Investigation of the Adsorption of Polystyrene by Plasmon Surface Polaritons on Metal Gratings

In this communication we report a new optical method to study the kinetics of adsorption of polymers onto a metal plate from solutions. This work was undertaken to demonstrate that the electromagnetic surface waves or plasmon surface polaritons (PSP) can be used to follow the kinetics of adsorption of polystyrene onto a silver grating from a toluene solution. This new optical method can also be applied to investigate various interfacial processes ranging from the adsorption of macromolecules as synthetic or natural polymers to the formation of monolayer films of small molecules. Moreover, the interfacial interactions can be modified by coating the metal grating by a thin dielectric film as SiO_2.

Among the various optical methods, ellipsometry is a suitable technique to measure simultaneously the two quantities, thickness and index of refraction. Indeed, several models have been developed to describe the concentration profile of polymer solution near a rigid wall,[1,2] but measurements are generally analyzed in the approximation of a homogeneous layer: the adsorbance and the thickness being deduced from data. Stromberg, Tutas, and Passaglia[3] have pioneered in the adsorption measurements of polystyrene onto a chrome plate from cyclohexane solutions. More recently, polystyrene adsorption onto various metal surfaces from different solvents have been investigated.[4]

In the present study, we have used the PSP resonance excitation on a silver grating surface. A TM polarized incident beam strikes the grating at the PSP resonance angle (Figure 1). A change of reflectivity due to the progressive adsorption of the polymer on the metal surface is observed. The sensitivity of the method allows one to measure low adsorbance with any type of solvent, even one with a very small refractive index increment ($\partial n/\partial c$). Moreover, experimentally the PSP appears simpler than ellipsometry.

In adsorption experiments, grating couplers present several advantages compared to the classical ATR[1] and to the Otto or Kretschmann's configurations.[5] First, a prism traversed by the laser beam places an upper limit on the refractive index of the solutions. Secondly, the experimental conditions can be optimized by choosing the grating[6] characteristics, i.e., grating constant and modulation amplitude, provided a grating with wavelengths shorter than the PSP wavelength can be produced.

Let us now describe how the presence of a homogeneous layer can be investigated by PSP. In absence of adsorbed film, the PSP propagate along the metal–dielectric interface decreasing exponentially in amplitude with the distance from this interface (typically on $\lambda/5$ in the dielectric). Resonant excitation of PSP is achieved for the optimum angle counting θ_p defined by[6]

$$n\frac{\lambda_0}{\Lambda} + \epsilon_i^{1/2} \sin \theta_p = \left(\frac{\epsilon\epsilon_i}{\epsilon + \epsilon_i}\right)^{1/2} \qquad (1)$$

with $n = \pm 1, \pm 2, \ldots$, where $\epsilon = \epsilon' + i\epsilon''$ and ϵ_i are the dielectric constants of the metal and isotropic medium, λ_0 is the wavelength of the laser beam in vacuum and Λ the grating constant. The reflection of the incident beam is attenuated and falls almost to zero at the resonance angle θ_p. A schematic representation of the reflectivity peak is shown on Figure 1. If the dielectric constant of one of the two media is known, the measurements of the angular position of the peak provides the value of the dielectric constant of the other medium. A growing adsorbed layer on the grating surface gives rise to several modifications

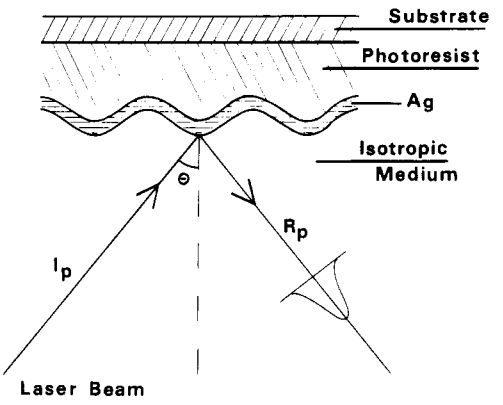

Figure 1. Schematic representation of the experimental geometry to excite the plasmon surface polaritons. The reflectance vs. the incident angle has a shape and a position θ_p strongly dependent of the thickness and of the dielectric constants of the dielectric medium.

in the PSP propagation. Three principal effects are observed on the reflectance curve: (1) a shift of the angular position of the minimum reflectivity, (2) a broadening in the shape of the reflectance curve, and (3) an increase or decrease of the minimum of reflectivity.

It has been shown[5] that the shift and the broadening are directly related to the modifications of the real and imaginary parts of the wavevector k on the interface metal/film. If δk is the modification of k for an ATR configuration, in the case where $d \ll \lambda$[7] and $\Delta n \ll 1$, we obtain

$$\delta k = 2\frac{(-\epsilon)^{1/2}}{\epsilon + \epsilon_i} k^2 \Delta n d \qquad (2)$$

where Δn is the difference between the refractive index of the interfacial layer and that of the bulk and d the thickness of the layer. So, let us emphasize that in the approximation of a homogeneous layer, δk is proportional to $\Delta n d$ and hence to the adsorbance. (Indeed the surface excess or adsorbance is equal to $\Delta n d\ (\partial c/\partial n)$).

We have used this PSP property to investigate the continuous increase in the excess material at the surface during adsorption of polystyrene onto a silver plate from a toluene solution. The variations in the value of the minimum and in the broadening of the reflectance curve are negligible during the adsorption process. So, we have used the following way to measure the shift of the angular position of the minimum vs. time. The angular position θ_m (see Figure 2) is chosen and fixed in order to be in the linear part of the reflectance curve. Hence, the measured reflectivity is continually proportional to the shift and thus to the surface excess.

Holographic metal gratings are made by first exposing a 1-μm thick film of photoresist (Shipley AZ-135) on a glass plate to two interferring expanded beams of an argon ion laser (λ = 457.9 nm). Then, after development of the resist, a layer of silver, 300–400-nm thick, was evaporated on top. The exposure times were selected to obtain gratings showing an effective sinusoidal modulation with an amplitude small compared to the wavelength λ_0. Typical gratings had dimensions 1 × 1 cm^2; the grating constant Λ and the half-depth of the modulation H are in the range of 480 and 20 nm, respectively. The strength of the coupling between PSP and incident light is determined by H and a good choice of this parameter leads to a minimum in reflectivity of almost zero.

The grating plate was immersed in a glass cell and the reflectivity curves with and without pure toluene were first determined at λ = 632.8 nm by using an accurate rotating table (Micro-Contrôle) (see Figure 3). In the air and in

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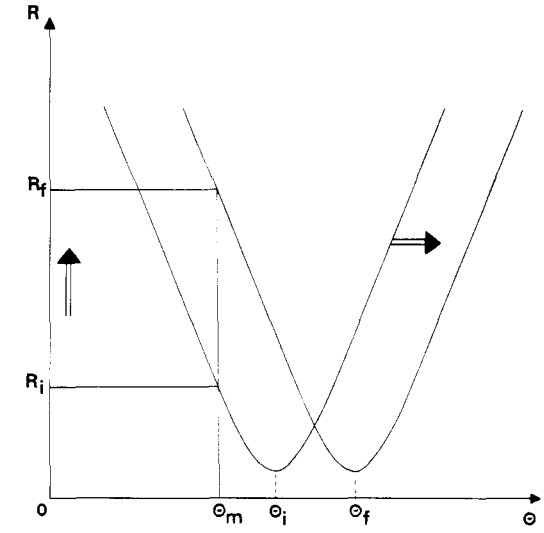

Figure 2. Principle of the measurement of the shift of the minimum reflectivity during polymer adsorption onto the metal grating. As the adsorbance of the polymer layer increases, the reflected intensity observed at a fixed angle θ_m increases from R_p^i to R_p^f.

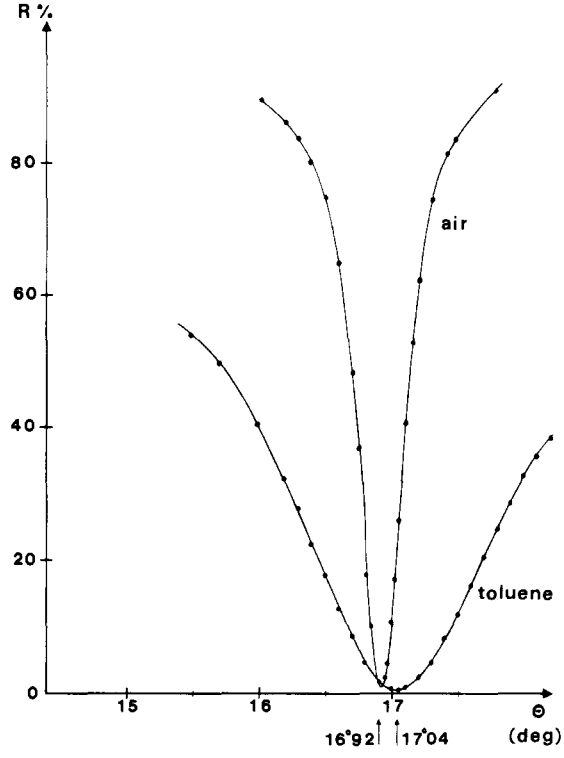

Figure 3. p-Polarized reflectivity of a silver grating with and without toluene. Using Fresnel's equations, we deduced the real part ϵ' of the silver and the refractive index of toluene from the experimental value θ_p. The results, $\epsilon' = -15.143$ and $n = 1.4947$, are in good agreement with often used values.

the toluene, the PSP resonance angles were at 16°92 and 17°04, respectively. The PSP resonance angles obtained with air and toluene as outside media allow us to calculate the dielectric constants of the silver and toluene from the expression (1). We found $\epsilon_{Ag} = -15.28 + j0.47$ and $\epsilon_{toluene} = 2.23$. Before removing the toluene from the cell, we fixed the incident angle of the beam at 16°65 in the linear part of the peak. Then the toluene was removed and a solution of polystyrene in toluene ($c = 10^{-2}$ g/cm^3 $M_w = 270\,000$) was introduced into the cell. The bulk solution has a dielectric constant close to $\epsilon = 2.24$. The reflectivity of the grating illuminated at the constant incidence angle was

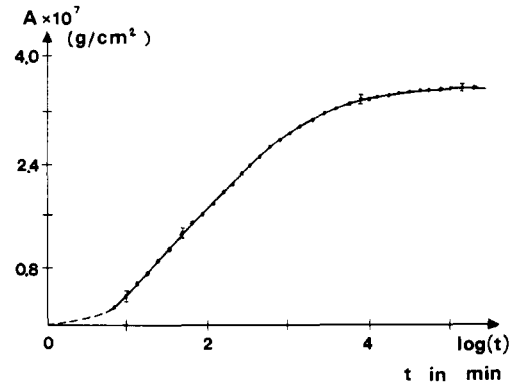

Figure 4. Adsorbance of polystyrene ($M_w = 270\,000$) from toluene solution ($c = 10^{-2}$ g/cm^3) during the adsorption period. The values have been deduced from the reflected intensity using a refractive index increment $\partial n/\partial c = 0.104$ cm^3/g. The bars represent the measurement accuracy.

measured as a function of time with a Moseley strip chart recorder. These measurements were continued for 8 days and more. The variation of the adsorbance which is simply proportional to the reflected intensity is presented in Figure 4. At the beginning the surface excess increases rapidly and then tends to saturate in agreement with previous studies.[1,4] Moreover, as the accuracy of our technique is very good $\Delta A/A \sim 10^{-2}$, a linear variation of the adsorbance vs. the logarithm of the time is clearly observed.

We have shown in this communication that plasmon surface polaritons can be used to follow the adsorption of polymer onto a metal plate from solution. As the thickness of the interfacial layer is small ($\Delta \ll \lambda$) and the increment of the refractive index is small ($\Delta n \ll 1$) the surface excess is simply proportional to the reflectivity. So, this new optical technique appears very suitable and simple to measure the surface excess and its variation during the adsorption process. An extension (currently in progress) of this method using simultaneously several wavelengths will allow us to measure both the adsorbance and the thickness of the adsorbed layers.

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Registry No. Polystyrene (homopolymer), 9003-53-6.

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