Formation and Loss of Orientation in Adsorbed PMMA Layers[†]

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The behavior of polymer chains at solid interfaces is of importance in understanding such diverse technological areas as coating processes, adhesion, and fouling.[1] It is believed that, at early times in the process of adsorption, the attached macromolecules have conformations deviant from the normal, isotropic state. We present here direct evidence of the changing structure of an adsorbed PMMA layer at the solid/solution interface during early stages in the process of adsorption.

Experimental Section. The adsorption of PMMA onto a silicon optical crystal was measured using an infrared internal reflection technique, similar to that developed by Granick.[2] Briefly, the experiment involves monitoring the mass of material adsorbed after the injection of a dilute polymer solution into a liquid cell. The experiments were performed at 30 °C, and the cell was thermostated to within 2 °C. The solution concentration of poly(methyl methacrylate) (M_w 107 000, M_w/M_n = 1.1) used, 2 mg/mL, is such that polymer adsorbed onto the silicon ATR crystal dominates the measurement; quantification of the adsorbed mass was performed by integrating the characteristic carbonyl band. This concentration is also below the region in which the adsorbed mass plateaus, as determined by measuring an adsorption isotherm. Automated sampling of dichroic data is made possible by mounting a germanium polarizer in an Oriel precision rotator, which is then interfaced to the Nicolet 60SX spectrometer used for spectra acquisition.

The polarized ATR experiment may be mathematically described in the following manner. The measured absorbance in any direction is equal to the dot product of the sum of transition moments and the square of the incident electric field

$$A_i = \alpha E_i^2 N_i$$

where α represents the magnitude of the transition moment, E_i is the electric field intensity in the ith direction, and N_i is the component sum of the number of transition moments pointing to the ith direction.

For s-polarization, only oscillators with some component of the transition moment in the y direction are sampled:

$$A_s = \alpha N_y E_y^2 \tag{1}$$

For p-polarization, oscillators with components in both the x and z directions are sampled:

$$A_p = \alpha(N_x E_x^2 + N_z E_z^2) \tag{2}$$

A dichroic ratio may be defined as the number of oscillators normal to the plane divided by the number in the plane of the surface:

$$\rho = \frac{N_z}{N_x + N_y} \tag{3}$$

In a dilute solution, orientational effects induced by the injecting flow field are rapidly destroyed, as evidenced by
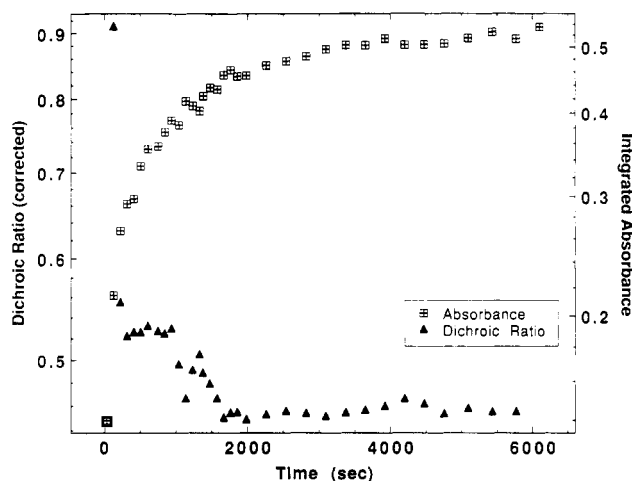
Figure 1. Dichroic ratio and integrated intensity of the carbonyl stretch of PMMA as a function of time during absorption onto a silicon ATR crystal. The initial orientation of the adsorbed polymer is completely erased within 0.5 h from the time of the injection of the sample.

the relatively large center of mass diffusivities found under these conditions.[3,4] Since the molecules arrive at the surface in an isotropic state, in-plane isotropy ($N_x = N_y$) can be assumed, and by substituting (1) and (2) into (3), we obtain the following expression for the dichroic ratio:

$$\rho = \frac{N_z}{N_x + N_y} = \frac{N_z}{2N_y} = \frac{E_y^2\{A_p - A_s(E_x/E_y)^2\}}{2A_s E_z^2} \tag{4}$$

The ratios of the electric field intensities at the surface may be calculated from expressions found by Harrick,[5] using the refractive indices of the ATR crystal and the contacting medium (CCl_4). In this manner, absorbance data taken with s- and p-polarizations may be converted directly into a dichroic ratio.

Results. The sum of the absorbances and the dichroic ratio for the adsorbing PMMA carbonyl stretch is illustrated in Figure 1. At early times the chains apparently stick in an oriented fashion, with the carbonyl oscillators possessing a preferential orientation normal to the plane of the surface. This could be explained by a tendency of the chains to spread out in the surface plane to maximize the number of segments participating in enthalpic interactions with the surface. At later times, as more molecules attach to the surface, the initial orientation is lost and the dichroic ratio reaches a value of 0.46, which given the uncertainties in the refractive indices used in evaluating the electric field strengths, is probably experimentally indistinguishable from the isotropic value of 0.5. Since the experiment measures the net orientation of all bound molecules, it is impossible to determine if the orientation of the initially bound molecules is lost or if late-arriving molecules of nearly isotropic conformation merely dominate the measurement. What is clear is that, although some degree of orientation of the molecules does occur early in the adsorption process, this effect is relatively small and is quickly erased by the attachment of more chains to the surface.

References and Notes

(1) Takahashi, A.; Kawaguchi, M. *Adv. Polym. Sci.* **1982,** *46,* 1. Cohen-Stuart, M. A. *Adv. Colloid Int. Sci.* **1986,** *24,* 143. Cohen-Stuart, M. A.; Tamai, H. *Macromolecules* **1988,** *21,* 1863.
(2) Johnson, H. E.; Granick, S. *Macromolecules* **1990,** *23,* 3367.
(3) Leger, L.; Hervet, H.; Rondelez, F. *Macromolecules* **1991,** *14,* 1732.

(4) The rapid loss of any flow-induced orientation can be illustrated by estimating an upper limit for the orientational relaxation time, which would be less than or equal to the longest characteristic relaxation time for the chain, i.e., that for center of mass motion. Assuming a center of mass diffusivity on the order of 10^{-7} cm^2/s,[3] the time required for a chain to random walk a distance of its radius of gyration of 70 Å is on the order of a few microseconds.

(5) Harrick, N. J. *Internal Reflection Spectroscopy*; Interscience: New York, 1967.