Adsorption of Poly(vinyl alcohol) onto Hydrophobic Substrates. A General Approach for Hydrophilizing and Chemically Activating Surfaces

Mikhail Kozlov,[†] Mamle Quarmyne,[‡] Wei Chen,*[,‡] and Thomas J. McCarthy*[,†]

Chemistry Department, Mount Holyoke College, South Hadley, Massachusetts 01075, and Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

Received November 13, 2002; Revised Manuscript Received May 14, 2003

ABSTRACT: The adsorption of poly(vinyl alcohol) onto hydrophobic surfaces is described. Three different commercial polymer film samples, poly(tetrafluoroethylene-*co*-hexafluoropropylene)(FEP), poly(ethylene terephthalate) (PET), and poly(4-methyl-1-pentene) (PMP), four different silicon-supported covalently attached monolayers prepared from tridecafluoro-1,1,2,2-tetrahydrooctyl-dimethylchlorosilane, *n*-decyldimethylchlorosilane, 10-(carbomethoxy)decyldimethylchlorosilane, and 3-[methoxy(polyethyleneoxy)]-propyltrimethoxysilane, and a gold-supported self-assembled monolayer of 1-dodecanethiol were used as adsorption substrates. The kinetics of the irreversible adsorptions and the concentration dependence of adsorbed layer thickness are reported for FEP and the fluoroalkyl monolayer. The adsorbed films render the surfaces of the substrates hydrophilic with advancing water contact angles ranging from 40 to 68°. PVOH films on hydrophobic alkyl and fluoroalkyl monolayers are 10−50 Å thick, depending on solution concentration, and less thick on the less hydrophobic carbomethoxy-containing monolayers. Crystallization is implicated as a major driving force for adsorption as evidenced by infrared spectroscopy and electron diffraction. The supported PVOH thin films are stable in water at room temperature but dissolve in hot water. Cross-linking of the PVOH with glutaraldehyde causes the films to be stable to hot water.

Introduction

The low surface energies of organic materials give rise to problems in certain applications when adhesion, wetting, or spreading is required. Typically these problems are overcome by increasing the surface energy of the materials by introducing polar functionality using chemical surface modification or reactive gas discharge treatment (plasma, corona) or by surface graft polymerization of polar monomers.[1] We reported[2] another approach in 1991 that involved the irreversible adsorption of a polar polymer, poly(L-lysine) (PLL), from aqueous solution to a fluoropolymer, poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP), surface. These experiments were carried out based on the observations that numerous natural polymers, specifically proteins, adsorb from water onto hydrophobic surfaces.[3] We found, however, that most water-soluble synthetic polymers do not adsorb irreversibly to fluoropolymers from aqueous solution and that PLL adsorbs only under certain conditions, at pH 11 when it exists as a neutral, hydrogen-bonded α-helix. We thought that PLL was unique and that some structure in solution was critical (as is the case for proteins) for entropic reasons. The adsorbed layer of PLL was extremely thin and likely not continuous as evidenced by water contact angle analysis and X-ray photoelecton spectroscopy (XPS).

We recently reported[4] that poly(vinyl alcohol) (PVOH) spontaneously adsorbs from aqueous solutions to FEP−water interfaces and behaves very differently than other water-soluble polymers. A robust adsorbed film on the order of 10 Å thick is formed that renders the FEP hydrophilic. XPS and contact angle analysis suggest that the film is continuous. This research was initiated based on the report of Akashi et al.[5] that showed that multiple ultrathin layers of PVOH can be built up on gold surfaces. We showed that multilayer films could be prepared on FEP as well and suggest that the driving force for the initial adsorption on gold is hydrophobic forces. The gold surfaces used by Akashi et al. likely had adventious carbonaceous impurities that rendered them hydrophobic. A recent report[6] indicates that PVOH adsorbs from water to polystyrene.

Here we show that adsorption of PVOH from aqueous solution onto hydrophobic surfaces is a general phenomenon that can be used for surface modification. This is a significant advance in polymer surface modification in that this technique is simple and works with most any hydrophobic surface (every one that we have tried). Other techniques to introduce discrete alcohol functionality to polymer surfaces[7−10] are specific to individual polymers and involve multistep chemistry. Three different commercial polymer film samples, four different silicon-supported covalently attached monolayers (CAMs), and a gold-supported self-assembled monolayer (SAM) were used as adsorption substrates. In addition, a carbon-coated electron microscopy grid and a polystyrene-coated ATR IR crystal were used for analytical objectives. The introduction of a discrete functional group (alcohol) to these surfaces rather than a mixture of functional groups (which is the case for many surface modifications) allows rational subsequent surface modification chemistry. This chemistry will be the subject of future publications.

PVOH is unusual because it is atactic yet semicrystalline. It is surface-active at hydrophobic surface/water interfaces and concentrates at these sites allowing adsorption/crystallization to occur.

---

* To whom correspondence should be addressed. Email: weichen@mtholyoke.edu, tmccarthy@polysci.umass.edu.

[†] University of Massachusetts.

[‡] Mount Holyoke College.

10.1021/ma021681g CCC: $25.00

Experimental Section

General Information. Two samples of poly(vinyl alcohol) were used; one was from Polysciences ($M_W = 108\,000$, 99.7% hydrolyzed) and one was from Aldrich ($M_w = 89\,000-98\,000$, 99+% hydrolyzed). FEP film (5 mil) was obtained from Berghof, poly(ethylene terephthalate) (PET) film (5 mil Mylar) was obtained from DuPont and poly(4-methyl-1-pentene) (PMP) film (2 mil) was obtained from Mitsui. Silicon wafers were obtained from International Wafer Service (100 orientation, P/B doped, resistivity 20−40 Ω-cm, thickness 450−575 μm). The thickness of the native oxide on these wafers was determined to be ~22 Å by ellipsometry. Tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane, *n*-decyldimethylchlorosilane, 10-(carbomethoxy)decyldimethylchlorosilane, and 3-[methoxy(polyethyleneoxy)]propyltrimethoxysilane were obtained from Gelest and used as received. House-purified water (reverse osmosis) was further purified using a Millipore Milli-Q system that involves reverse osmosis, ion-exchange, and filtration steps (10^{18} Ω/cm). Other reagents and solvents were obtained from Aldrich or Fisher and used as received.

X-ray photoelectron spectra (XPS) were recorded with a Perkin-Elmer−Physical Electronics 5100 instrument with Mg Kα excitation (15 kV, 400 W). Spectra were obtained at two different takeoff angles, 15 and 75° (between the plane of the surface and the entrance lens of the detector optics). Contact angle measurements were made with a Ramé-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. The probe fluid used was water, purified as described above. Dynamic advancing (θ_A) and receding angles (θ_R) were recorded while the probe fluid was added to and withdrawn from the drop, respectively. The values reported are averages of three to five measurements made on different areas of sample surfaces. Ellipsometric measurements were made with a Rudolph Research model Auto SL-II automatic ellipsometer. The light source was a He−Ne laser with $\lambda = 632.8$ nm. The angle of incidence (from the normal to the plane) was 70°. Measurements were performed for three to five different locations on each sample. The thicknesses of the layers were calculated from the ellipsometric parameters (Δ and Ψ) using DafIBM software. Calculations were performed for the transparent double layer model (silicon substrate/silicon oxide + alkylsilane layer/PVOH/air) with the following parameters: air, $n_0 = 1$; PVOH, $n_1 = 1.5$; silicon oxide + alkylsilane layer, $n_2 = 1.462$, the thickness of this layer varied in a close range 29−31Å depending on the alkylsilane used; silicon substrate, $n_S = 3.858$, $k_s = 0.018$ (imaginary part of the refractive index). AFM images were obtained with a Digital Instruments NanoScope III atomic force microscope operated in tapping mode. Infrared spectra of PVOH films were obtained using a Bio-Rad FT IR spectrometer equipped with an MCT detector. Germanium 45° ATR crystals (1 × 5 × 10 mm) were purchased from Harrick Scientific. To render the surfaces of these crystals hydrophobic, they were submerged in a 0.1% (w/v) solution of polystyrene in toluene and withdrawn at a slow constant rate to form a thin uniform coating. A Harrick Scientific 45° fixed angle beam condenser was employed for operating the spectrometer in ATR mode. Background spectra were recorded on polystyrene-coated germanium crystals, and these were subtracted from the PVOH spectra. Each spectrum was obtained using 1024 scans. Electron diffraction studies were performed using a JEOL 2000FX Mark II 200 kV transmission electron microscope. Copper grids with square 400 mesh were coated with a continuous film of amorphous carbon; PVOH was deposited on them in the fashion described below for silicon substrates.

Polymer Film Preparation. FEP film was cleaned by immersing the film samples in 25 mL of concentrated sulfuric acid containing 0.5 g of potassium chlorate for 2 h. The film samples were then rinsed with five aliquots of water and then THF and dried at reduced pressure overnight. PET film was rinsed with water and then methanol, extracted with hexane for 2 h, and dried at reduced pressure overnight. PMP film samples were extracted with refluxing dichloromethane for 1 h and then dried at reduced pressure overnight.

Preparation of Silicon-Supported Substrates. These procedures are adaptations of one previously reported.[11] Silicon wafers were cut into 1.5 × 1.5 cm pieces and cleaned by submerging (overnight) in a freshly prepared mixture of seven parts concentrated sulfuric acid containing ~3 wt % sodium dichromate and three parts 30% hydrogen peroxide. Upon preparation, the solution warms to ~90 °C and foams extensively due to the formation of oxygen and ozone. Wafers were then removed and rinsed with copious amounts of water and dried in a clean oven at 120 °C for 1 h. Silanization reactions were carried out immediately after treating the wafers in this fashion. Silanization with alkyldimethylchlorosilanes was performed in the vapor phase at 70 °C for 3 days using ~1 mL of silane. There was no contact between the liquid silanes and the wafer. The reaction between the wafers and 3-[methoxy(polyethyleneoxy)]propyltrimethoxysilane was carried out overnight at room temperature using 2 mM silane in toluene. After silanization, all wafers except those modified with the fluorinated silane were rinsed with toluene, ethanol, 50:50 ethanol/water, and water (in this order). The $C_6F_{13}(CH_2)_2Si(CH_3)_2Cl$ − modified silicon wafers were soaked in perfluoro-2-butyltetrahydrofuran for 30 min and then rinsed with acetone, ethanol, and water (in this order).

Preparation of the Self-Assembled Monolayer. Gold surfaces were prepared on clean silicon wafers by sequentially evaporating and condensing 100 Å of chromium and 300 Å of gold. Samples were submerged in 10 mM 1-dodecanethiol in anhydrous ethanol overnight followed by rinsing in pure ethanol and drying at reduced pressure.

PVOH Solutions. Stock solutions of ~10% w/v PVOH were prepared by heating (85−100 °C) the polymer−water suspension for ~1 h and allowing it to cool. Solutions of lower concentration were prepared shortly thereafter by diluting the stock solutions. A PVOH film sample was prepared by casting a 0.5 M (based on repeat units) solution on a glass microscope slide. After it was allowed to dry in air, it was further dried at reduced pressure overnight.

Adsorption Experiments. Substrates were submerged in PVOH solutions at room temperature for the desired amount of time. Both glass and polypropylene vessels were used and we observed no differences in product structure. After the desired time, the samples were removed and rinsed with copious amounts of water and dried, either under a stream of nitrogen for 1 h or at reduced pressure overnight. Out of concern that some deposition (Langmuir−Blodgett-like) might occur when samples were removed through the solution−air interface, we diluted adsorption solutions repetitively after adsorption and removed the samples from pure water.

Cross-Linking of Adsorbed PVOH Films and Film Stability. A PVOH adsorbed layer on a silicon-supported $C_6F_{13}(CH_2)_2Si(CH_3)_2Cl$-derived monolayer was submerged in a 0.075 M aqueous solution of glutaraldehyde containing 0.2 M sulfuric acid for 45 min at 40 °C. The sample was removed from the solution and rinsed with copious amounts of water. An identical procedure was used with an FEP-supported PVOH film. Both un-cross-linked and glutaraldehyde-cross-linked films were submerged in water at 80 °C for 30 min and then rinsed and dried before analyses.

Results and Discussion

Poly(vinyl alcohol) (PVOH) is an unusual polymer in that it is both atactic and semicrystalline ($T_g = 85$ °C, $T_m = 258$ °C). It is prepared by hydrolysis of poly(vinyl acetate), and a number of "grades" are available that vary in their degree of hydrolysis; a range of molecular weights is also available. We briefly studied the effects of the degree of hydrolysis and the molecular weight on the adsorption behavior early in this work and decided to focus on completely hydrolyzed polymers at one molecular weight. Both of these factors affect the adsorption behavior and in particular the wettability of the resulting thin film, but these effects are not discussed further here. Two samples were used for the

Table 1. Substrates and Water Contact Angle Data

substrate	θ_A (deg)	θ_R (deg)
FEP	117	93
PMP	115	89
PET	77	55
Si/SiO_2-CF_3	116	107
Si/SiO_2-CH_3	107	90
$Si/SiO_2-CO_2CH_3$	86	76
Si/SiO_2−PEG	57	35
$Au-CH_3$	106	95

work described here: one was "99.7% hydrolyzed" and had a reported molecular weight (M_w) of 108 000, the other was "99+% hydrolyzed" and had a reported molecular weight (M_w) of 89 000−98 000. Neither showed evidence of residual acetate content by infrared spectroscopy.

Neither of these PVOH samples dissolves in water at room temperature (a general behavior of PVOH), but both dissolve to form apparently homogeneous solutions at elevated temperatures (80−100 °C) in tens of minutes. Dilute solutions are apparently stable for months after they are cooled to room temperature, and no crystallization or precipitation is observed. These solutions likely owe their kinetic stability to the slow rate of PVOH crystallization from water. The chains are highly hydrated. Three literature reports[4−6] indicate that PVOH adsorbs rapidly onto hydrophobic surfaces (FEP, gold, polystyrene) that are placed in contact with the aqueous solutions, and our report[4] suggests that the adsorption is irreversible under the conditions of adsorption (no desorption was observed after exposure to water for 14 days). It is also reported that PVOH adsorbs onto aqueous solution−air interfaces.[12] These results and the fact that PVOH adsorption is unique among the water-soluble polymers we have studied led us to the hypothesis that interface activity (at the hydrophobic surface−water interface) and crystallization drive the adsorption. We surmised that adsorption that lowers interfacial free energy increases the concentration of PVOH near the interface to a value in excess of its "kinetic solubility" and crystallization occurs in concert with adsorption. The experiments described here were designed to test this hypothesis.

Eight substrates, three commercial polymer films, four silicon-supported covalently attached monolayers (CAMs), and a gold-supported self-assembled alkanethiol monolayer (SAM) were chosen for study. These are summarized in Table 1 along with their water contact angle data. In addition a polystyrene-coated ATR IR crystal and a carbon-coated electron microscopy grid were used for analytical objectives. The three polymers were chosen to represent hydrophobic fluoropolymers (FEP), hydrophobic polyolefins (PMP), and a less hydrophobic polymer (PET). Three of the CAMs were chosen as models for these polymers and contain fluoroalkyl, alkyl, and ester functionality. The fourth CAM contains oligo(ethylene oxide) chains and represents hydrophilic surfaces. The SAM was studied to show generality. The surfaces abbreviated Si/SiO_2-CF_3, Si/SiO_2-CH_3, and $Si/SiO_2-CO_2CH_3$ were prepared using silicon wafers and a vapor phase reaction using $CF_3(CF_2)_5CH_2CH_2Si(CH_3)_2Cl$, $CH_3(CH_2)_9Si(CH_3)_2Cl$, and $CH_3OC(O)(CH_2)_{10}Si(CH_3)_2Cl$, respectively, that are monofunctional silanes that do not self-assemble, but form dense covalently attached monolayers.[11] The surface abbreviated Si/SiO_2−PEG was prepared from $CH_3O(CH_2CH_2O)_{6-9}Si(OCH_3)_3$ in toluene solution using conditions that should favor monolayer formation.[13] The surface abbreviated, $Au-CH_3$ was prepared by self-assembly of $CH_3(CH_2)_{11}SH$ from ethanol solution on evaporated gold. We note that the contact angle hysteresis is higher for the polymer films than the monolayers, and this is likely due to their greater roughness. The thicknesses of all four CAMs (plus the native oxide) were estimated by ellipsometry to range between 29 and 31 Å.

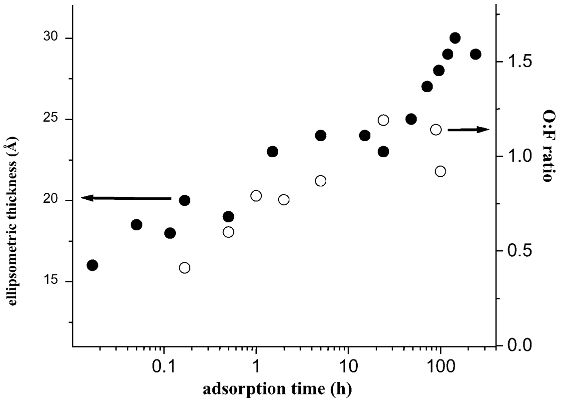

Figure 1. Kinetics of adsorption of PVOH to FEP (○, 0.01 M PVOH in water, room temperature) determined by XPS and to Si/SiO_2-CF_3 (●, 0.023 M PVOH in water, room temperature) determined by ellipsometry. Concentrations are based on repeat units.

Adsorption kinetics were determined for a number of conditions and substrates and were observed to be rapid in all cases. Figure 1 shows data for two systems, adsorption of PVOH onto FEP from a 0.01 M solution and onto Si/SiO_2-CF_3 from a 0.023 M solution. The relative adsorbed amounts are reflected by the O:F ratio for the FEP samples, determined by XPS and by the ellipsometric thickness of the layer for the Si/SiO_2-CF_3 substrates. Both of these measures must be regarded as estimates as the mean free paths of the photoelectrons in the thin films and the refractive indices of the thin films are unknown, but the relative thickness values should be quite accurate. Both adsorptions are initially rapid and then slow as the interfaces saturate. Adsorption to FEP reaches a plateau value after 24 h or less. The adsorption onto Si/SiO_2-CF_3 reaches a plateau from 90 min − 24 h, but a slow further growth in thickness is observed. This slow growth stops by 120 h as evidenced by the fact that the thickness after 240 h is unchanged relative to the thickness after 120 h. All subsequent adsorption experiments were carried out for 24 h, conditions that yielded reproducible film thicknesses as assessed by these techniques. We cannot readily explain the slow further film growth on the monolayer, but make several comments in this regard. If the polymer film is removed from the solution, dried, and resubmerged, another layer of PVOH adsorbs. Multilayers can be built up on Si/SiO_2-CF_3; this has been observed for FEP[4] and gold[5] (from solutions containing salt) as well. This indicates that the surface of the PVOH thin film must reconstruct on drying to a structure very different than that of the as-adsorbed polymer in contact with water. It is likely that the hydroxyl groups hydrogen bond with one another and orient away from the surface to minimize surface energy causing the film to become more hydrophobic. It is possible that the adsorbed PVOH layer on Si/SiO_2-CF_3 reconstructs to some extent at late adsorption times giving rise to the additional slow PVOH adsorption. A

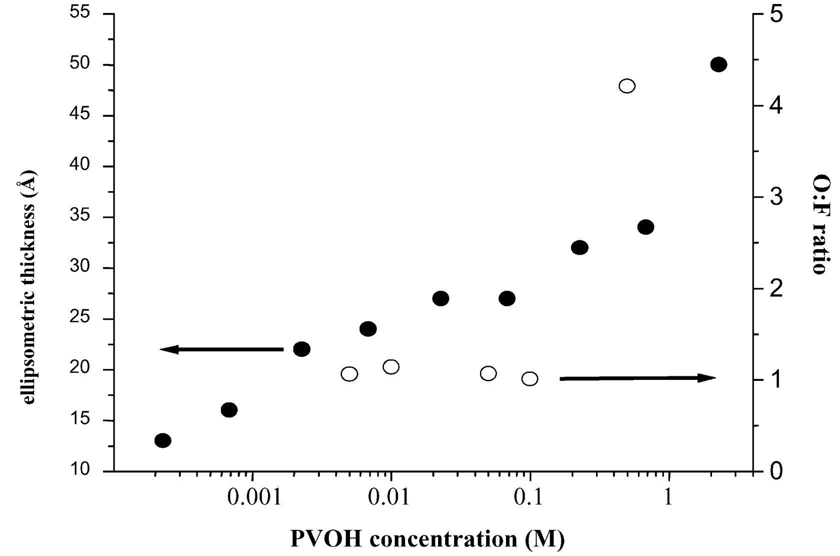

Figure 2. Ellipsometric thickness of PVOH thin films on Si/SiO_2-CF_3 (●) and O:F ratios (XPS) of PVOH thin films on FEP (○) as a function of PVOH solution concentration (based on repeat units) at room temperature.

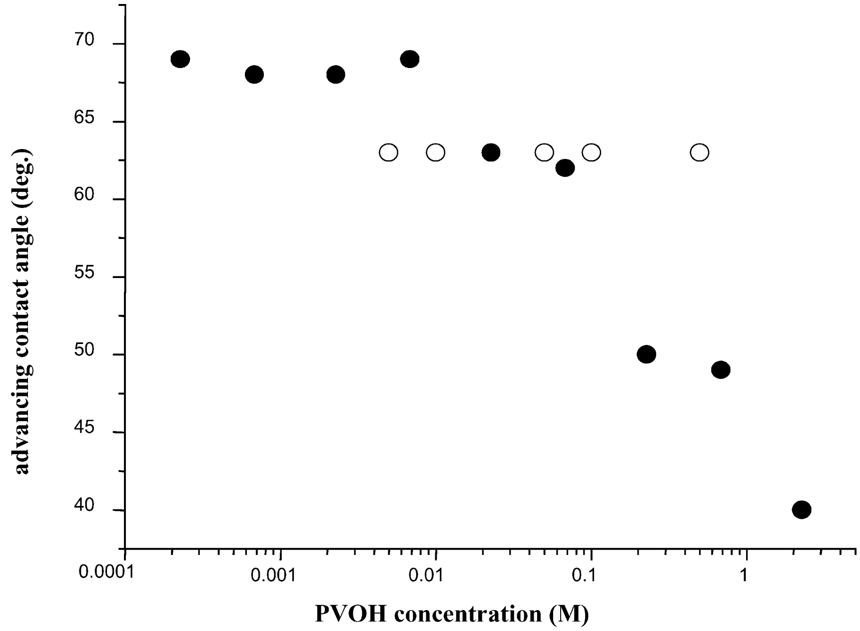

Figure 3. Advancing water contact angles for PVOH thin films adsorbed on Si/SiO_2-CF_3 (●) and FEP (○) as a function of PVOH solution concentration (based on repeat units) at room temperature.

comparison between the two systems described in Figure 1 and some of the data that follow suggest that PVOH adsorbs onto different surfaces in slightly different fashions.

The effect of PVOH concentration on adsorbed layer structure was assessed for Si/SiO_2-CF_3, and FEP and concentration isotherms are shown in Figure 2, again with ellipsometry data for the monolayer substrate and XPS data for the polymer substrate. For the case of Si/SiO_2-CF_3, PVOH thickness increases gradually with concentration, levels at intermediate concentrations and then rises further at higher concentrations. For FEP, the PVOH thickness is constant until high concentration and then increases significantly. We ascribe the rise in adsorbed amount at high concentration to solution viscosity and polymer entanglements. At low concentration, only single molecules adsorb, but at high concentration, entangled molecules that are stabilized by intermolecular hydrogen bonding adsorb as well. We note, but do not provide data here, that this effect is more pronounced with higher molecular weight PVOH. Water contact angles decrease substantially for both of these substrates upon PVOH adsorption. Advancing contact angles decrease from 116 and 117° to less than 70° at all concentrations. Receding contact angles decrease from 93 and 107° to less than 20°. Advancing water contact angles for supported PVOH films on Si/SiO_2-CF_3 and FEP as a function of adsorption solution concentration are shown in Figure 3. For Si/SiO_2-CF_3 the data mirror the trend seen in Figure 2. Contact angles decrease and level at ~65° at low concentrations and then decrease sharply to 40–50° at higher concentrations. The wettability of FEP-supported PVOH is independent of PVOH concentration, and advancing values are ~63°, that of cast PVOH films.

The trends in the Si/SiO_2-CF_3 data are consistent with our analysis of the thickness data (Figure 2) and suggest that at higher concentrations, entangled chains adsorb and give rise to more loosely packed PVOH chains. These chains are less hydrogen bound to one

Table 2. Water Contact Angle and Ellipsometric Thickness Data for Adsorbed PVOH Films

substrate	θ_A (deg)	θ_R (deg)	thickness (Å)
FEP	65	18	
PMP	58	16	
PET	40	13	
Si/SiO_2-CF_3	62	9	26 ± 2
Si/SiO_2-CH_3	61	9	27 ± 2
$Si/SiO_2-CO_2CH_3$	68	10	13 ± 1
Si/SiO_2-PEG	57	35	0 ± 1
$Au-CH_3$	62	11	
PVOH	63	17	

another and more available to interact with water. We hypothesize above (and show below) that crystallization is a driving force for PVOH adsorption, and from this perspective, we argue that the PVOH adsorbed onto Si/SiO_2-CF_3 at higher concentration is less crystalline than that adsorbed at lower concentrations. At high concentrations, entangled molecules adsorb and are forced to assume conformations that reflect their solution structure and crystallization is inhibited. Crystalline PVOH is characterized by doubly hydrogen-bonded alcohols.[14] PVOH films with lower degrees of crystallinity have more nonbonded hydrophilic groups.

We emphasize that PVOH adsorption differs between FEP and Si/SiO_2-CF_3; differences are seen in each of the first three figures. The monolayer surface is composed of predominately CF_3 groups, and the FEP surface has predominately less hydrophobic CF_2 groups. We believe that the details of the adsorption mechanism differ between these substrates and suspect that the initial adsorption steps on FEP are more reversible than for Si/SiO_2-CF_3. Entangled polymer chains are more likely to get “trapped” at the Si/SiO_2-CF_3−water interface than at the FEP−water interface. Table 2 shows water contact angle data for adsorbed PVOH films on all of the substrates studied and ellipsometric thickness data for the CAM substrates. The contact angle values for a cast film of PVOH are also included. The polymer-film-supported samples were prepared from 0.01 M PVOH and the monolayer-supported samples were prepared using 0.023 M PVOH (concentrations are based on repeat units). The data presented in Figures 2 and 3 indicate that the data in Table 2 can be compared directly, despite the differences in concentration. Several points are noteworthy. PVOH adsorbs onto all of the surfaces except the most hydrophilic one, Si/SiO_2-PEG. This supports our hypothesis that hydrophobic interactions or displacement of water molecules from the hydrophobic solid−water interface drives the initial steps of the adsorption. This is likely the reason that surfaces containing PEG oligomers are protein-resistant.[15] We note that PVOH does not adsorb to clean hydrophilic silicon wafers. Wettability increases significantly in all cases that adsorption is observed (compare with data in Table 1), but the contact angle data differ significantly substrate-to-substrate. The very low contact angle data observed for PVOH on PET suggest that the PVOH is highly disordered and less capable of ordering or crystallizing. PET is significantly less hydrophobic than the other substrates that PVOH adsorbs onto, and likely the adsorption mechanism differs. It is very different chemically from the other substrates, and the PET−water interface is likely very different in structure. PET contains aromatic diesters that are capable of hydrogen bonding with both water and PVOH. The thickness of the PVOH layer on the less hydrophobic $Si/SiO_2-CO_2CH_3$ surface is half that of the layers on the more hydrophobic Si/SiO_2-CF_3 and Si/SiO_2-CH_3 surfaces.

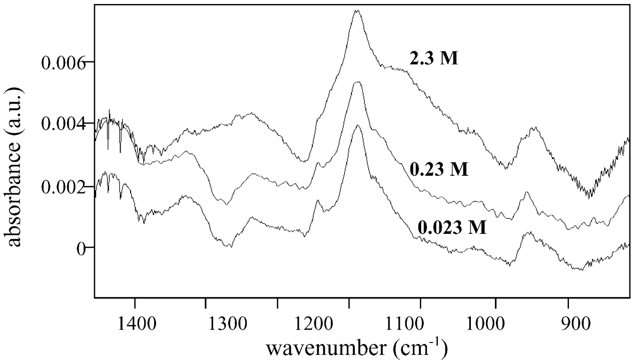

Figure 4. ATR IR spectra of PVOH thin films adsorbed onto polystyrene-coated germanium as a function of concentration (based on repeat units).

To implicate crystallization as a driving force for PVOH adsorption, ATR IR spectra were recorded. The C−O bond stretching vibration in PVOH is sensitive to the crystalline state of the polymer and allows assessment of crystallinity.[16] PVOH was adsorbed onto polystyrene-coated germanium ATR elements from solutions of 0.023, 0.23, and 2.3 M PVOH. The PVOH thicknesses ranged from 20 to 40 Å. Infrared spectra were recorded, and the C−O stretching regions of these are shown in Figure 4. A clear difference in the spectra is the relative intensity of the peaks at 1142 cm^{-1} (C−O stretch in the crystalline regions) and 1096 cm^{-1} (C−O stretching in the amorphous regions). The degree of crystallinity can be assessed using geometrical construction and a suitable calibration technique[17] and was found to vary from ∼10% for thin films adsorbed from 2.3 M PVOH to ∼30% for thin films adsorbed from 0.023 M PVOH. This difference in crystallinity is consistent with the arguments we make above regarding thickness and wettability. Thinner films adsorbed from more dilute solutions are more highly crystalline and less hydrophilic. Electron diffraction was performed to verify the crystallinity of adsorbed PVOH films. PVOH was adsorbed onto a carbon-coated copper TEM grid from a 2.3 M solution. The diffraction image shown in Figure 5 clearly indicates the presence of the PVOH crystalline phase. We have performed detailed AFM studies on the monolayer-supported surfaces and have observed only smooth conformal coatings. There are no visible crystallites on the film, and atomic force microscopy indicates that the PVOH films are smooth, featureless, and continuous with an rms roughness of ∼6 Å. Under other conditions (higher temperatures, added salt), the topography of the surface is affected, and this will be detailed in a future publication.

We emphasize that PVOH adsorbs onto all hydrophobic surfaces and also that the structure of the film differs surface-to-surface. We used the polystyrene-coated ATR IR crystal and the carbon-coated electron microscopy grid for experimental efficiency. The extent to which these data can be used to infer structure in the polymer film/PVOH and monolayer/PVOH samples is suspect. We believe, however, that crystallization is what sets PVOH apart from other water-soluble polymers at hydrophobic solid/water interfaces and that the crystallization observed at polystyrene and carbon reflects what is occurring at the other hydrophobic surfaces.

The supported PVOH thin films discussed here are stable to water (are not dissolved) at room-temperature

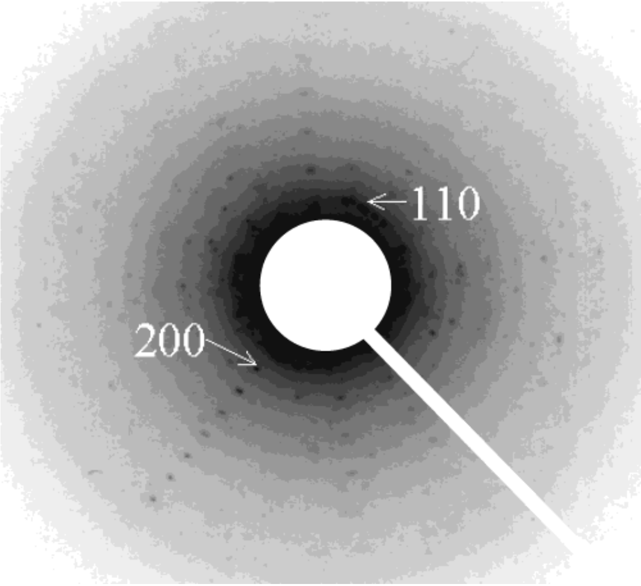

Figure 5. Electron diffraction pattern of a PVOH thin film adsorbed onto a carbon-coated copper TEM grid. The PVOH solution was 2.3 M based on repeat units.

Table 3. Water Stability Experiments for PVOH and Glutaraldehyde-Cross-linked PVOH Films

sample	θ_A (deg)	θ_R (deg)	thickness (Å)
as adsorbed Si/SiO_2-CF_3-PVOH	63	11	28
after water treatment[a]	112	16	14
cross-linked Si/SiO_2-CF_3-PVOH	56	11	39
after water treatment[a]	56	11	39

[a] Immersed in water at 80 °C for 30 min.

indefinitely, but do dissolve in hot water (the same behavior as solid PVOH). To prepare samples that are stable to hot aqueous solutions, we cross-linked the PVOH with glutaraldehyde using a modification (no Na_2SO_4 was used) of a procedure reported for the preparation of PVOH hydrogels.[18] Table 3 shows the results of the water stability experiments using samples of PVOH adsorbed onto Si/SiO_2-CF_3 from 0.023 M solution. The as-adsorbed PVOH layer has a thickness of 28 Å and water contact angles of $\theta_A/\theta_R = 63°/11°$. After immersion in water at 80 °C for 30 min, the thickness is reduced to 14 Å and the contact angle values change to $\theta_A/\theta_R = 112°/16°$. About half of the PVOH is dissolved under these conditions, and the advancing contact angle indicates that the fluoroalkyl monolayer is exposed. Cross-linking with glutaraldehyde causes the thickness of the film to increase to 39 Å and the contact angles to change to $\theta_A/\theta_R = 56°/11°$. After immersion in 80 °C water for 30 min, no polymer is dissolved and the contact angles do not change, indicating that this cross-link density stabilizes the PVOH film. It is interesting that in this case the advancing contact angle decreases upon cross-linking, which decreases the total number of alcohol groups and introduces nonpolar methylene groups and relatively nonpolar acetal groups. Evidently the reaction frees up some hydrogen-bonded alcohols.

Summary

Poly(vinyl alcohol) adsorbs irreversibly from aqueous solutions onto hydrophobic solids in contact with the solutions. Lowering interfacial free energy (hydrophobic interactions or displacement of water molecules from the hydrophobic solid−water interface) drives the initial steps of the adsorption. The polymer concentrates at the interface, exceeds its “kinetic solubility” in this region and crystallization ensues yielding adsorbed continuous thin films of PVOH that are 10−50 Å thick. The thickness, wettability, and crystallinity of the PVOH thin films depend on PVOH concentration and the structure of the hydrophobic substrate. Cross-linking the PVOH renders it stable to hot water and does not decrease (in fact can increase) wettability. This is a versatile technique to hydrophilize hydrophobic solids and introduce alcohol functionality to surfaces. Seven hydrophobic substrates including three polymer film samples, three silicon-supported CAMs, and one gold-supported SAM as well as polystyrene (for the ATR IR experiments) and carbon (for the electron diffraction experiment) adsorb PVOH and become hydrophilic.

Acknowledgment. We thank the NSF-funded Research Site for Educators in Chemistry, the Office of Naval Research, and the NSF-funded Research in Undergraduate Institutions for financial support. Use of the central facilities of the NSF-supported Materials Research Science and Engineering Center at the University of Massachusetts is also acknowledged.

References and Notes

(1) For a review see: Ward, W. J.; McCarthy, T. J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley and Sons: New York, 1989; Suppl. Vol., p 674.
(2) Shoichet, M. S.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 1441.
(3) Young, B. R.; Pitt, W. G.; Cooper, S. L. *J. Colloid Interface Sci.* **1988**, *125*, 246.
(4) Coupe, B.; Chen, W. *Macromolecules* **2001**, *34*, 1533.
(5) Serizawa, T.; Hashiguchi, S.; Akashi, M. *Langmuir*, **1999**, *15*, 5363.
(6) Barrett, D. A.; Hartshorne, M. S.; Hussain, M. A.; Shaw, P. N.; Davies, M. C. *Anal. Chem.* **2001**, *73*, 5232.
(7) Lee, K.-W.; McCarthy, T. J. *Macromolecules* **1988**, *21*, 1, 2318.
(8) Bening, R. C.; McCarthy, T. J. *Macromolecules* **1990**, *23*, 2648.
(9) Franchina, N. L.; McCarthy, T. J. *Macromolecules* **1991**, *24*, 3045.
(10) Chen, W.; McCarthy, T. J. *Macromolecules* **1998**, *31*, 3648.
(11) Fadeev, A. F.; McCarthy, T. J. *Langmuir* **1999**, *15*, 3759.
(12) Glass, J. E. *J. Phys. Chem.* **1968**, *72*, 4450.
(13) Fadeev, A. F.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7268.
(14) Bunn, C. W. *Nature (London)* **1948**, *161*, 929.
(15) Harris, J. M., Zalipsky, S., Eds. *Poly(ethylene glycol): Chemistry and Biological Application*; American Chemical Society: Washington, DC, 1997.
(16) Tadokoro, H.; Seki, S.; Nitta, I. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 559.
(17) Kenney, J. F.; Willcockson, G. W. *J. Polym. Sci., Part A* **1966**, *4*, 679.
(18) Kim, K. J.; Lee, S. B.; Han, N. W. *Polym. J.* **1993**, *25*, 1295.

MA021681G