

Water Adsorption on and Desorption from Crystalline Copolymers of Vinylidene Fluoride with Trifluoroethylene

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Received: September 10, 2004; In Final Form: October 15, 2004

Water adsorption and absorption on crystalline polyvinylidene fluoride with 30% trifluoroethylene, P(VDF–TrFE, 70:30), was examined by thermal desorption spectroscopy. Two distinctly different water adsorption sites are identified: one adsorbed species that resembles ice and another species that interacts more strongly with the polymer thin film. The existence of the latter species is consistent with X-ray diffraction studies of water absorbed into the bulk of copolymers of polyvinylidene fluoride with trifluoroethylene crystalline thin films. There are strong steric effects observed in the angle-resolved thermal desorption that may be a result of the large polymer thin film surface dipoles.

1. Introduction

Water adsorption on surfaces (and the formation of ice) has been a major part of surface science for decades,^{1,2} but there is not yet a corresponding level of understanding of water (or indeed any adsorbate) interaction with polymer surfaces.³ Unlike single-crystal metal surfaces, polymers are typically not very good electrical or thermal conductors and are notorious for having very heterogeneous surfaces,³ adding considerable impediments to the undertaking of otherwise standard surface science techniques. In complex polymer mixtures, segregation of one component^{4–10} complicates attempts to prepare a reproducible surface. Yet, water absorption by polymers is not only a subject of considerable research, but also an issue with considerable industrial applications in gels and in vivo implants, not to mention water-resistant coatings.

Despite the complexities of polymer surface characterization, water has been identified as a cause of reorientation at polymer surfaces,^{11–14} including the surface structure of fluorinated polymers.^{15–17} Water has a strong dipole, so it is not surprising that water absorption is also known to change the dielectric properties of polymers, including copolymers of polyvinylidene fluoride with trifluoroethylene.^{18–20}

Copolymers of polyvinylidene fluoride with trifluoroethylene, P(VDF–TrFE), have a number of advantages for the surface scientist interested in adsorption and absorption studies in that ultrathin crystalline films of these polymers can be formed, thin enough for sufficient thermal conductivity for thermal desorption experiments as described here. The Langmuir–Blodgett technique for fabricating the P(VDF–TrFE) films provides sufficient crystalline order for scanning tunneling microscopy,^{21–24} low-energy electron diffraction,^{22,23} and even band structure mappings,^{22–23} so that in many respects adsorbate interactions can be investigated in much the same way as traditional surface science studies undertaken on single-crystal metal surfaces. The Teflon-like polymer and tetrafluoroethylene are a rich system for the study of ferroelectricity,^{24–26} with a number of applications^{26,27} in electronic devices, including piezoelectric transducers.²⁸ In all ferroelectric applications of P(VDF–TrFE) in most ambient environments, there is the question of whether the strong dipole of water results in absorbed water adopting

behavior as an actor (contributing to the ferroelectric transition) or as a spectator (merely responding to the ferroelectric transition). Angle-resolved thermal desorption spectroscopy provides some indication of dipole–dipole interactions. We chose copolymers of polyvinylidene fluoride with trifluoroethylene for these studies because the trifluoroethylene results in a polymer system that is still crystalline but with a surface and bulk ferroelectric transition that is within the vicinity of room temperature (20 and 80 °C, respectively, for P(VDF–TrFE, 70:30)^{23,26,27}) and well below the melting temperature of the polymer (about 160 °C).

2. Experimental Section

Ultrathin ferroelectric films of a copolymer such as 70% vinylidene fluoride with 30% trifluoroethylene, P(VDF–TrFE, 70:30), by molecular percent (not by weight percent) and 80% vinylidene fluoride with 20% trifluoroethylene, P(VDF–TrFE, 80:20), by molecular percent (not by weight percent) were fabricated by the Langmuir–Blodgett (LB) deposition technique on graphite substrates from the water subphase, which can produce films with thickness ranging from 1 monolayer (1 ML, 0.5 nm) to over 500 ML.²⁷ The bulk crystallinity has been confirmed by X-ray diffraction on films from 4 to 150 ML thick.^{18,23,29} The angle-resolved thermal desorption studies were undertaken in an ultra-high-vacuum chamber with sample cooling to 120–135 K as described elsewhere.^{30,31} The temperature was determined using a calibrated chromel–alumel thermocouple, as has been described elsewhere.^{30,31} To undertake the angle-resolved thermal desorption experiments, the quadrupole mass spectrometer (Dycor) operated by the new Ametek software, with an angular acceptance of $\pm 3^\circ$ of the spectrometer axis, was differentially pumped by an ion pump. P(VDF–TrFE, 70:30) samples 3 and 425 molecular layers thick, on graphite, were cleaned in ultrahigh vacuum by annealing at 110 °C before and after each experiment for 30 min, which has proved to be an effective recipe in prior studies.^{21–23} The heating rates for obtaining the thermal desorption spectra were 0.5 deg/s throughout this work.

X-ray diffraction (XRD) studies in a water vapor ambient and in a vacuum at room temperature were undertaken to study

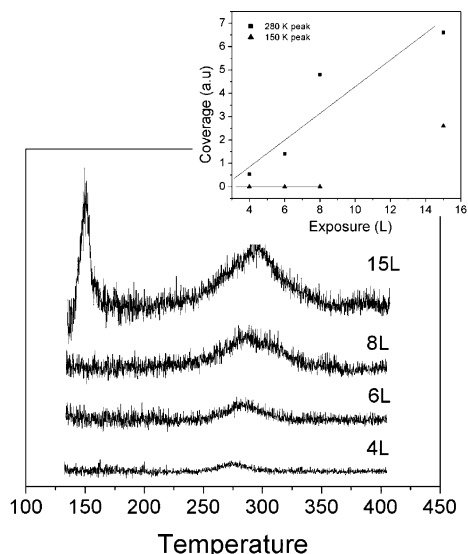


Figure 1. Thermal desorption spectra of water from a thin (15 Å thick) P(VDF-TrFE, 70:30) film on graphite for 4, 6, 8, and 15 langmuirs of exposure to water at 130 K (1 langmuir = 1×10^{-6} Torr·s). The inset shows the integrated thermal desorption intensities of water associated with ice, desorbing at about 160 K (▲), and absorbed water, desorbing at 280–300 K (■).

water absorption effects on the lattice constant of the well-ordered copolymer films nominally 100 molecular P(VDF-TrFE) layers thick.^{18,29} A small stainless steel vacuum chamber, with a Mylar window largely transparent to the X-ray radiation, was built²⁹ and mounted in a Rigaku D/MAX-B θ - 2θ X-ray diffractometer. This allowed scans of 2θ through nearly 180° , and determination of the lattice constant in the normal direction. The main Mylar contribution to the θ - 2θ diffraction intensity was in the vicinity of 26° , well away from the P(VDF-TrFE) copolymer film contribution near 20° in the ferroelectric phase and 18 – 19° in the paraelectric phase.^{18,23,29}

3. Evidence of Water Absorption

The thermal desorption spectra of water desorption from thin (roughly 14 Å thick) crystalline films of P(VDF-TrFE, 70:30) are characterized by two desorption peaks, as indicated in Figure 1. With smaller exposures to water of up to 4–10 langmuirs (1 langmuir = 1×10^{-6} Torr·s), the water desorbs at 275–300 K. With increasing water exposure, a second feature appears in the thermal desorption spectra at roughly 160 K. In thicker films (roughly 115 Å thick), the water desorption at roughly 160 K does not appear until much higher exposures to water in the vicinity of 100 langmuirs.

The desorption water at 150–160 K resembles the thermal desorption of water from graphite³² and ice from Cu(100),^{33,34} which exhibit largely zero-order thermal desorption kinetics (sublimation) at very similar temperatures. This thermal desorption feature in the thermal desorption spectra is characteristic of sublimation of water and does not saturate with increasing water exposure, but continues to increase in intensity. We associate this water species with the formation of surface “ice” or similar species. What is interesting is that the formation of this icelike species is not observed with small exposures of water to the P(VDF-TrFE) thin film sample cooled to 130 K. For samples roughly 14 Å thick, more than 10 langmuirs is required for formation of ice. For thicker films, roughly 115 Å thick, more than a 100 langmuir exposure to water is required for the formation of ice, as determined in thermal desorption spectra. We therefore conclude that, as indicated in Figure 1, the water

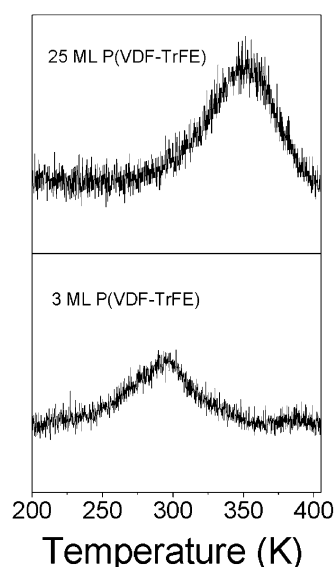


Figure 2. Thermal desorption spectra of water from two films of P(VDF-TrFE) on graphite, with different P(VDF-TrFE) film thicknesses of 115 Å (nominally 25 monolayers) and 15 Å (nominally 3 monolayers). The films were exposed to water at 130 K at 40 and 5 langmuirs, respectively, exposures well below that for formation of ice. Note that the thermal desorption of water occurs at a higher temperature (365 K) for the thicker P(VDF-TrFE) film than the thinner P(VDF-TrFE) film (280 K).

is not adsorbed into a site characterized by weak substrate-adsorbate interactions, but a more strongly bound water adsorption or, more appropriately, absorption site. Indeed, by delaying the thermal desorption experiments for various time durations following the adsorption of water, it is very evident that water sublimates more rapidly from the ice species (desorbing at 160 K) than the absorbed species (desorbing at 280–350 K).

The peak temperature, for this more strongly bound water species, increases in temperature with the thickness of the P(VDF-TrFE) film, as indicated in Figure 2. Because the desorption temperature of water from P(VDF-TrFE) above 280 K is associated with film thickness and water exposure, we associate this water species with absorbed water, not a surface species. The assignment of this desorption peak to an absorbed species of water in P(VDF-TrFE) is consistent with the extremely broad thermal desorption temperature width that does not match exactly with first- or second-order reaction rate kinetics. This thermal desorption feature has a width that increases with increasing integrated thermal desorption intensity. For thicker films, roughly 115 Å thick, this thermal desorption feature can span a temperature range of more than 50 K. Because the desorption characteristics scale with P(VDF-TrFE) film thickness and the desorption temperature is well above 280 K at high coverages, we can exclude water intercalated in the graphite substrate as a contribution to this water species.³² Because of the huge temperature width in the thermal desorption, Arrhenius plots of the pressure versus temperature provide very low desorption energies, much lower than the expected 0.49 eV per molecule sublimation energy of water.^{32,35} Diffusion of water within the P(VDF-TrFE) film to the surface, prior to desorption, is implicated in the width of the thermal desorption peak and the peak temperature.

There is other evidence of water absorption from X-ray diffraction.^{18,29} Although water is not considered a standard solvent for P(VDF-TrFE), the well-ordered P(VDF-TrFE) copolymer films swell when immersed in water^{18–20} and some similar fluorinated polymers.^{36,37} For a 100 ML P(VDF-TrFE,

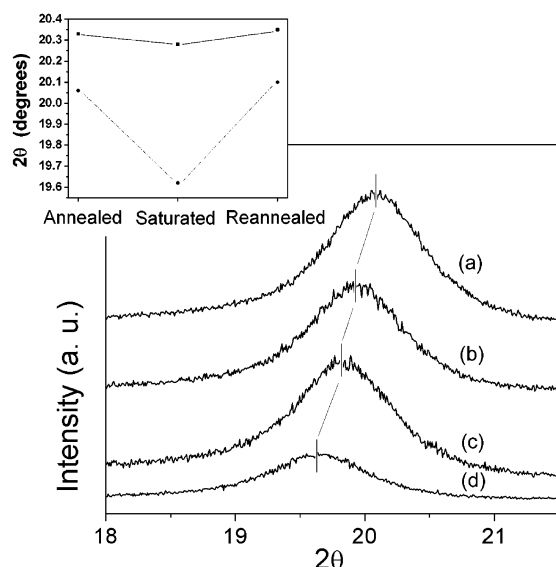


Figure 3. Increase in the layer lattice spacing along the film normal for crystalline copolymer Langmuir-Blodgett films of 80% vinylidene fluoride with 20% trifluoroethylene with water exposure. The θ - 2θ X-ray diffraction scans, recorded at room temperature, are shown for increasing times of exposure to water as described in the text. The film is nominally 100 monolayers thick. The inset summarizes that reannealing to remove water restores the interlayer lattice constant and that the absorption of water is reversible.

80:20) film (with a slightly higher ferroelectric transition temperature than P(VDF-TrFE, 70:30)) annealed in a vacuum, there is an increase in the $\langle 110 \rangle$ lattice interlayer spacing ranging from 4.35 to 4.45 Å for the water-free films to as much as 4.55 Å with long exposure to water. This is seen in the XRD measurements shown in Figure 3: the annealed (nominally 100 layers or roughly 450–500 Å thick) P(VDF-TrFE) film (a) and after contact with liquid water at room temperature for 50 h (b), 120 h (c), and 240 h (d). Even in contact with liquid water, the copolymer films may not reach equilibrium for hours or days. This again is consistent with a diffusion-limited process, consistent with the thermal desorption data.

While the degree of lattice expansion varied considerably among samples, all exhibited the same trend: an increase in the $\langle 110 \rangle$ layer spacing by 0.2–0.8 Å after exposure to water or water vapor. A large initial lattice constant, for the annealed film, leads to greater swelling (by as much as a 4% increase in the lattice constant). For films with the smallest lattice constant, there is still some increase in the lattice constant (0.5%) and a decrease in the $\langle 110 \rangle$ X-ray diffraction intensity. By gradually increasing the annealing temperature and then annealing for 3 h at 110 °C, the water was removed from P(VDF-TrFE) thin films. After the film is annealed, both diffraction intensities and the original, film-specific, lattice constant are recovered, as indicated by the inset to Figure 3.

4. Evidence of Steric Effects

Water has a strong dipole as does P(VDF-TrFE). Although P(VDF-TrFE) is a known ferroelectric, some ferroelectric properties have been ascribed to ice as well.^{38–40} Adsorbate/adsorbate dipole interactions with large P(VDF-TrFE) dipoles are expected, particularly since water is known to cause polymer reorientation with a number of polymers.^{11–17} This water to polymer interaction may be manifest in a number of ways, beyond simply affecting the P(VDF-TrFE) dielectric properties,^{18–20} as noted above.

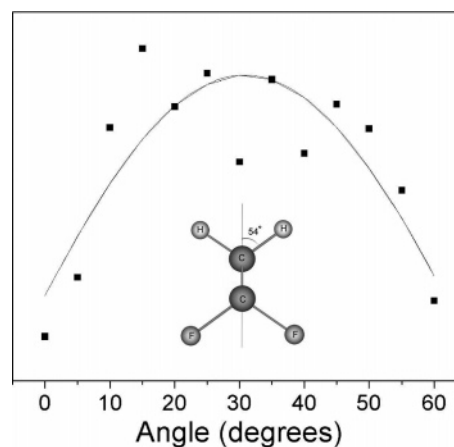


Figure 4. Integrated intensity of water desorbing from P(VDF-TrFE) as a function of the angle with respect to the surface normal, showing an enhancement of the desorption signal at 30°. The data were abstracted from the angle-resolved thermal desorption spectra taken following 5 langmuir water exposure of P(VDF-TrFE) thin films at 130 K. The \sin^2 curve is meant only to guide the eye.

With this potential for dipole-dipole coupling, we investigated the possibility that steric effects might occur in the water desorption process. Angle-resolved thermal desorption was undertaken at various take-off angles ranging from 0° to 65° with respect to the film surface normal. Angle-resolved thermal desorption studies were undertaken with thinner films (about 15 Å thick) to avoid dramatic temperature gradients through the P(VDF-TrFE) film and were undertaken at smaller water exposures of the P(VDF-TrFE) film to avoid any complications of ice formation. The desorbing water species, following 5 langmuir water exposure of 15 Å thick P(VDF-TrFE) films at 120 K, is attributable solely to the absorbed water species (thermal desorption occurs in the vicinity of 280–300 K) not the surface “ice”, as indicated in Figure 1. The intensity of the integrated thermal desorption peak in the vicinity of 280–300 K (the only desorption water peak at this water exposure) is plotted showing the normalized water desorption intensity peaks at 30° off normal (Figure 4), strong evidence of steric or geometric effects.

This favored off-normal desorption of water and the example of nickelocene in the canted configuration³¹ are among the very examples where steric effects in the thermal desorption process cause the angle-resolved thermal desorption to deviate strongly from the expected $\cos^2 \theta$ distribution.⁴¹ Unlike the example of nickelocene, adsorbate to adsorbate interactions³¹ cannot be implicated as the origin of the favored off-normal desorption. Rather the increase in the desorption signal at 30° off normal appears to be related to the off-normal orientation of each $-\text{C}-\text{H}$ and $-\text{C}-\text{F}$ bond that forms the dipole moment of each monomer (CH_2-CF_2) of the P(VDF-TrFE, 70:30) copolymer (roughly 54°),^{25–27} or the $-\text{C}-\text{C}-$ bond angle of 30° that runs from CF_2 to CH_2 in the monomer. In fact, the $\cos^2 \theta$ distribution contribution is largely absent in the case of water desorption from P(VDF-TrFE), but still evident in the case of nickelocene desorption from Ag(100).³¹ This suggests that the origins of the steric effects in the thermal desorption spectra of these two systems are significantly different.

The off-normal desorption of water suggests that there are steric effects due to water interaction with P(VDF-TrFE), though more work will be needed to demonstrate this interaction directly. Such dipole-dipole interactions would do much to explain the influence of water on the dielectric properties of P(VDF-TrFE) with water absorption.^{18–20} Unfortunately, we

have not been able to identify the possible absorption sites within the bulk of the P(VDF–TrFE) film as yet. The loss of diffraction intensity (Figure 3) suggests that there are several sites and/or the water is not necessarily well ordered once absorbed within the bulk of the polymer films.

5. Summary

We find evidence for at least two different adsorbed species of water on P(VDF–TrFE): an icelike species and an adsorbed species. The desorption of water from the adsorbed phase is associated with strong interactions with the substrate leading to steric effects that favor desorption of water off the surface normal. The desorption of adsorbed water is complicated by diffusion processes to the P(VDF–TrFE) surface.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE-0415421 and the by the Petroleum Research Fund administered by the American Chemical Society.

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