Macromolecules **1992,** *25,* 6693–6695

Polymer Brushes in Mixed Solvents: Chromatography and Collapse

Pik-Yin Lai*

Institut für Physik, Johannes-Gutenberg-Universität Mainz, Postfach 3980, D-6500 Mainz, Germany

Avi Halperin

Materials Department, University of California, Santa Barbara, Santa Barbara, California 93106

Received April 7, 1992
Revised Manuscript Received July 23, 1992

I. Introduction

Liquid chromatography and the collapse of brushes are seemingly unrelated subjects. Yet, a close relationship is found when one explores the potential of polymer brushes, comprising terminally anchored chains[1], as the stationary chromatographic phase.[2] The mobile phase considered is a mixture of low molecular weight liquids. In particular, it is possible to modify the performance of the particles used as a stationary phase via dense grafting of terminally anchored polymers. Such coatings may be used to improve the performance of chromatographic columns with regard to the target component, i.e., to extend the linear adsorption regime and to enhance the selective adsorption.[3] As we shall see, the optimal regime is found when the majority component, the carrier, is a poor solvent and the brush is largely collapsed. The problem is also of interest from another perspective. Polymer brushes attract considerable current interest. Their properties, thickness for example, may be adjustable by immersion in a mixed solvent.[4] It is often assumed that the mixed solvent is the "average" of the two components. However, in reality it is necessary to allow for preferential adsorption of the better solvent. As we shall see, this indeed gives rise to a strongly nonlinear dependence of the layer thickness on the bulk composition.

Our discussion concerns the properties of a flat polymeric brush immersed in a binary mixture of two solvents of low molecular weight. We focus on the dependence of the brush thickness, H, and the adsorption isotherm on the polymerization degree of the grafted chains N, the grafting density σ, and the quality of the solvents. In particular, we characterize the relative surface excess, Γ, and the extent of the linear regime in the adsorption isotherm. These two last properties are of special interest in the characterization of chromatographic columns.[3] The grafted chains are assumed to be flexible, neutral, and monodisperse. The brush is described within the framework of the Alexander model:[1] The polymer concentration profile within the layer is constant and the chains are uniformly stretched. Similarly, we assume step functions for the concentration profiles of the two solvents. For simplicity, we ignore scaling correction and use the Flory exponents. The bulk solution is modeled as a regular mixture. Furthermore, we confine the discussion to the case of two solvents which are miscible in all proportions and have no preferential attraction to the grafting surface. In this situation the use of the Alexander model is permissible and, indeed, it allows us to recover the experimentally observed[4] features of the brush thickness as a function of solvent composition. In the opposite case, in the vicinity of a wetting transition, the description of the brush by means of self-consistent field theories is required.[5] The equilibrium conditions of a brush immersed in a mixed solvent are derived in section II. In section III we describe the behavior of the layer thickness. The adsorption isotherm is considered in section IV.

II. Polymer Brush Immersed in a Two-Component Solvent

We consider polymer chains of length N and monomer size a with one end grafted on a flat wall with area per chain S and surface coverage $\sigma = a^2/S$. The polymer brush is immersed in a mixture of two solvents, A and B. The volume fractions of the monomer, solvent A, and solvent B within the brush are denoted respectively by ϕ, ϕ_A, and ϕ_B where $\phi_A + \phi_B + \phi = 1$. ϕ and ϕ_A serve as the two independent variables in our calculation.

Upon denoting the number of A molecules per chain within the brush by M, the volume fractions of interest are given by

$$\phi = N\sigma a/H \tag{1}$$

$$\phi_A = M\sigma a/H \tag{2}$$

where H and M are to be determined from the equilibrium conditions. The free energy per unit area of a brush of given values of H and M is

$$F(H,M) = F_{el} + a^{-3}HF_{mix} \tag{3}$$

The first term is the elastic free energy per unit area. It arises because of the stretched configurations adopted by the densely grafted chains. The second term is due to interactions among solvent molecules and monomers. The Flory mixing free energy is used for F_{mix}

$$F_{mix}(\phi_A,\phi) = \phi_A \ln \phi_A + (1-\phi-\phi_A)\ln(1-\phi-\phi_A) + \chi_A\phi_A\phi + \chi_B(1-\phi-\phi_A)\phi + \chi_{AB}\phi_A(1-\phi-\phi_A) \tag{4}$$

To allow for situations with high surface coverage σ, where the finite extensibility of the chains is important, the elastic free energy is expressed in terms of the inverse Langevin function[7,8]

$$F_{el} = \frac{\sigma}{a^3}\int_0^H \mathcal{L}^{-1}\left(\frac{z}{Na}\right) dz \tag{5}$$

where $\mathcal{L}(x) = \coth x - 1/x$. This form reduces to the Gaussian stretching expression for small deformation, namely $F_{el} \simeq {}^3/_2\sigma H^2/(Na^4)$ for $H \ll Na$. Thus, when appropriate, we will use the Gaussian form for the derivation of certain analytical expressions. As noted, earlier, the bulk is modeled as a regular solution. Accordingly, the associated free energy density, f, is given by $f(\Phi) \equiv F_{mix}(\Phi,\phi = 0)$ as defined by eq 4 where Φ is the A volume fraction in the bulk.

The equilibrium state of a brush immersed in a mixed solvent is determined by equating the exchange chemical potential μ and the osmotic pressure Π at the brush and in the bulk. We have

$$S\frac{\partial F(H,M)}{\partial M} = f'(\Phi) = \mu \tag{6}$$

$$a^3\frac{\partial F(H,M)}{\partial H} = f(\Phi) - \Phi f'(\Phi) = -\Pi \tag{7}$$

---

* To whom correspondence should be addressed. Address after September 1, 1992: Institute of Physics, National Central University, Chung-Li, Taiwan 32054, ROC.

0024-9297/92/2225-6693$03.00/0

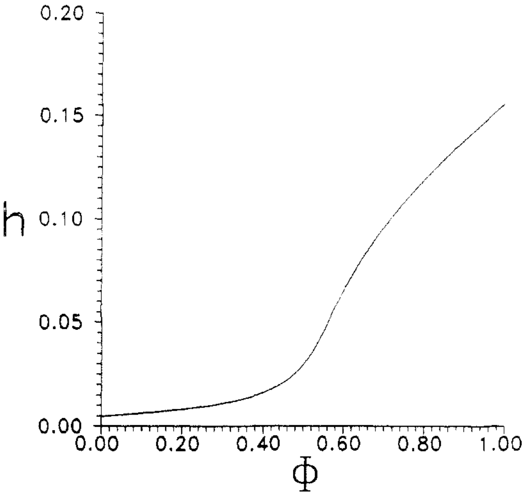

Figure 1. Reduced brush height h vs the fraction of solvent A (good solvent) in the bulk Φ for $\chi_A = -3$, $\chi_B = 1$ and $\chi_{AB} = 0$.

Using the explicit form of $F_{mix}(\phi_A, \phi)$ and $f(\Phi)$, after some algebra, we finally get

$$\ln\left[\frac{\phi_A}{1-\phi-\phi_A}\frac{1-\Phi}{\Phi}\right] + 2\chi_{AB}(\Phi-\phi_A) - \bar{\chi}\phi = 0 \quad (8)$$

$$\sigma\mathcal{L}^{-1}\left(\frac{\sigma}{\phi}\right) + \phi + \chi_B\phi^2 + \bar{\chi}\phi\phi_A + \ln\left[\frac{1-\phi-\phi_A}{1-\Phi}\right] + \chi_{AB}({\phi_A}^2 - \Phi^2) = 0 \quad (9)$$

where $\bar{\chi} \equiv \chi_B - \chi_{AB}$. Equations 8 and 9 specify the equilibrium condition of the brush for given values of σ, Φ, and χ's. In general only a numerical solution is possible but for certain regimes one may also obtain analytical results.

III. Layer Thickness

A given equilibrium value of ϕ, as obtained from eqs 8 and 9, specifies the relative thickness of the brush $h \equiv H/(Na) = \sigma/\phi$. The behavior of h as a function of Φ, the bulk volume fraction of solvent A, is of special interest when solvent B is poor. In such cases the h vs Φ diagram exhibits an inflection point: the function is convex for small Φ values and concave when Φ is close to unity. This is illustrated in Figure 1 which shows the variation of h as a function of Φ at a surface coverage of $\sigma = 0.003\,25$, close to the experimentally encountered values. The shown features are qualitatively similar to those observed experimentally by Auroy and Auvray.[4] One should note that the change in h takes place continuously, and no phase transition is involved.

For certain simple cases one may obtain analytical expressions for h at limiting values of Φ. Assuming $\chi_A < {}^1/_2$, $\chi_B \gg 1$, $\bar{\chi} > 0$, and $\sigma \ll 1$, we obtain

$$h \simeq \sigma[1 + \gamma + (e^{\bar{\chi}} - 1)\gamma\Phi + \mathcal{O}(\Phi^2)] \quad (10)$$

for low Φ values. In the opposite limit of high Φ, we find

$$h \simeq b\sigma^{1/3}[1 + \alpha(1-\Phi) + \mathcal{O}(1-\Phi)^2] \quad (11)$$

where $b = [(1 - 2\chi_A)/6]^{1/3}$, $\gamma = \exp[-1 - 3\sigma^2 - \chi_B]$, and $\alpha = 2(\bar{\chi} - 2\chi_{AB})/[2\chi_A - (3b^2 + b^{-1}]\sigma^{2/3})$. The crossover between these two regimes is smooth and occurs around

$$\Phi_* \simeq \frac{b(1+\alpha) - \sigma^{2/3}(1+\gamma)}{b\alpha + \gamma\sigma^{2/3}(e^{\bar{\chi}} - 1)} \quad (12)$$

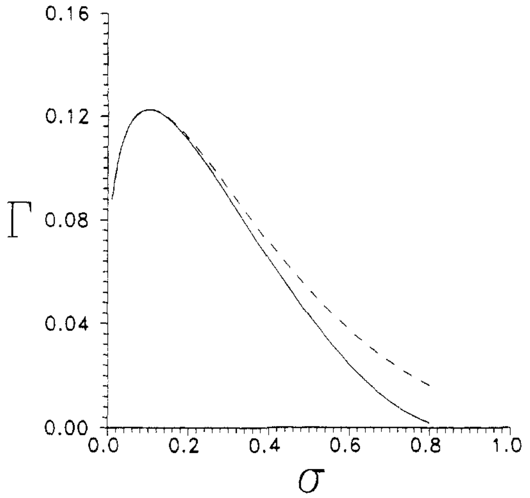

Figure 2. Γ vs σ for $\chi_B = 1$, $\chi_A = \chi_{AB} = 0$, and $\Phi = {}^1/_2$. The two curves are the results using inverse Langevin function (solid curve) and Gaussian (dashed curve) elastic free energies.

IV. Adsorption Isotherm and Chromatography

One may use polymer brushes to tailor stationary phases for certain chromatographic separations. In such situations the mobile phase is a multicomponent dilute solvent of various components dissolved in solvent B. When component A has a stronger affinity for the polymer, the grafted brush can enhance the separation of the mixture. To this end, it is desirable to have strong preferential adsorption of the target material and an extended linear regime in the adsorption isotherm.[3] With this in mind we attempt to characterize the σ and χ's dependences on the following quantities: (i) the surface excess of component A over solvent B, Γ defined as

$$\Gamma = \phi_A - \phi_B - (2\Phi - 1) = 2\phi_A + \phi - 2\Phi \quad (13)$$

(ii) the volume fraction of component A inside the brush, ϕ_A, as well as the relative composition of the mobile components within the brush, $p = \phi_A/(1 - \phi)$; (iii) the extent of the linear regime of the adsorption isotherm, that is, Φ_l, such that for $\Phi < \Phi_l$, $\phi_A \propto \Phi$.

As σ increases from 0, Γ shows a maximum Γ_m, at $\sigma = \sigma_m$, as illustrated in Figure 2. This implies an optimal surface coverage at which the selectivity is maximal. (We also display the result of using the Gaussian stretching energy instead of the inverse Langevin function. The maximum occurs at almost the same coverage. Weak deviations are found at higher coverages.) This phenomenon reflects the balance of two effects. The selectivity of the brush grows with the polymer concentration. However, when the polymer density approaches unity the total amount of adsorbed material, $1 - \phi$, decreases and eventually vanishes. Γ_m and σ_m depend on the χ's. The optimal coverage σ_m can be obtained by solving eqs 8 and 9 together with

$$1 - \phi - 2\phi_A + 2\Delta\phi_A(1 - \phi - \phi_A) = 0 \quad (14)$$

where $\Delta \equiv \chi_B - \chi_A$. Equation 14 can be derived by setting $d\Gamma/d\phi = 0$ and using eq 8. For illustrative purpose, we fix χ_A, χ_{AB}, and Φ, but vary χ_B. Figure 3 shows the variation of σ_m as χ_B increases with $\chi_A = 0$ and $\chi_{AB} = 0$ and 1. As shown, σ_m decreases as χ_B increases. When Δ is sufficient large, σ_m is around a few percent, well within the experimentally accessible regime. Figure 4 displays the variation of the optimal surface excess Γ_m, as a function of Δ. Note that Γ_m depends only on Δ, rather than on χ_A and χ_B independently. Γ_m increases almost linearly with Δ. Furthermore, for a given value of Δ, Γ_m grows with

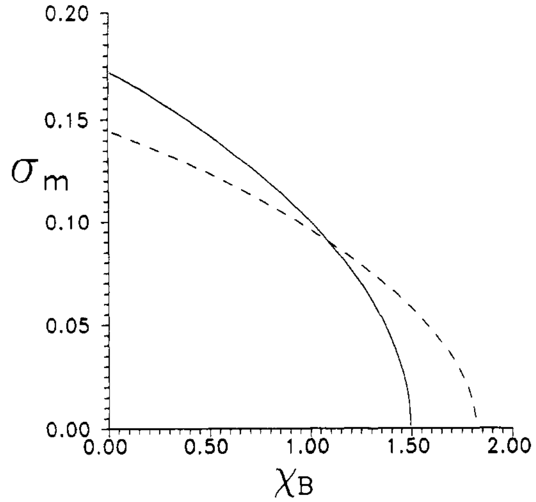

Figure 3. Optimal surface coverage σ_m vs χ_B for $\chi_A = 0$, $\Phi = 1/2$, and $\chi_{AB} = 0$ (solid) or 1 (dashed).

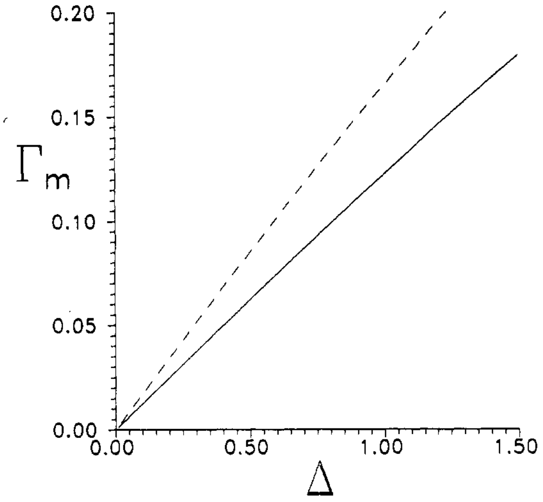

Figure 4. Γ_m vs Δ for $\Phi = 1/2$ and $\chi_{AB} = 0$ (solid) or 1 (dashed).

χ_{AB}. This is because preferential adsorption is favored by the greater tendency of the the bulk to demix.

Optimizing the performance with respect to Φ_l and the selectivity as measured by ϕ_A or p poses conflicting demands. It is possible to extend the linear regime by choosing polymers with lower $\bar{\chi}$. However, ϕ_A and p will also decrease at the same time. Conversely, for large $\bar{\chi}$, Φ_l is small while p and ϕ_A are large. In particular, Φ_l is given by

$$\Phi_l^{-1} \simeq \gamma[\bar{\chi} + (2\chi_{AB} - \bar{\chi})e^{\bar{\chi}}] - 2\chi_{AB} \qquad (15)$$

For $\Phi < \Phi_l$ we have $\phi_A \simeq K\Phi$ where K specifies the adsorption isotherm in the linear regime and is given by

$$K = \exp(\chi_{AB} - \chi_A - 3\sigma^2 - 1) \qquad (16)$$

V. Discussions

Mixed solvents are often used to attain intermediate solvent quality. While the possibility of preferential adsorption is well recognized, it is frequently difficult to allow for its effects. A simple treatment of the phenomenon is possible for flat grafted layers within the framework of the Alexander model. A strongly nonlinear dependence of the layer thickness on the solvent composition is found. The results are in qualitative agreement with recent experimental results.[4]

Grafted chains afford a route for tuning the properties of stationary phases used in chromatography. Judicious choices of the chemical nature of the polymer and the grafting density provide a method of adjusting the adsorption isotherms. In particular, one may improve selectivity and enlarge the linear regime of the isotherm.

Acknowledgment. The authors would like to acknowledge the financial support by the Bundesministerium für Forschung und Technologie (BMFT) Grant No. 03M4040A (P.-Y.L), the Ford Motor Co., and DOE Grant No. DE-FG03-87ER45288 (A.H.). We thank Dr. E. B. Zhulina for many useful discussions.

References and Notes

(1) Halperin, A.; Tirrell, M.; Lodge, T. *Adv. Polym. Sci.* **1992**, *100*, 31.
(2) Hennion, M.; Picart, C.; Caude, M.; Rosset, R. *Analysis* **1978**, *6*, 369.
(3) (a) Giddins, J. C. *Dynamics of Chromatography*; Marcel Dekker: New York, 1965. (b) Snyder, L. R. *Principles of Adsorption Chromatography*; Marcel Dekker: New York, 1968. (c) Rajcsanyi, P. M.; Rajcsanyi, E. *Adv. Chromatogr.* **1971**, *6*.
(4) Auroy, P.; Auvray, L. *Macromolecules*, submitted for publication.
(5) Johner, A.; Marques, C. *Europhys. Lett.*, submitted for publication.
(6) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.
(7) Flory, P. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(8) Lai, P.-Y.; Halperin, A. *Macromolecules* **1991**, *24*, 4981.