Adsorption of Polymers at the Free Surface of a Good Solvent: A Spectroscopic Ellipsometry Study

Gilbert Zalczer* and Véronique Gurfein

Commissariat à l'Energie Atomique, DSM/DRECAM/SRSIM, CEN/Saclay, 91191 Gif-sur-Yvette Cédex, France

Received October 3, 1991; Revised Manuscript Received January 15, 1992

ABSTRACT: We have studied the adsorption of a low surface tension polymer (PDMS) at the free surface of a good solvent (toluene). Assuming a scaling type profile, the short distance parameter of the profile can be determined when the molecular weight is high. We found a value of 0.42 nm in fair agreement with the expected monomer size, indicating the consistency of the model.

Introduction

The study of the adsorption of polymers at interfaces has attracted much attention both theoretically and experimentally. When the surface tension of the polymer is lower than that of the solvent, a polymer-rich layer is formed at the interface (otherwise a polymer-depleted layer is formed). The monomer concentration is high close to the substrate that is within a distance z from the interface on the order of the monomer size. Parts of the chains extend into the solution, creating an average concentration profile $\varphi(z)$. Beyond twice the radius of gyration R_z of the polymer coil the monomer density falls off very quickly.

Several theoretical approaches have been employed for computing this profile based on either mean-field approximations[1-3] or scaling concepts.[4-7] For a good solvent both predict that $\varphi(z)$ decreases as $(1/z)^{\mu}$ in the central region with $\mu = 2$ and $^4/_3$, respectively.

The existence of an extended profile has been evidenced by several experimental techniques including spectroscopic techniques,[8-11] ellipsometry,[12] hydrodynamic techniques,[13,14] electrophoretic mobility,[15,17] and surface force measurements.[16-21] However, a detailed investigation of the profile was possible only using neutron scattering. Some experiments confirmed the scaling exponent $^4/_3$[22,23] while other exhibited significant discrepancies.[24,25] The case of a free surface has been the object of neutron reflection experiments,[26] but the deduction of the profile from the reflecting data is not straightforward and some of the results could not be satisfactorily interpreted. We felt that it was useful to study the same system with a different technique, namely, spectroscopic ellipsometry. While this work was completed, new neutron reflectivity data were obtained and consistently interpreted[27] on the same system, but this cross-check is still useful.

Experimental Section

The system comprises poly(dimethylsiloxane) (PDMS) as the polymer and toluene as the good solvent. In the neutron experiment either the solvent or the polymer had to be deuterated. Only the former case led to results which could be interpreted in terms of the present theories. Because optical techniques are insensitive to isotopic effects, we used hydrogenated species. The solvent was Prolabo RP grade toluene taken from freshly opened bottles. The polymer was a fraction ($M_w/M_n = 1.26$) of high molecular weight ($M_w = 4.35 \times 10^6$) PDMS. The radius of gyration of this polymer in toluene is $R_z = 128$ nm. The polymer weight concentration was 6.13×10^{-4}. The segregation of PDMS at the free surface was shown first by surface tension measurements.[28] The surface tension of toluene and PDMS are respectively 28.5 and 20 nN/m. The surface tension of solutions can be extrapolated to 25.6 nN/m for dilute solutions at room temperature.

Ellipsometry is a technique which measures the ratio of the reflectivities of electromagnetic (light) waves of the two polarization states. When there is no anisotropic medium involved, the propagation equations reduce to a scalar form. For the s polarization state, the electric field is parallel to the interface and its amplitude E obeys

$$\frac{d^2E}{dz^2} + (n^2k_0^2 - q^2)E = 0 \tag{1}$$

while in p polarization, the magnetic field is parallel to the interface and obeys

$$\frac{1}{n^2}\frac{d}{dz}\left(\frac{1}{n^2}\frac{dH}{dz}\right) + (n^2k_0^2 - q^2)H = 0 \tag{2}$$

where k_0 is the wavevector in vacuum, and n the refractive index at depth z, and q the wavevector component along the interface. The ratio of the reflected field amplitudes R_p/R_s is a complex number usually written as

$$R_p/R_s = \tan\psi \exp(i\Delta) \tag{3}$$

With a transparent substrate, the angle of incidence can be chosen, for a given wavelength, so that R_p would be zero for a step interface (Brewster angle). This makes the method very sensitive to departures from this perfect interface. The opportunity of measuring at different wavelengths allows the consistency to be checked and provides more information on the refractive index profile when its range is not too small. The instrument we used was a SOPRA ES3G type.[29] The ratio of the amplitudes was found to be as low as a few 10^{-3}, and its precise determination required an elaborated operating method which has been reported elsewhere.[30]

The liquid samples were placed in a glass container enclosed in a metal box with windows normal to Brewster incidence light rays. By comparing successive spectra obtained with and without the windows, we could check that they did not show any appreciable birefringence. The cell was placed on a heavy-vibration filtering device which prevented vibration-driven capillary waves at the free surface. Thermally-driven capillary waves cannot be avoided and imply a finite interface thickness even for a pure liquid. When the cell was cleaned with the usual solvents (methanol, trichloroethane), successive spectra obtained for pure toluene showed a progressive thickening of the apparent overlayer due to surface segregation of low surface tension impurities on a time scale of a few hours. By repeatedly cleaning the cell with fresh toluene this thickening could be made slower and of smaller amplitude. However, a small scatter of the measured thicknesses could not be avoided. We therefore chose the spectrum with the thinnest overlayer as the pure solvent reference (Figure 1). On the other hand, the spectra obtained with the polymer solution were quite reproducible over several days. One is shown in Figure 2. It is immediately visible that the effect of the polymer layer is of the same magnitude as that of the roughness (the minima of $\tan\psi$ are $\sim 3.3 \times 10^{-3}$ and 2×10^{-3}, respectively), so both effects have to be taken accurately into account in the data analysis.

0024-9297/92/2225-2634$03.00/0

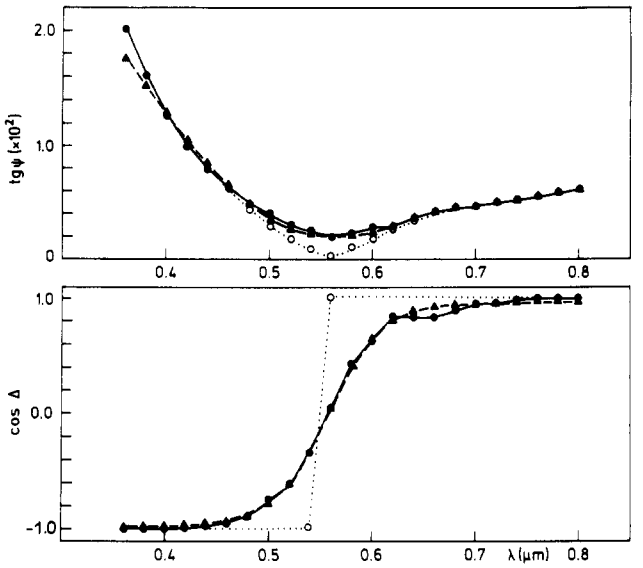

Figure 1. Experimental spectrum from a pure toluene surface (full line) and simulated spectra for a perfect interface (dotted line) and an interface with the profile in Figure 3a with t = 1.5 nm (dashed line).

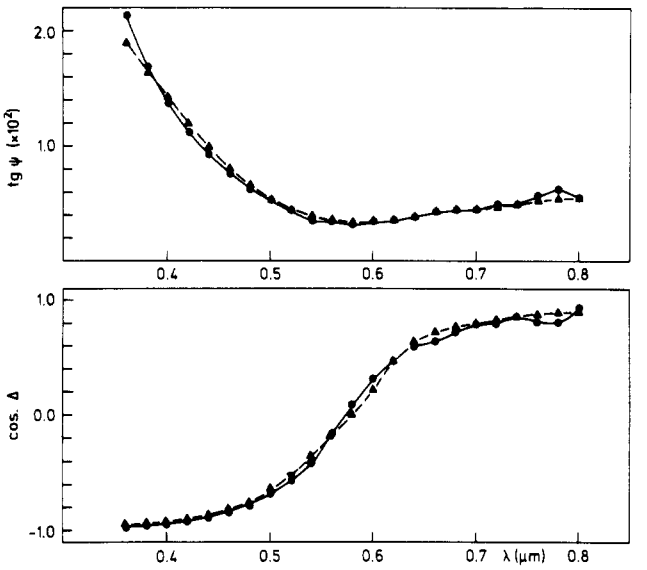

Figure 2. Experimental spectrum from the PDMS solution (full line) and simulated spectrum for an interface with the profile in Figure 3c with t = 1.6 nm and d = 0.42 nm.

Discussion

A profile normal to the interface cannot be unambiguously derived from ellipsometric spectra. As with other experimental techniques, we have to simulate the effect of a parameterized profile of reasonable assumed shape and select the best parameters. In order to avoid additional approximations arising from the computation, we numerically integrated the propagation equations for the s- and p-polarized waves using a fourth-order Runge–Kutta algorithm with a step of about 0.1 nm.

The intrinsic profile of a liquid–gas interface is also a subject of debate, but we need at most a convenient realistic approximation. In the capillary wave model of interface structure, the average profile has the shape of an error function. Our technique is insensitive to the exponential tails, and we limited our analysis to a linear variation of the concentration and the refractive index between both bulk values on a range t (Figure 3a). The spectrum shown in Figure 1 is consistent with a value of t of 1.5 nm.

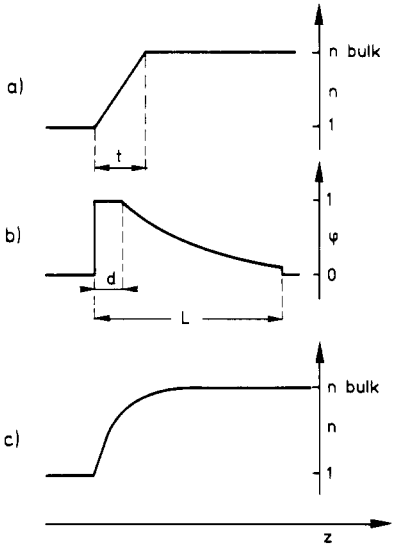

Figure 3. Sketch of the different profiles involved: (a) linear profile as an approximation for the pure toluene free surface structure; (b) theoretical monomer concentration profile as defined by eq 4 and used in ref 26; (c) convolution of the monomer concentration profile by the interface average structure.

Table I
Fitted Value of the Characteristic Length of the Profile d for Different Values of Its Total Extension L

L, nm	10	20	40	⩾60
d, nm	0.55	0.48	0.43	0.42

The simulation of the spectrum recorded from the polymer solution must include both roughness and concentration profile effects. According to the capillary wave theory, the interfacial thickness behaves as the square root of the surface tension (apart from logarithmic corrections which can be neglected here). The roughness t of the solution free surface was therefore taken equal to 1.6 nm. The model profile was defined as

$$\varphi = 1 \quad z < d \tag{4a}$$

$$\varphi = (d/z)^{\mu} \quad \mu = {}^4/_3, d < z < L \tag{4b}$$

$$\varphi = 0 \quad L < z \tag{4c}$$

where d is on the order of the monomer size and L of the radius of gyration R_z (Figure 3b).

This profile was convoluted by the roughness function and the composite profile (Figure 3c) introduced in the simulation program. We did not succeed in determining simultaneously the polymer dependent parameters d and L due to the correlation between these variables. So we determined the best value of d for different values of L, which are reported in Table I.

We expect L to be comparable with R_z. For $L > R_z/2$ the best value of d is constant and equal to 0.42 nm. With our hypotheses the relative uncertainty is about 10%. The main approximations concern the roughness of the free surface and its combination with the profile, and the linear relationship between the refractive index and the concentrations. These approximations should not strongly bias the results of the simulations. This value of d is in fair agreement with that of 0.37 nm reported in ref 26. It is somewhat smaller than the value 0.52 nm reported in ref 27. Determining the relevance of this discrepancy will require further investigation. Our study therefore confirms the overall relevance of the theoretical profile which

fitted the neutron reflection data for hydrogenated PDMS in deuterated toluene.

Acknowledgment. We thank the authors of ref 27 and M. Daoud for helpful discussions and A. Lapp for providing the PDMS.

References and Notes

(1) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.
(2) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1980**, *84*, 178.
(3) Jones, I. S.; Richmond, P. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1062.
(4) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(5) de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637.
(6) de Gennes, P.-G.; Pincus, P. *J. Phys. Lett.* **1983**, *44*, L241.
(7) Eisenreigler, E.; Kremer, K.; Binder, K. *J. Chem. Phys.* **1982**, *77*, 6296.
(8) Robb, I. D.; Smith, R. *Eur. Polym. J.* **1974**, *10*, 1005.
(9) Bloch, J. M.; Sansone, M.; Rondelez, F.; Peiffer, D. G.; Pincus, P.; Kim, M. W.; Eisenberger, P. M. *Phys. Rev. Lett.* **1985**, *54*, 1039.
(10) Kawaguchi, M.; Hayakawa, H.; Takahashi, A. *Macromolecules* **1983**, *16*, 631.
(11) Priel, Z.; Silberberg, A. *J. Polym. Sci.* **1978**, *16*, 1917.
(12) Varoqui, R.; Déjardin, P. *J. Chem. Phys.* **1977**, *66*, 4395.
(13) Koopal, L. K.; Lyklema, J. *Faraday Discuss. Chem. Soc.* **1975**, *59*, 230.
(14) Brooks, D. E. *J. Colloid Interface Sci.* **1973**, *43*, 687.
(15) de Gennes, P.-G. *C. R. Acad. Sci. Paris* **1983**, *297*, II883.
(16) Israelachvili, J. N.; Tirrell, M.; Klein, J.; Almog, Y. *Macromolecules* **1984**, *17*, 204.
(17) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.
(18) Tirrell, M.; Patel, S.; Hadziioannou, G. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 4725.
(19) Ansarifar, M. A.; Luckham, P. F. *Polymer* **1988**, *29*, 329.
(20) Taunton, H. J.; Toprakcioglu, C.; Klein, J. *Macromolecules* **1988**, *21*, 3333.
(21) Marra, J.; Hair, M. L. *Colloids Surf.* **1988**, *34*, 215.
(22) Auvray, L.; de Gennes, P.-G. *Eur. Phys. Lett.* **1986**, *2*, 647.
(23) Auvray, L.; Cotton, J. P. *Macromolecules* **1987**, *20*, 202.
(24) Cosgrove, T.; Health, T. G.; Ryan, K.; Crowley, T. L. *Macromolecules* **1987**, *20*, 2879.
(25) Cosgrove, T. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1990.
(26) Bouchaud, E.; Farnoux, B.; Sun, X.; Daoud, M.; Jannink, G. *Eur. Phys. Lett.* **1986**, *2*, 315. Sun, X.; Bouchaud, E.; Lapp, A.; Farnoux, B.; Daoud, M.; Jannink, G. *Eur. Phys. Lett.* **1988**, *6*, 207.
(27) Lee, L. T.; Guiselin, O.; Farnoux, B.; Lapp, A. *Macromolecules* **1991**, *24*, 2518.
(28) Ober, R.; Paz, L.; Taupin, C.; Pincus, P.; Boileau, S. *Macromolcules* **1983**, *16*, 50.
(29) SOPRA, 26, Rue Pierre Joigneaux, F92270 Bois-Colombes, France.
(30) Zalczer, G.; Gurfein, V., to appear in *Rev. Sci. Instrum.*