Adsorption Studies of Poly(N-vinylcarbazole) on Sapphire by a Fiber-Optic UV-Attenuated Total Reflection Technique

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Received March 1, 1991; Revised Manuscript Received June 17, 1991

ABSTRACT: The adsorption of polydisperse poly(*N*-vinylcarbazole) on the surface of α-Al_2O_3 (sapphire) was studied from four solution concentrations in toluene at the Θ temperature (37 °C). The technique of attenuated total reflection (ATR) using the evanescent wave was employed in the ultraviolet (UV) region by designing an optical setup based on a specially designed ATR crystal and a fiber-optic UV spectrometer. The adsorption kinetics occurred over a period of 10 h. The concentration profiles of the adsorbed layers in contact with solution were examined by performing angle-resolved experiments, which probe about a thousand-angstrom range. An exponential concentration profile was used to extract characteristic adsorption parameters. The adsorbed amount was found to be in the range of 1.4–1.8 mg/m^2. The adsorption isotherm was rounded and seemed to level off at the highest solution concentration. The root-mean-square thickness was found to be in the range of 300–400 Å, which is less than 2 times the radius of gyration at the Θ condition. On the other hand, the mean thickness values of the adsorbed layer were comparable to the radius of gyration.

Introduction

Polymer adsorption is a common phenomenon that determines the interfacial properties of many polymer-modified surfaces. Theoretical treatments have been recently formulated to attempt to explain the characteristics of polymer adsorption at the solid–liquid interface.[1-3] However, experimental data are required to test the predictions of these theories and to help in their further development. Experimental data on the structure of the adsorbed layer during actual adsorption are limited since only a few experimental techniques are sensitive to this thickness scale under the required experimental conditions. This research is concerned with the characteristics of the adsorption of polydisperse poly(*N*-vinylcarbazole) on the surface of α-Al_2O_3 (sapphire) from dilute solutions in toluene at the Θ temperature. An experimental technique based on absorption spectroscopy in the ultraviolet region utilizing the evanescent wave is employed, and a new optical system is designed and tested for this purpose based on a specially designed crystal and a fiber-optic UV spectrometer.

Attenuated total reflection (ATR) is a phenomenon that occurs when light is introduced through a denser medium at an angle greater than the critical angle. At the interface between a denser medium and a less dense medium, however, an evanescent field is established in the less dense medium, which can absorb the light, thus attenuating the original intensity. When the denser medium is transparent while the less dense medium absorbs the light, the ATR spectrum contains information on the structure and composition of the less dense medium. With UV–vis light, the penetration depth is usually in a thousand-angstrom range. The ATR technique is thus inherently suitable for the study of the adsorption of organic materials. The ATR crystal can be used directly as the inorganic adsorbing surface, or it can be coated with another organic thin layer. Haller and Rice studied the adsorption of alcohols and the molecular orientation of a Langmuir–Blodgett monolayer of calcium stearate.[4] They measured adsorption isotherms at several temperatures for three faces of sapphire and postulated an adsorption site involving a coordinately unsaturated pair of Al^{3+} ions and O^{2-}. Sung et al. studied the interaction of organosilanes as coupling agents with sapphire and found the adsorbed silanes to form cross-linked polysiloxane networks.[5] The adsorption of proteins was investigated in many studies which have shed light on the factors influencing the biocompatibility of the materials.[6] A limited body of experimental work exists for the study of synthetic polymer adsorption with ATR. Granick et al. studied the adsorption of poly(methyl methacrylate) from carbon tetrachloride on a germanium IR-ATR crystal.[7] Due to a deeper penetration depth (micron range), the underlying polymer solution in addition to the thin adsorbed layer was sampled and, hence, the quantitative characteristics of the adsorbed layer were not obtained. However, their polymer exchange experiments yielded interesting results. It was found that the polymer adsorbed first was replaced with a higher molecular weight deuterated polymer and it displayed a residence time on the surface of at least several hours. In a subsequent paper, they studied the influence of shear on the kinetics of polymer adsorption.[8] They found a steady-state plateau level of mass adsorbed for a stagnant solution. For a moderate shear rate of 3 s^{-1}, they found no sign of a plateau on the logarithmic time scale. In 1967, Peyser and Stromberg studied the adsorption of polystyrene from cyclohexane at the Θ temperature, using ultraviolet radiation and a conventional quartz ATR crystal.[9] Since the penetration depth in UV-ATR is in the hundreds or the thousand angstroms, they were able to measure the extension and the concentration of the adsorbed layer directly at a single angle of incidence by assuming a homogeneous adsorbed layer. They highlighted the possibility to determine the concentration distribution of adsorbed segments normal to the surface, if incidence angles were changed. This possibility prompted us to undertake the experiments described in this paper, where incidence angles were changed.

Tompkins showed that the functional form of the concentration distribution can be determined by measuring the absorbance at various values of the angle of incidence, by assuming a low absorption approximation and a uniform refractive index distribution.[10] Hirschfeld has shown that the measurements at different angles of incidence yield spectra that are weighed differently with respect to successive layers within the sample.[11] ATR intensities at a given point in the spectrum can give the functional form of the concentration profile by inverse

Laplace transformation, if the measurements were available throughout the whole range of angles of incidence with an angular resolution within the crystal of at least ±1°. Muller et al. have given a comprehensive treatment of ATR spectra on the basis of the Lorentz–Lorenz law and Fresnel equations.[12] They derived equations for the attenuated case where absorbances are substantial enough to affect the physics of the evanescent wave and showed that the depth of penetration is significantly reduced due to the effect of the absorption index.

The evanescent wave is far from being restricted to absorption spectroscopy. In this final paragraph we shall briefly introduce other spectroscopic measurements utilizing the evanescent wave. The possibility of performing internal reflection fluorescence and Raman spectroscopy was suggested at an early date by Harrick.[13] Andrade and co-workers have used evanescent wave induced fluorescence to measure adsorbed protein concentration profiles by varying the angle of incidence or observation.[14] Rondelez and co-workers have used the technique to measure the depletion layer thickness present near a polymer solution and a nonadsorbing, fused-silica wall.[15a–c] More recently, they studied the adsorption of poly(methyl methacrylate) from toluene onto a clean flat sapphire surface at 20 °C, by measuring the surface excess and the mean thickness of the adsorbed layer which are in good agreement with results by ellipsometry and small-angle neutron scattering experiments.[15d,e] Suci et al. analyzed the determination of fluorescence depth profiles by depositing well-defined film thicknesses by the Langmuir–Blodgett technique.[16] They found that variable incident angle data were more reliable than variable observation angle data. Time-resolved ATR fluorescence spectroscopy has been demonstrated in a series of papers of Masuhara and coworkers,[17] where a sapphire crystal was used with polystyrene films with different dopants. Fluorescence rise and decay curves were obtained as a function of the angle of incidence with a time resolution of 60 ps. Takenaka and co-workers first used ATR Raman spectroscopy to examine the orientation of molecules adsorbed at the liquid–liquid interface.[18] By using various assumptions about the relative magnitudes of the components of the polarizability tensor, they were able to arrive at average molecular orientations for dyes at the water–carbon tetrachloride interface. The seminal work on solid–liquid interfaces was done by Iwamoto et al.[19a] They chose sapphire as the ATR crystal due to its low scattering efficiency, small birefringence, and excellent mechanical properties. They performed careful investigations of the dependence of the Raman signal on sample thickness and on incident angle and observed polystyrene film spectra down to a thickness of 60 Å. An evanescent wave ellipsometry study was recently reported for a polymer concentration profile near a liquid–solid interface.[19b]

Experimental Section

Materials and Their Characteristics. Poly(*N*-vinylcarbazole) (PVK), from Polysciences, Inc., had a weight-average molecular weight of 840 000 with a polydispersity of 3.50. It was purified by three repeated precipitations into methanol from *p*-dioxane solution followed by drying at 120 °C for 24 h under vacuum to remove any solvent. Kuwahara and co-workers have measured the unperturbed dimensions of free-radically polymerized PVK and found a Θ temperature of 37 ± 1 °C in toluene,[20] which was chosen as the condition for our adsorption experiment. The absorption spectrum of PVK has been compared to that of *N*-alkyl-substituted carbazole.[21] The band at 344 nm is polarized in the short axis of the chromophore, while the bands at 293 and 261 nm are polarized in the long molecular axis. The absorption coefficient of our polymer was measured by collecting the spectra of a stock toluene solution at four different concentrations. The values were 15.63 ± 0.10 and 5.64 ± 0.07 mL/mg·cm for the 293- and 344-nm bands, respectively. One of the primary reasons for our choice of PVK in adsorption studies was this high value of the specific absorption coefficient which is an order of magnitude higher at 293 nm than the specific absorption coefficient of polystyrene at 262 nm. This value is close to the measured value for *N*-ethylcarbazole for the 298-nm band.[22] Spectrograde toluene (Aldrich), which was stored over molecular sieves (Aldrich type 4A), was distilled before making the polymer solutions. Pyrex Erlenmeyer flasks with Pyrex stoppers were cleaned with an ethanol solution of acetic acid, rinsed several times with pure ethanol, and placed in an oven at 120 °C. Four concentrations of purified PVK were prepared in toluene (0.1, 0.5, 1.0, and 5.0 mg/mL). Each solution was prepared before an adsorption experiment and was allowed to equilibrate at 40 °C for 5 days.

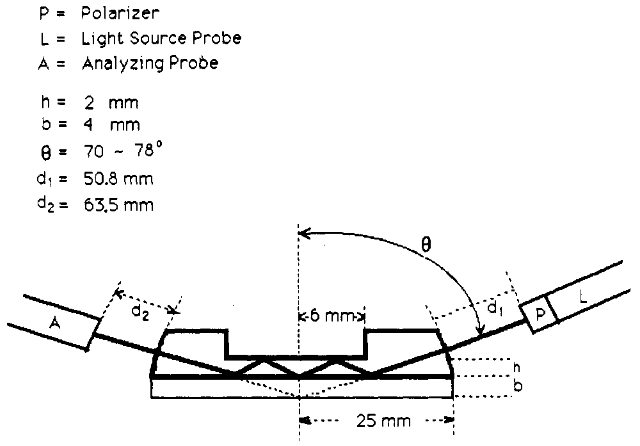

Figure 1. Schematic diagram of the specially designed truncated hemispherical crystal and fiber probes.

Instrumental Setup. An attenuated total reflection (ATR) setup was designed, meeting the requirement of well-defined angles of incidence, multiple reflections, and axial symmetry. Synthetic sapphire was selected due to a high value of refractive index (1.81 at 313 nm) and transparency in the ultraviolet region. As the birefringence of this material is small, the angle of incidence can be precisely defined and is almost independent of the polarization of the incident beam. The structural and electron diffraction characteristics of sapphire are well-known.[23] Haller and Rice have studied the adsorption of *n*-amyl alcohols on three distinct crystallographic faces of sapphire by IR-ATR and observed that the (4150) surface was free of depolarization effects.[24] Figure 1 illustrates our design of a truncated hemispherical crystal and the positions of the light source probe, polarizer, and analyzing fiber probe. The diametrical face which is the (4150) crystallographic face is used as the reflecting surface. The curved surface serves as the entrance and the exit windows for the UV beam. When the UV beam is focused outside the curved surface by a distance R (equal to 3.09 cm), a fairly parallel light beam is obtained inside the crystal and the angle of incidence can be accurately set. Geometric considerations show that when b/h is an integer of m, the number of reflections will be independent of the angle of incidence and equal to $2m + 1$, as long as the incident beam is directed toward the origin of the sphere.[25] A disadvantage of this design is that only a limited range of angles of incidence is accessible. Our design parameters set the minimum angle of incidence (measured from the axis perpendicular to the crystal) at 66.5° and the maximum at 78.5°. The crystal was manufactured by Harrick Scientific Corp. It was supplied in two pieces including the bottom disk (with a thickness of 2 mm), with sharp edges and polished surfaces. The two-part design of the crystal was very convenient, since the surface must be rigorously cleaned for adsorption studies, and, with this design, only the bottom disk was handled. The reproducibility of the cleanliness of the bottom surface is very important for adsorption studies. On the basis of several cleaning procedures tried, the procedure that proved to give reasonably reproducible results is as follows. The crystal was cleaned with ultrasound for 10 min in dioxane, heptane, and ethanol (spec-

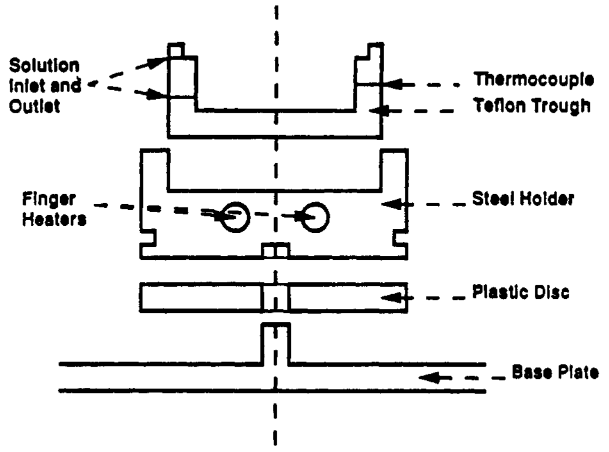

Figure 2. Schematic diagram of the components of the crystal cell and holder.

trograde), successively, followed by placement on top of two small hemispherical sapphire supports with ultrasound-cleaned Teflon-coated tongs. While the adsorption surface was free standing in air, the furnace was heated to 900 °C for 2 h and then allowed to cool to room temperature with a flow of dry argon in the chamber of the muffle furnace. The crystal was then placed onto a Teflon trough and left overnight in a desiccator. The Teflon trough with a volume of 10 mL was designed to have a tight fit to the crystal. As shown in Figure 2, two holes were drilled on the side of the trough. The bottom hole was used for the injection of the polymer solution while the top hole served as an air outlet. A smaller hole was drilled to fit a needle-type thermocouple for temperature control of the polymer solution. A stainless steel holder was designed to have a tight fit to the Teflon trough. Two cylindrical holes were drilled on the side of the holder to fit two finger heaters that were connected along with the thermocouple outlet to a microprocessor temperature controller. This served as a hot stage for the temperature control of the polymer solution inside the Teflon trough. The holder was separated from the aluminum base with an insulating plastic disk. A clamp was attached to the holder that held the crystal in place using a torque wrench. The whole mechanism sat on a pin that was normal to the reflecting surface and passed through the origin of the sphere. This could be rotated throughout the entire 360° without unclamping the crystal and was held tightly in position using T-clamps attached to the base plate with two diagonally opposed screws. The reflecting surface was 4 mm above the origin of the sphere. A fiber-optic UV-vis spectrometer (Guided Wave 200 analyzer) was used as the light source and detector system. Fiber optics eliminate the need for guiding mirrors and lenses that are a source of loss, particularly in the UV range. The spectrometer used here launches polychromatic light from a deuterium bulb (30 W) into a high-light-throughput, multimode silica fiber bundle containing seven silica fibers. The diameter of each silica single fiber is 320 μm. The fiber-optic cable connector is fitted to a radiance probe that has a fused-silica lens for collimating the diverging light emanating from the fiber bundle. We modified the tip of the radiance probe by installing a second fused-silica lens (Guided Wave) with a focal length of 1 in. and a Glan Thompson polarizer (Oriel). The analyzer probe and cable were identical to those from the light source. The ATR-modified light was collected by this probe and introduced to the monochromator and photomultiplier detector.

Adsorption Procedures. The cleaning procedure for the crystal has been described in the previous section. The Teflon trough was also cleaned with ultrasound for 10 min in dioxane, heptane, and ethanol, successively, followed by drying in a vacuum oven at a temperature of 40 °C overnight. The 20-mL glass syringe, hypodermic needles, and the top piece of the crystal were cleaned in a similar fashion except that they were placed in an oven at 120 °C overnight. On the day of the experiment, the trough/holder assembly was fastened to the base plate. A small amount of spectrograde glycerol was applied with an optical lens tissue to the top part of the crystal, before it was placed on the bottom part. The clamp was tightened with a torque wrench at 80 psi. Finger heaters and the cleaned hypodermic thermocouple were placed in their respective holes, and the temperature controller was turned on and set at 37 °C. Within $^1/_2$ h, the holder and crystal were equilibrated at 37 ± 0.4 °C and the background spectra were taken for nine angles of incidence for both TE and TM polarizations. The analyzer was required to detect the intensity at each wavelength interval 12 times. The lowest and the highest readings were dropped, and the other 10 readings were averaged. A single scan of 270–370 nm took approximately 1 min. Light was only allowed to run through the fibers during scanning to reduce the possibility of photodegradation of the fiber. The light source and the analyzer were allowed to warm up for at least 30 min before scanning. The polymer solution was then injected at 37 °C with the glass syringe through the bottom hole in the Teflon trough. The top hole was fitted with a stainless steel hypodermic needle, and after the trough was filled with the exit of the last air pocket, it was sealed with a clean glass cork. The first sample spectra were collected 10 min after the sealing of the top needle. Sample spectra were taken every 10 min up to 2 h and then every 1 h up to 10 h. These spectra were taken at an angle of incidence of 76° and TM polarization. An additional spectrum was recorded at 20 h, and if no significant change in the magnitude of the spectra was observed, the spectra were recorded for the eight other angle settings for both polarizations. This angle sweep was performed twice, with the second angle settings progressing in the opposite direction to compensate for any systematic errors introduced by taking the average of corresponding pairs. All spectra were ratioed to the corresponding background spectra.

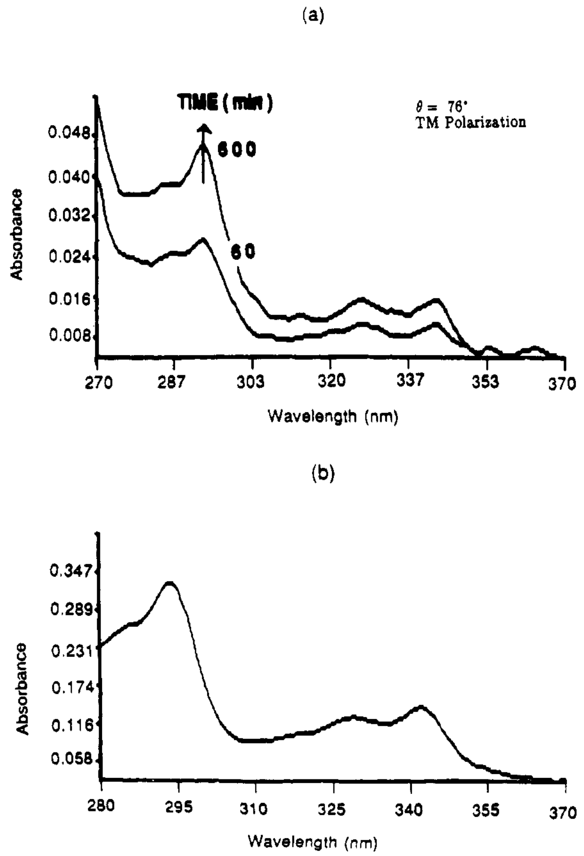

Figure 3. (a) Typical ATR spectra as a function of adsorption time. Spectra collected for the 0.1 mg/mL solution concentration and 76° angle of incidence and TM polarization. (b) Transmission spectra of dilute PVK solution in toluene.

Results and Discussion

Figure 3a illustrates a typical ATR spectrum as a function of adsorption time for the 0.1 mg/mL solution. It can be seen that the spectra remain similar in shape; only the magnitude of UV absorption increases as a function of time, due to the adsorption of PVK onto the

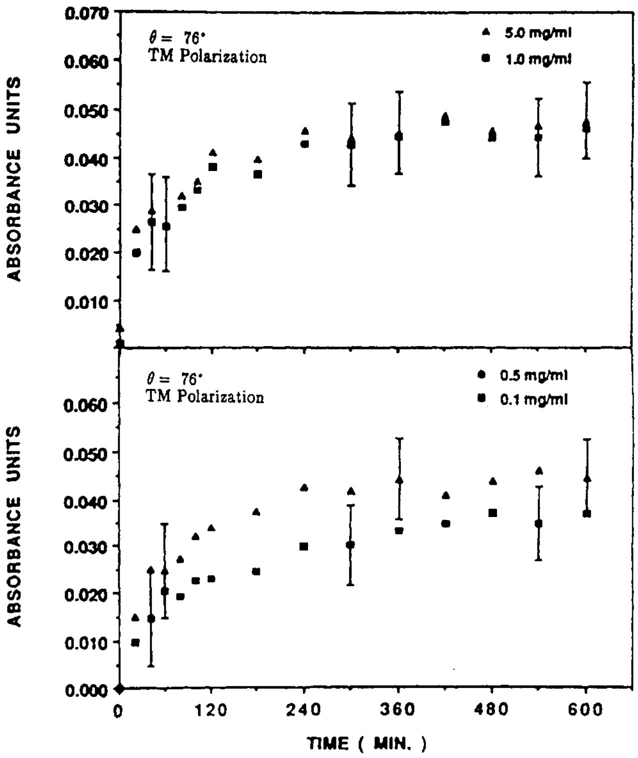

Figure 4. Absorbances at 298 nm plotted against adsorption time for various solution concentrations. Error bars represent twice the standard deviation from multiple experiments.

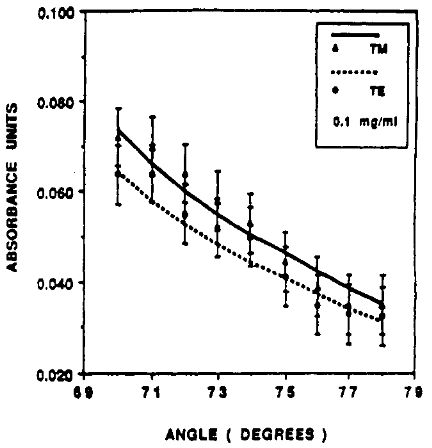

Figure 5. Absorbances at 293 nm as a function of the angle of incidence, for a 0.1 mg/mL solution concentration and TM and TE polarizations. Theoretical curves are for an exponential concentration profile: d = 210 Å, c_s = 65 mg/mL. Error bars represent twice the standard deviation from multiple experiments.

sapphire surface. These sample spectra were ratioed against background spectra obtained with the crystal in contact with air. Background spectra obtained with pure toluene in the cell do not have an effect on the resulting PVK spectra in the region from 270 to 370 nm, since the absorption coefficient of toluene is essentially zero beyond 280 nm and the spectra are obtained under total reflection.[22] These UV-ATR spectra can be compared with transmission UV spectra (Figure 3b) obtained for a dilute PVK solution in toluene by the same fiber-optic spectrometer with the probes in a transmission position. While the absorbance is higher for the transmission UV spectra as expected, the spectral features showing three main peaks are almost identical.

Figure 4 (bottom) shows the absorbance at 293 nm with the maximum value of twice the standard deviation as a function of adsorption time for a 0.1 mg/mL solution. For a 0.5 mg/mL solution, a similar time dependence is observed, except for the generally higher absorbances. In all solution concentrations, we observe an initially fast adsorption, followed by a slow buildup of the polymer on the sapphire surface. Figure 4 (top) also illustrates the results obtained for solution concentrations of 1.0 and 5.0 mg/mL. The absorbances in these data are comparable to each other and slightly greater than those in the data for a 0.5 mg/mL solution. Similar trends have been observed by other techniques.[7b,15e,26]

The average absorbances at 293 nm along with the maximum value of twice the standard deviation for variable angle settings and TM and TE polarizations are illustrated in Figure 5 for the 0.1 mg/mL solution concentration. It can be seen that the values for TM polarization are higher than those for TE polarization. There is also a significant increase in the absorbances at 293 nm from 78° to 70°. This increase is expected due to the greater depth of penetration (d_p) at lower angles of incidence. Quantitative comparison between the absorbance, A, and the prediction by the physics of the evanescent wave is possible through eq 1[10] where $c(z)$ is the concentration profile normal to the

$$A = [(Nn_{21}E_{0\text{-}p}^{2}\epsilon)/\cos\theta]\int_0^\infty c(z)\exp(-2z/d_p)\,dz \quad (1)$$

boundary, $E_{0\text{-}p}$ is the electric field amplitude at the boundary, θ is the incident angle, n_{21} ($=n_2/n_1$) is the ratio of the refractive index for the adsorbed layer divided by that for the sapphire, N is the number of reflections, and ϵ is the molar extinction coefficient. This equation assumes a homogeneous refractive index profile as a first approximation and requires an analytical expression for the concentration profile $c(z)$. The most basic expression that can be used for $c(z)$ is the exponential function predicted by the ground-state solution of the self-consistent-field theory[2] and the loop profile in the mean-field theory.[1] Therefore, $c(z)$ was assumed to decay exponentially according to eq 2 where c_s is the surface concentration and

$$c(z) = c_s\exp(-z/d) \quad (2)$$

d is the distance over which the concentration decays to c_s/e. There are two adjustable parameters, c_s and d, in eq 2. In addition, an "effective" refractive index (n_2) for the material in contact with the sapphire crystal has to be defined for eq 1. This refractive index determines the value of the depth of penetration and also affects the prefactors of the integral. Due to the nonuniform refractive index, the effective refractive index is difficult to determine, since it depends on the angle of incidence. The value of this refractive index has to be assumed based on physical rationale. A physical insight that helped in estimating the value of n_2 was the plateau in the experimental data for lower angles of incidence. This trend seemed to hint that the experiments at these lower angles were approaching the critical angle. We chose a value of 1.69, which is reasonable on the basis of the refractive indices of pure toluene and PVK which were determined as 1.60 and 1.76, respectively. For this refractive index, the depth of penetration decays from a value of 2400 Å at an angle of incidence of 70° to a value of 900 Å at an angle of 78°. Next, c_s and d were adjusted until the theoretical curves were of the same magnitude and varied over a comparable range with the angle of incidence. This type of analysis yields the theoretical curves illustrated in Figure 5 for the same solution concentration. These curves were calculated with a d value equal to 210 Å and a c_s value equal to 65 mg/mL. In reality, the value of 65 mg/mL for

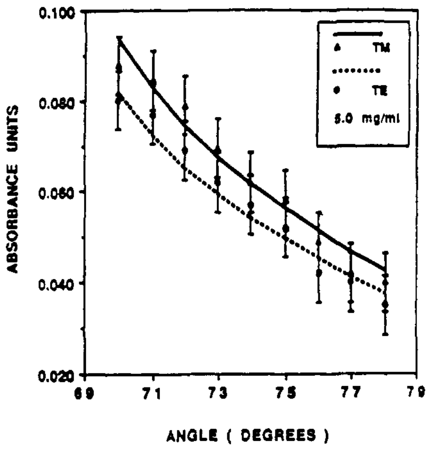

Figure 6. Absorbances at 293 nm as a function of the angle of incidence, for a 5.0 mg/mL solution concentration and TM and TE polarizations. Theoretical curves are for an exponential concentration profile: d = 280 Å, c_s = 65 mg/mL. Error bars represent twice the standard deviation from multiple experiments.

Table I
Model Parameters and Calculated Adsorption Parameters for PVK from Toluene Solution on Sapphire at 37 °C[a]

c, mg/mL	c_s, mg/mL	d, Å	Γ, mg/m^2	t_{RMS}, Å
0.1	65	210	1.37	297
0.5	65	230	1.50	325
1.0	65	260	1.69	368
5.0	65	280	1.82	396

[a] Errors in the values of d, Γ, and t_{RMS} are about ±3%.

the surface concentration was obtained after much trial and error and comparison with the other solution concentrations by assuming the surface concentration to remain constant at all concentrations. On the basis of adsorption theories, this is expected to be a good assumption for high molecular weight polymers. The theoretical curves assume an isotropic sample, and since the calculated values for TM and TE polarization compare reasonably well with the experimental data, no global orientation seems to be present. Figure 6 illustrates the results for the highest solution concentration of 5.0 mg/mL. The data exhibit a higher magnitude in absorbance and thus adsorbed amount for this solution concentration when compared with Figure 5. When the value of c_s was kept at 65 mg/mL, the value of d for this highest concentration was estimated to be 280 Å. For intermediate concentrations of 0.5 and 1.0 mg/mL, the values of d were estimated to be 230 and 260 Å. The errors in the values of d are about 3%. Therefore, the differences in the d values for various concentrations appear to be real.

We used these values to calculate the adsorbed amount (Γ) and the root-mean-square thickness (t_{RMS}), according to eqs 3 and 4, respectively.

$$\Gamma = c_s \int_0^\infty \exp(-z/d)\,dz \tag{3}$$

$$t_{RMS} = [(c_s \int_0^\infty \exp(-z/d) z^2\,dz)/\Gamma]^{1/2} \tag{4}$$

The model parameters and the calculated adsorption parameters are listed in Table I. The adsorbed amount (mg/m^2) is plotted against solution concentration (mg/mL) in Figure 7 and represents the adsorption isotherm of the system PVK/toluene/sapphire. The adsorption isotherm is of the low-affinity type as generally found for polydisperse polymer.[27] The adsorbance seems to level off with a value of 1.82 mg/m^2 in agreement with most polymer adsorbances. Figure 8 is a plot of the root-mean-square thickness (angstroms) versus solution concentration (mg/mL). The requirement of an identical value for surface concentration forces the RMS thickness dependency to be identical to the adsorbed amount. The RMS thickness values extend from 300 to 400 Å, approximately. These values are less than twice the radius of gyration of PVK at the Θ condition since the radius of gyration based on the measured weight-average molecular weight of 840 000 is estimated to be 240 Å. The mean thickness values extend from 210 to 280 Å and are more comparable to the radius of gyration of PVK at the Θ condition.

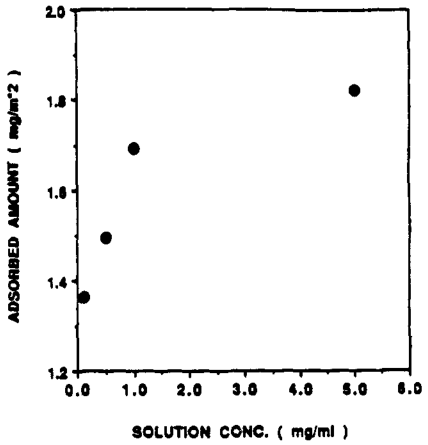

Figure 7. Adsorbed amount versus solution concentration. Errors are about ±3%.

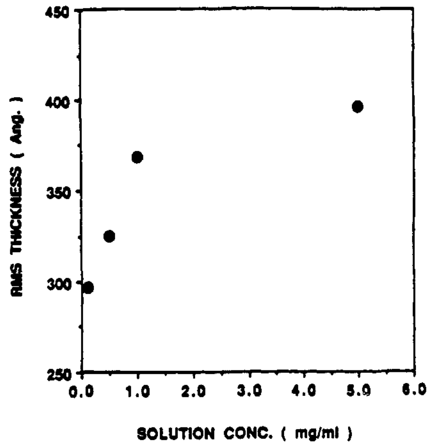

Figure 8. Root-mean-square (RMS) thickness versus solution concentration. Errors are about ±3%.

It should be noted that, for an exponential profile of characteristic distance d, the mean thickness of the adsorbed layer is equivalent to the characteristic distance d. It has been shown that this mean thickness is equivalent to the layer thickness measured by ellipsometry.[28]

In summary, a technique of attenuated total reflection (ATR) using the evanescent wave in the ultraviolet region was developed by designing an optical setup based on a specially designed ATR crystal and a fiber-optic UV spectrometer. This technique was applied to the in situ adsorption studies of polydisperse poly(*N*-vinylcarbazole) on the surface of a sapphire from toluene solution at the Θ temperature. The concentration profiles of the adsorbed layers in contact with solution were examined by performing angle-resolved experiments, which probe the 900–2500-Å range. Some characteristic parameters of the adsorbed layer were extracted with certain assumptions. Their values were reasonable on the basis of other adsorption studies.

The UV-ATR technique is similar to the fluorescence ATR technique extensively used by Rondelez and coworkers for polymer adsorption studies.[15] They both require the presence and the high intensity of the chromophores or the fluorophores in the polymer. While a fluorescence signal can be mixed with some scattering, a UV-ATR signal is free from such effects. On the other hand, fluorescence ATR can be more sensitive than UV-ATR.

Acknowledgment. This work was in part supported by the Office of Naval Research. We thank Drs. H. Hervet and F. Rondelez and Prof. S. Granick for helpful discussions and providing the manuscripts prior to publication.

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