

# Formation and Characterization of an Ultrathin Polysiloxane Film onto Mica

JACQUES-EMILE PROUST, ERIC PEREZ, YVAN SEGUI,\*  
AND DOMINIQUE MONTALAN\*

*Physicochimie des surfaces et innovation en pharmacotechnie, UA CNRS 1218, Centre d'études pharmaceutiques,  
5 rue Jean Baptiste Clément, Châtenay-Malabry 92296 France*

Received October 15, 1987; accepted February 4, 1988

The plasma polymerization technique used on mica provided us with ultrathin hydrophobic polymer layers which were homogeneous and water stable but not resistant to peeling in water. These layers did not seem to alter the molecular smoothness of the mica cleavage planes. It was therefore possible to measure force/distance profiles between such polymer surfaces with a comparable accuracy to that usually obtained with multiple beam interferometry. Moreover, such surfaces did not produce any detectable contact angle hysteresis. © 1988 Academic Press, Inc.

## INTRODUCTION

The formation of thin polymer layers on a solid surface has a considerable technological interest (1-4) in such domains as microelectronics, biomaterials (5), etc. . . . Moreover, theoretical progress in wetting science refers to ideal surfaces which are therefore needed for experiments. As an example, the experimental study of dynamics of wetting necessitates homogeneous low energy surfaces without any chemical or geometrical defect (6). Other studies, such as the measurements of surface forces, require molecularly smooth surfaces such as mica. Hydrophobic mica has been obtained by adsorption from solution (7, 8), Langmuir-Blodgett deposition (9), etc.

The aim of the present work was to obtain and characterize a homogeneous ultrathin polymer layer (a few millimicrons) on mica by plasma polymerization hoping that it would be firmly anchored on the mica cleavage plane while leaving the surface molecularly smooth. Films obtained by this method have already been studied (10) with thicknesses ranging from a few tens of millimicrons to a few mi-

croons. Here, we will characterize the polymer films by multiple beam interferometry, wettability, and surface forces measurements.

## MATERIALS AND METHODS

Mica was freshly cleaved from ruby muscovite plates.

The monomer used for plasma polymerization was Hexamethyldisiloxane (Fig. 1).

The water was tridistilled from acid permanganate. The *n*-octane was Merck reference substance for gas chromatography and was used without any further purification. The octane/water interfacial tension was measured by the Wilhelmy plate method at room temperature:

$$\gamma_{ow} = 50.6 \text{ mN} \cdot \text{m}^{-1}.$$

NaCl was Merck suprapur roasted at 700°C for 6 h.

## Plasma Polymerization Method

The method and apparatus for glow-discharge deposition of a polymer film has been described in detail in Ref. (10). The film is obtained by creating an electrical discharge between two electrodes in a monomer gas at a given pressure. Here, the mica samples were

\* Laboratoire de génie électrique de l'Université Paul Sabatier 31000 Toulouse France.

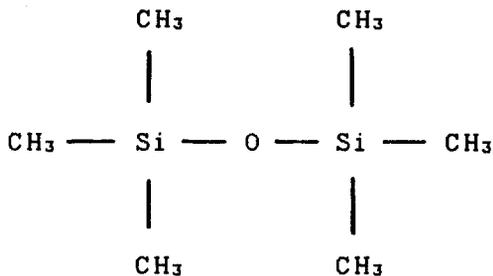


FIG. 1. Hexamethyldisiloxane.

put on one of the two electrodes. After vacuum was obtained in the bell jar, the monomer was introduced at a pressure of  $45 \pm 5$  Pascals and the electrical discharge forming a homogeneous plasma was started at a frequency 2.5 KHz, with a current of  $1.6 \pm 0.2 \text{ A} \cdot \text{m}^{-2}$  for 30 s.

#### Interferometry

Multiple beam interferometry was used to measure thickness, refractive index, and to characterize the homogeneity of the polymer layers. This method is extensively described in Ref. (11). It requires two mica sheets of equal thickness (a few microns), silvered on one side (the polymer films are deposited on the other side). The two sheets are brought into contact with the two silver layers on the outside, thus forming a Perot-Fabry interferometer. With a suitable optical setup, fringes of equal chromatic order can be observed. The accuracy of this method is 0.1–0.2 nm for the thickness, and 0.03 for the refractive index at thicknesses of a few nm. When optimal optical conditions are realized, the fineness of the fringes ultimately depends on the rugosity of the studied surfaces. This interferometric method has a very high depth resolution, but a much lower lateral resolution (a few microns). For instance, a hole in a 5 nm thick film will be optically seen only if it is larger than a few microns.

The thickness and refractive index of the polymer layers were measured by comparing identical samples of treated and nontreated mica.

#### Surface Forces

The forces between two treated mica surfaces immersed in a liquid (aqueous NaCl  $10^{-3} \text{ M}$  solution) were measured as a function of the distance between the two solid surfaces, by the technique developed by Israelachvili, extensively described in Ref. (12). The above mentioned interferometric method was used in combination of a calibration procedure in order to determine the force to  $10^{-7} \text{ N}$ . One of the two mica sheets was fixed to a force measuring leaf spring with a stiffness coefficient 100 N/m. We could measure attractive forces only if their gradient was smaller than 100 N/m, otherwise the surfaces would jump into contact (12).

#### Surface Characterization by Contact Angle Measurements

The purpose of the present work was to create a hydrophobic surface. We want to characterize it by its surface energy and its hydrophobicity. Several methods based on wettability have been proposed. The state equation proposed by Neumann allows, from liquid surface tension and its advancing contact angle on the solid, to obtain values for solid/vapor and solid/liquid surface energies.

In order to evaluate the hydrophobic character of the surface, we have used the Hamilton-Andrade method which has the advantage of providing a competition between water and a hydrophobic liquid. It is based on Fowkes' approach (13) and on the fact that octane and water have an equal dispersion component to their surface energy.

Although both approaches may be incompatible from a theoretical point of view (14, 15), they provide us with parameters which allow comparison with other surfaces.

Contact angles were measured with a goniometer in two different configurations as shown in Fig. 2 (16):

(a) Drop-on-plate method using a thermostated contact-angle apparatus described in Ref. (17). A drop of liquid is deposited on the

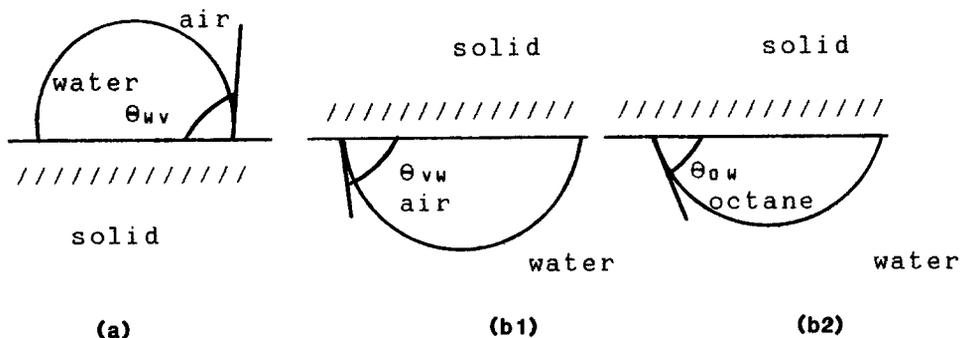


FIG. 2. The contact angles were measured in the configurations: (a) sessile drop of water; (b1) air bubble on the solid immersed in water; (b2) octane drop on the solid immersed in water.

solid substrate by means of a micrometric syringe. This allows measurement of both static advancing and receding contact angles.

(b) vapour/water/solid and octane/water/solid systems where we could only measure the receding angle.

Using the advancing water contact angle obtained by the drop-on-plate method (Fig. 2a), and the equation proposed by Neumann (18), the solid surface free energy  $\gamma_{sv}$  and the solid-water interfacial energy  $\gamma_{sw}$  were obtained for all surfaces by computation from the following equations:

$$\cos \theta_{wv} = \frac{(0.015\gamma_{sv} - 2.00)(\gamma_{sv}\gamma_{wv})^{1/2} + \gamma_{wv}}{\gamma_{wv}[0.015(\gamma_{sv}\gamma_{wv})^{1/2} - 1]} \quad [1]$$

$$\gamma_{sw} = \frac{[(\gamma_{sv})^{1/2} - (\gamma_{wv})^{1/2}]^2}{1 - 0.015(\gamma_{sv}\gamma_{wv})^{1/2}} \quad [2]$$

Using the Hamilton-Andrade approach (19, 20) and the contact angles measured at the triple line solid-air-water  $\theta_{vw}$  and solid-octane-water  $\theta_{ow}$  (see Fig. 2b), we can deduce (20) the polar  $W_{sw}^p$  and nonpolar  $W_{sw}^d$  contributions to the solid/water adhesion free energy:

$$W_{sw}^p = 50.6(1 - \cos \theta_{ow}) \quad [3]$$

$$W_{sw}^d = \gamma_{wv}(1 - \cos \theta_{vw}) - W_{sw}^p \quad [4]$$

RESULTS AND DISCUSSION

*Water Stability of the Polysiloxane Layer Deposited onto Mica*

The plasma polymerization treated mica surfaces were resistant to water and did not show any alteration either after contact with a drop or after one day immersion. This water stability was also noticed during all the characterization experiments. In the difficult problem of finding a stable hydrophobic treatment of such an inert surface as mica (9), this plasma polymerization method seems satisfactory.

*Optical Characterization*

The fringes of equal chromatic order obtained with two polysiloxane treated mica sheets in contact did not show any holes in the polymer film. They were as fine as those obtained with clean mica surfaces. This proves that the new surface was smooth within the resolution of the technique.

In the above described deposition conditions, each of the polysiloxane layers had a thickness:

$$4.5 \pm 0.4 \text{ nm}$$

and a refractive index:

$$1.44 \pm 0.04.$$

The indicated errors correspond to the dispersion of the results which may be due to the

imperfect reproducibility of the deposition conditions.

### *Surface Force Measurements*

The measurements were performed in successive movements of bringing together and separating the surfaces in NaCl  $10^{-3}$  M aqueous solution. After the first contact, the forces measured in subsequent cycles were not reproducible. Therefore, special care was taken to make sure that the treated mica sheets were not brought into contact prior to the first force measurement run.

In this run (not shown here), only an attractive regime was observed, with a jump into contact from about 12 nm. The absence of repulsion indicates that the electrostatic charge of the surface is negligible. Without going into great detail for these preliminary measurements, we can observe that van der Waals forces are not large enough for explaining this jump at large distances, even with an overestimation of the Hamaker constant. The occurrence of hydrophobic forces should be a satisfactory alternative explanation, as shown by other authors with surfactant-coated hydrophobic mica surfaces (8, 9).

On subsequent cycles, we could observe nonreproducible double-layer type repulsions, showing that the layer is damaged after the first separation from contact. We think that this damage may be due to a shear that would take place on reversing one translation stage of the force measuring system in order to separate the surfaces. Another explanation, as suggested by one of the referees is that the damage caused on separating the treated surfaces in water is due to the strong adhesion in water ( $\gamma_{SL} = 31.6 \text{ mJ} \cdot \text{m}^{-2}$ , see next paragraph) which may be stronger than the adhesion of the polymer to mica.

In some cases, under great compression, the extrusion of the polymer layer could be directly observed on the fringes of equal chromatic order, where the flattened portions (corresponding to the contact zone) were, within a few seconds, shifted to a new position,

allowing an accurate measurement of the thickness and refractive index of the polysiloxane layer.

### *Contact Angle and Surface Energy Parameters for Treated Mica*

The contact angle of water on the treated mica surface, measured by the drop-on-plate method is

$$\theta_{wV} = 95^\circ \pm 0.5^\circ$$

for both advancing and receding angles, showing no hysteresis. This is quite different from the behavior of polydimethylsiloxane sheets (21) which showed, with water, an advancing contact angle of  $98^\circ$  and a receding one of  $66^\circ$ .

Recent progress of theory has been achieved in understanding wetting hysteresis (6): contact angle hysteresis is influenced by surface chemical and geometrical heterogeneities. Here, the absence of wetting hysteresis confirms our optical characterization of the smoothness of treated mica surfaces. We can, moreover, deduce that those surfaces are chemically homogeneous.

The contact angle  $\theta_{wV}$ , when vectorized in Eqs. [1] and [2] gives values  $\gamma_{SV}$  and  $\gamma_{SW}$  respectively for the surface free energy of treated mica in equilibrium with water vapor and for the treated mica/water interface free energy:

$$\gamma_{SV} = 25.3 \text{ mJ} \cdot \text{m}^{-2}$$

$$\gamma_{SW} = 31.6 \text{ mJ} \cdot \text{m}^{-2}.$$

Using the configuration of Fig. 2b1, we could deduce the same values for  $\gamma_{SV}$  and  $\gamma_{SW}$  from the contact angle data  $\theta_{vW}$ .

The  $\gamma_{SV}$  value is close to the critical surface tension  $\gamma_c$  of polymethylsiloxane found by Zisman (22):

$$\gamma_c = 24 \text{ mJ} \cdot \text{m}^{-2}.$$

Values for  $\gamma_{SL}$  and  $\gamma_{SV}$  of mica coated by a hydrophobic monolayer have been obtained independently by direct force measurements (9) and Neumann's equation of state (23).

The results are fairly close to those of our different but hydrophobic mica surfaces.

The contact angles measured on treated mica immersed in water (Fig. 2) were

$$\theta_{OW} = 49^\circ \pm 0.5^\circ$$

$$\theta_{VW} = 85^\circ \pm 0.5^\circ.$$

The polar and nonpolar contributions to the solid/water interface free energy are obtained from [3] and [4],

$$W_{SW}^p = 17.2 \text{ mJ} \cdot \text{m}^{-2}$$

$$W_{SW}^d = 48.5 \text{ mJ} \cdot \text{m}^{-2},$$

and the polar/nonpolar ratio,

$$W_{SW}^p/W_{SW}^d = 0.35.$$

This parameter characterizes the polarity of the surface which is, in this case, very low. It is more hydrophobic than silane grafted glass where this ratio is 0.56 (from Ref. (16)). This parameter has been shown to have an important bearing on the interaction of the surface with solutes (for example, protein adsorption (24)).

With this plasma polymerization technique, we have obtained a hydrophobic polymer surface which is very smooth and homogeneous.

#### ACKNOWLEDGMENT

We thank Dr. A. Baszkin for fruitful discussions.

#### REFERENCES

1. Yasuda, H., "Plasma Polymerization," Academic Press, New York, 1985.
2. Vincett, R. S., and Roberts, G. G., *Thin Solid Films* **68**, 135 (1980).
3. Tredgold, R. H., and Winter, C. S., *Thin Solid Films* **99**, 81 (1983).
4. Larkins, G. L., Jr., Thompson, E. G., Ortiz, E., Burkhart, C. W., and Lando, J. B., *Thin Solid Films* **99**, 277 (1983).
5. Clark, D. T., Dilks, A., and Shuttleworth, D., in "Polymer Surfaces" (D. T. Clark and W. J. Feast, Eds.), p. 185. Wiley, Chichester, 1978.
6. de Gennes, P. G., *Rev. Mod. Phys.* **57**, 827 (1985).
7. Pashley, R. M., and Israelachvili, J. N., *Colloid Surf.* **2**, 169 (1981).
8. Israelachvili, J. N., and Pashley, R. M., *J. Colloid Interface Sci.* **98**, 500 (1984).
9. Claesson, P. M., Blom, C. E., Herder, P. C., and Ninham, B. W., *J. Colloid Interface Sci.* **114**, 234 (1986).
10. Segui, Y., and Bui, Ai, *J. Appl. Polym. Sci.* **20**, 1611 (1976).
11. Israelachvili, J. N., *J. Colloid Interface Sci.* **44**, 259 (1973).
12. Israelachvili, J. N., and Adams, G. E., *J. Chem. Soc. Faraday Trans. 1* **74**, 975 (1978).
13. Fowkes, F. M., *Ind. Eng. Chem.* **56**, 40 (1964).
14. Spelt, J. K., Absolom, D. R., and Neumann, A. W., *Langmuir* **2**, 620 (1986).
15. Spelt, J. K., and Neumann, A. W., *Langmuir* **3**, 588 (1987).
16. Barbucci, R., Baszkin, A., Benvenuti, M., Costa, M. L., and Ferruti, P., *J. Biomed. Mater. Res.* **21**, 443 (1987).
17. Baszkin, A., and Ter-Minassian-Saraga, L., *Polymer* **15**, 759 (1974).
18. Neumann, A. W., Good, R. J., Hope, C. J., and Sejpal, M., *J. Colloid Interface Sci.* **49**, 291 (1974).
19. Hamilton, W. C., *J. Colloid Interface Sci.* **40**, 219 (1972).
20. Andrade, J. D., King, R. N., Gregonis, D. E., and Coleman, D. L., *J. Polym. Sci. Polym. Symp.* **66**, 313 (1979).
21. Baszkin, A., Boissonade, M. M., Proust, J-E., Tchaliowska, S., Ter-Minassian-Saraga, L., and Wajs, G., *J. Bioeng.* **2**, 527 (1978).
22. Zisman, W. A., *Ind. Eng. Chem.* **55**, 19 (1963).
23. Moy, E., and Neumann, A. W., *J. Colloid Interface Sci.* **119**, 296 (1987).
24. Baszkin, A., and Lyman, D. J., *J. Biomed. Mater. Res.* **14**, 393 (1980).