivity of fluorescence, the Evanescent

Wave Induced Fluorescence Technique (E.W.I.F.) has been developed.[30] It has proven to be powerful in the case of depletion, and its application to adsorption is under development.

DYNAMICAL PROBLEMS

Except for grafted chains, the question which arises for adsorbed chains is how stable is such a layer ?

STABILITY UNDER WASHING

If we wash out with pure solvent an adsorbed polymer layer of long chains after a long incubation time, we observe that the layer does not redissolve.

EXCHANGE WITH THE BULK AT FINITE CONCENTRATIONS

It is well established that adsorbed polymer chains can be displaced by homopolymers of larger molecular weight.[31] Nevertheless extreme preferential adsorption is usually not observed.[32] Precise isotopic exchange experiments performed by Pefferkorn and al.[33] have shown that desorption of surface molecules occurs only in the presence of a polymer solution. The rate of desorption increases proportionally to the bulk concentration.

THEORETICAL EXPLANATION [34]

An important feature of the adsorbed layer is the strong repulsive interaction between adjacent chains in good solvent. When at equilibrium if we try to add more chains, their free energy becomes higher than in the bulk solution and they are repelled out. Thus at equilibrium the energy balance tends to maintain Γ constant. If we take into account this feature in the adsorption or desorption rate equations, we find that the chains can escape from the adsorbed layer at equilibrium only if there are free chains in the solution which can replace the missing one, and keep Γ constant. This condition of nearly constant Γ is called the "saturation condition". This mechanism explains why Pefferkorn and al.[33] found that the desorption rate was proportional to the bulk concentration, and the stability of adsorbed layers in pure solvent.

ADSORBED POLYMERS AND LIQUID CRYSTALS

What will happen to the adsorbed layer when facing a liquid crystal phase ? Our knowledge in this area is very restricted and a lot a work has still to be done. Some experimental data are available for bulk mixtures.[35,36] Also some theoretical conjonctures on the behavior of adsorbed polymer layers in the presence of liquid crystals have been suggested.[37]

BULK SOLUTIONS

An important result is that polymer chains with molecular weights larger than 10^4 are immiscible with liquid crystal. Theoretical models have been proposed[36] with a crucial parameter Win which is the change in energy for a monomer going from the isotropic phase to the liquid crystal phase. If Win is large , this is the regime of "strong perturbation", the liquid crystal is in the isotropic phase inside the polymer chain. Otherwise the liquid crystal phase still exists inside the polymer coil.

GRAFTED LAYERS

A more interesting situation, is that of grafted chains on a surface in a nematic phase. A theoretical study has been done by F. Brochard[37] with the following assumptions :

a) no polymer adsorption : the chains are attached by one extremity to the wall, but the rest of the chains does not stick to the wall.

b) the wall has no influence on the nematic order parameter : with no grafted chains the boundary condition for S is $\partial S/ \partial z = 0$ on the wall.

c) the nematic order is suppressed inside the chains.

d) the chains are in good solvent in the isotropic phase.

e) the nematic order parameter is a scalar (instead of a traceless tensor of rank two). This amounts to neglect any spatial variation of the preferred axis, and to consider only the magnitude of the molecular alignment

The results of the theoretical calculations are condensed in figure 5.Five regimes are found for the structure of grafted chains , which can be described in reduced coordinates R_0/ξ vs $(\xi/D)^2$. Where R_0 is the ideal radius of the chains ($R_0 \sim aN^{1/2}$), and ξ is the nematic coherence length.

- $D > \xi$ and $R_0 < \xi$ this corresponds to separate coils with no interactions, each chain occupies roughly a half sphere of radius R_0 and destroys the nematic order up to a distance ξ (region N,Id).

- $D > \xi$ and $R_0 > \xi$. The chains are collapsed ($R \sim N^{1/3}$) but still contain a large amount of solvent (region N,C).

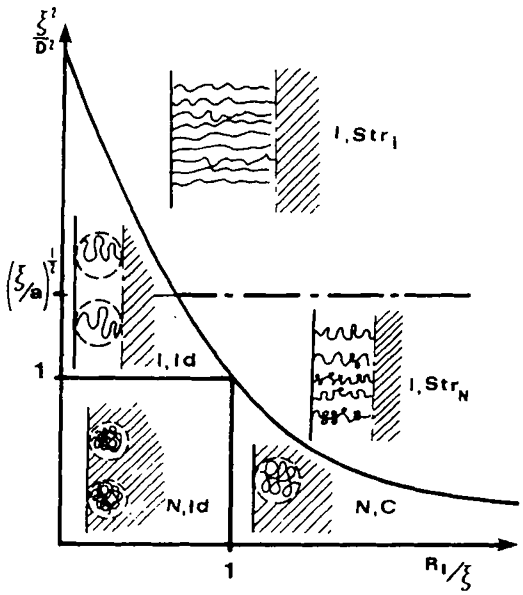


FIGURE 9. The five regimes of a grafted surface in a nematic solvent.

- $D < \xi$ and $R_0 < \xi$. The chains are separated but with interactions due to the nematic phase. The distorsions due to different coils overlap and S is now a function of the distance z to the wall. Inside the chain of radius R_0, $S = 0$. Outside this layer, $S(z)$ increases on a scale ξ up to S_0 (region I,Id).
- $D > \xi^{3/4} a^{1/4}$. The coils overlap directly and there is a competition between an internal osmotic pressure (due to excluded-volume) and an external osmotic pressure (due to S). In this regime of medium grafted density the chains are moderately stretched (region I,Str$_N$). The thickness L of the layer is :

$$L = N\ \xi (a/D)^2 \tag{14}$$

- $D < \xi^{3/4}\ a^{1/4}$. The elastic term becomes dominant and the chains are more stretched (region I, Str_I) with a layer thickness :

$$L = Na\ (a/D)^{2/3} \tag{15}$$

These different regimes could be studied by macroscopic methods such as contact angles measurements, ellipsometry or EPR. However the regime I_{Str}. could be difficult to obtain because of the difficulty of getting high density for grafted layers.

CONCLUSION

From this brief review on the knowledge of the structure and of the properties of adsorbed and grafted polymer chains, it appears that the theoretical models and experimental tools are in progress, but there is still much work to do. For the behavior of adsorbed layer interacting with liquid crystals, the whole field is still open for theoreticians and experimentalists.

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