

# Water Absorption and Desorption from the Dipole Ordered Polymer Poly(methylvinylidene cyanide)

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From thermal desorption studies, we find evidence that absorbed water in the bulk of poly(methylvinylidene cyanide) is more weakly bound than is the case for copolymer films of poly(vinylidene fluoride—trifluoroethylene). Ultraviolet laser enhanced thermal desorption of absorbed water exhibits little light polarization dependence for poly(methylvinylidene cyanide) in contrast to absorbed water in copolymer films of poly(vinylidene fluoride—trifluoroethylene). The implications of these differences are discussed.

## Introduction

The ferroelectric crystalline copolymer films of vinylidene fluoride with trifluoroethylene (70%:30%), P(VDF-TrFE), strongly interact with the dipoles of adsorbed and absorbed water molecules.<sup>1,2</sup> Recently, this interaction has been probed by using laser assisted thermal desorption techniques<sup>2</sup> and the UV light enhancement of water desorption was found to be strongly light polarization dependent.<sup>2</sup> Several explanations have been put forward to explain these phenomena.<sup>2</sup> A comparison of these recent results with water absorption studies of crystalline thin films of poly(methylvinylidene cyanide) (PMVC) provide an opportunity to determine whether surface dipoles alone influence the light polarization dependent enhancement of water desorption or dipole reversal and/or local point group symmetry plays a role.

Surface dipole interactions have long been implicated as important in surface adsorption and surface catalysis.<sup>3–6</sup> Furthermore, water absorption is seen to alter the dielectric properties of the ferroelectric crystalline copolymer films of vinylidene fluoride with trifluoroethylene (70%:30%).<sup>7–11</sup>

Surface dipoles can affect the binding site of water species adsorbed at the surface and sterically hinder or enhance the desorption of adsorbed and absorbed water.<sup>1,2,7</sup> We show that the strong light polarization effects in ultraviolet laser enhanced thermal desorption of absorbed water, which have been found in copolymer films of poly(vinylidene fluoride—trifluoroethylene), are not as significant for a similar dipole ordered polymer—poly(methylvinylidene cyanide).

## Experimental Section

Thin films of poly(methylvinylidene cyanide) or PMVC were prepared by the Langmuir–Blodgett (LB) method from a water subphase, as described elsewhere.<sup>12,13</sup> Films used for this study

were 8 ML (6.5 nm) thick and grown on highly ordered pyrolytic graphite (HOPG) substrates. The LB method produces highly crystalline films of PMVC as is evident from the surface structure investigated by STM and experimental band structure mappings.<sup>13</sup>

Thermal desorption spectra were taken with a quadrupole mass spectrometer (Dycor), monitoring mass 18 amu, in an ultrahigh vacuum (UHV) chamber as described elsewhere.<sup>1,2,14</sup> The graphite substrate (chosen for the flat surface and better thermal conductivity) supporting the PMVC was held between tantalum mounts and heated resistively at a rate of 0.5 deg/s. This slow heating rate was used to minimize the effect of thermal gradients in the thin film. To remove any water remaining from the fabrication the sample was vacuum annealed at 350 K for 60 min before any desorption spectra were taken. Before each experiment the thin film was annealed in a vacuum at 350 K for 20 min. A similar annealing treatment has been used on copolymers of poly(vinylidene fluoride—trifluoroethylene), P(VDF-TrFE).<sup>1,2,14</sup>

For the experiments undertaken here, the thin films of PMVC were exposed to water vapor at substrate temperatures of 160 K, to avoid the complication of surface ice formation observed with water adsorption on P(VDF-TrFE) at 130 K.<sup>1,2,14,15</sup> After exposing the sample to water, the chamber was pumped for 5 min to reduce the UHV chamber background pressure (largely water vapor) to below  $2 \times 10^{-9}$  Torr. No multilayer water ice formation thermal desorption peak was seen, nor any expected, in the work presented here (as the thermal desorption temperature for ice is expected to be about 150–160 K).<sup>1,2,14,15</sup>

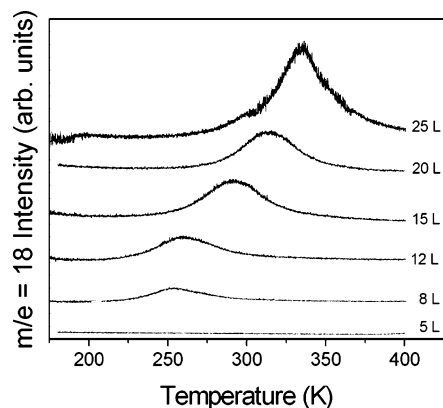
For the laser assisted thermal desorption, a pulsed nitrogen laser (337 nm, 3.66 eV) operated at 20 Hz with an intensity of 120  $\mu\text{J}/\text{pulse}$  was used. This corresponds to approximately 1 photon per surface dipole per 4 ns pulse in the geometry of our experiment. In our experiments, we have compared linearly polarized light with the electric field vector **E** (and the vector potential **A**) of the incident radiation parallel with the surface to a polarization with the electric field vector **E** (and the vector potential **A**) of the incident radiation perpendicular to the

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**Figure 1.** Coverage-dependent thermal desorption sequence from PMVC. Water is observed leaving the film after exposures of 8 L and greater. The peak center shifts with coverage from 260 to 340 K.

surface, but with the same radiation intensity/area and no change in light incidence angle. This technique of UV laser assisted thermal desorption has been described in considerable detail elsewhere.<sup>2</sup> Briefly, the laser assisted thermal desorption process occurs following water vapor exposure to the sample, with resistive sample heating and UV laser illumination beginning simultaneously.

### The Theoretical Models

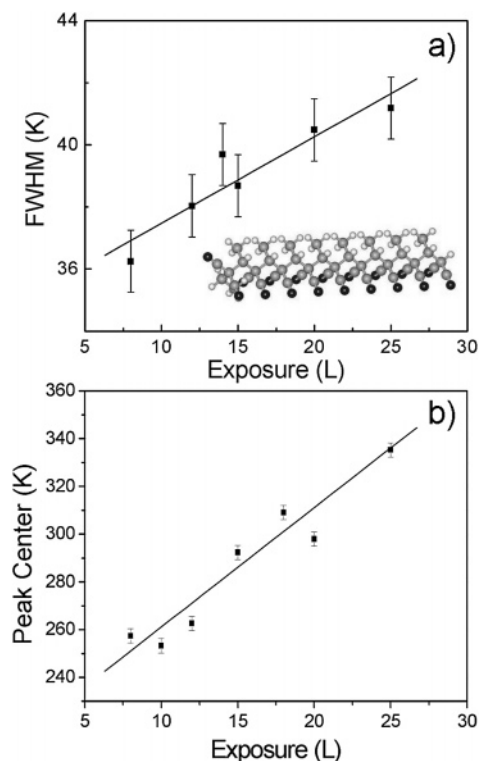
As we have done previously,<sup>1</sup> to obtain a qualitative picture of the behavior of a water molecule at the polymer surface, both structure optimization and molecular dynamics (MD) simulations were undertaken with use of HyperChem code within a semiempirical (SE) quantum mechanical method.<sup>1</sup> This includes parametrization of overlap integrals in the framework of the restricted Hartree–Fock (RHF) method. The semiempirical calculational approach, with the PM3 parameter set, has been recognized as sufficiently accurate, while very efficient for estimating the favored structures of molecular systems, in particular polymers,<sup>1,13,15,16</sup> by minimization of total energy. This semiempirical method provides structures that are in qualitative agreement with density functional theory.<sup>15</sup> While somewhat simplistic, this approach is also adequate for simulations modeling the evolution of molecular systems at finite temperatures by molecular dynamics methods, which take into account the molecular and atomic kinetic energies.

### Water Absorption in PMVC

Polymer chains have been shown to reorient in response to nearby water molecules;<sup>16–18</sup> polymer chain displacement could occur in PMVC, and should occur as indicated by theory, discussed below, allowing water access to bulk absorption sites. As water exposure increases the ordering of the polymer chains is expected to decrease,<sup>1,7</sup> and evidence of water absorption is found in the thermal desorption of water.

At low water exposures (performed at 160 K), less than 5 L ( $1 \text{ L} = 1 \times 10^{-6} \text{ Torr}\cdot\text{s}$ ), the thermal desorption spectra (for water, i.e.,  $m/e$  18) are largely featureless, as seen in Figure 1. For water exposure less than 8 L, water desorption occurs near 260 K as is apparent in the thermal desorption spectra.

We observe that the water desorption peak from PMVC shifts to higher temperatures with increasing water exposure (at 160 K), as seen in Figures 1 and 2. As there is no evidence of surface states becoming saturated with increasing water exposure and the water thermal desorption peak shifts to much higher



**Figure 2.** The water thermal desorption peak position (a) and full width half-maximum (fwhm) (b) as a function of coverage. The fwhm increases linearly with coverage indicating diffusion of water into the bulk of the film.

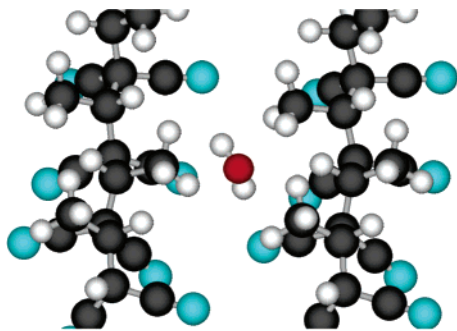
temperatures (from 260 to 340 K or greater), we can safely ascribe this thermal desorption to an absorbed water species in PMVC.

In thermal desorption spectra, water ice layers have a zero-order desorption (sublimation) peak at 150–160 K.<sup>1,2,14,15</sup> The shape of the water desorption feature in the thermal desorption spectra obtained for PMVC is inconsistent with sublimation of multilayer water ice from the surface, leaving a bulk absorbed species or a non-ice surface sensitive species as the possible origins of this thermal desorption feature.

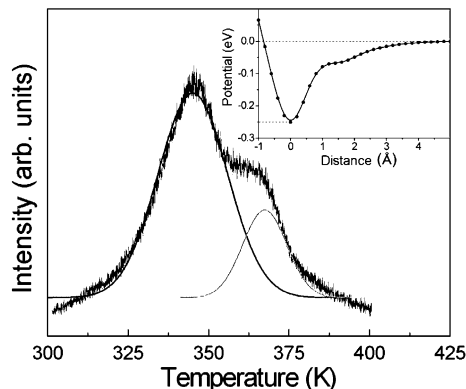
In similar studies with crystalline films of the ferroelectric P(VDF-TrFE 70%:30%), absorbed bulk water was seen as a high-temperature desorption peak.<sup>1,2,14,15</sup> For PMVC, this water desorption feature (Figure 1) occurs at much lower temperatures than the desorption of absorbed bulk water from P(VDF-TrFE),<sup>1,2,14,15</sup> for an equivalent water exposure. This argues that absorbed water is more weakly bound to PMVC than is the case for P(VDF-TrFE).

This attribution of the desorption spectra features to a weakly bound absorbed water species is further illustrated by results of modeling of water behavior in a monolayer PMVC (Figure 3). If the PMVC chains were “rigid”, a water molecule would not penetrate into the film because of a high potential barrier originating from electrostatic interaction. Even physisorption of the water ice in this case would be unfavorable. Due to the “flexibility” of the chains, an approaching water molecule can slightly distort the PMVC chains (with a 12% increase of local spacing) so that a favorable position for the water molecule between the chains is created (Figure 3). This distortion due to water absorption probably contributes to the loss in X-ray diffraction intensity, from the PMVC.

The “hands down” orientation of the molecule, shown in Figure 3, is not the only possible water molecule orientation (other orientations such as “hands up” also were found to be



**Figure 3.** The structure of two relaxed PMVC chains with the H<sub>2</sub>O molecule at the equilibrium position between the chains. The cyano groups are seen to “tilt” toward the water molecule.

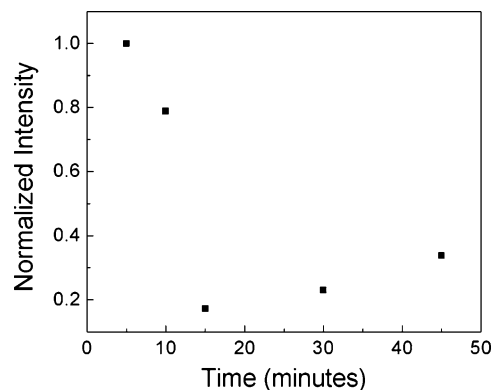


**Figure 4.** The thermal desorption of water following 50 L of water exposure to PMVC at 160 K is illustrated, and can be fit by two thermal desorption features. In the inset, the potential energy of the water molecule moving between the two chains upward, i.e., along the normal to the surface, is plotted. The chains, after optimization of the structure, were fixed. The origin ( $z = 0$ ) corresponds to the position of the equilibrated H<sub>2</sub>O molecule between the chains (shown in Figure 3). Zero potential energy corresponds to the system with evaporated water molecule.

favorable in the course of MD modeling and optimization starting from different original configurations), but does correspond to the global minimum of the potential energy (Figure 4), that is, to the ground state of the system. In contrast with water in P(VDF-TrFE),<sup>1</sup> for the PMVC layer, the position of the water molecule between the chains is more favorable than under the layer (that is, near the hydrophilic side of the layer). In other words, the water molecule will be absorbed preferably by the top surface layer between the PMVC chains.

The estimated potential energy of the water molecule moving between two PMVC chains along the normal to the surface is shown in Figure 4. The binding energy for water (with respect to evaporated state of the water molecule) in the potential well is 0.25 eV, similar to the values calculated for water at the surface of P(VDF-TrFE).<sup>1</sup> The potential barriers to the left and to the right from the minimum depend on orientation and actual trajectory of the molecule moving through the PMVC film and therefore the particular shape of the potential plot presented in the insert to Figure 4 should be considered as an example that is representative for some typical case, which illustrates absorption–desorption behavior of water molecules. As follows from MD simulations, the chains adjust their shape to facilitate transfer of the approaching water molecule, so the molecule will easily penetrate into the bulk of the PMVC film.

The time scale for distortion of the polymer chains is long compared to the surface residence time, in the P(VDF-TrFE) and PMVC crystalline polymer chains.<sup>1</sup> The sticking coefficient



**Figure 5.** The water thermal desorption intensity following 15 L of water exposure to PMVC at 160 K, as a function of the delay time between water exposure and the onset of thermal desorption. Intensity is normalized to the maximum value observed above background.

for absorption is therefore expected to be small, especially in the initial stages of water absorption (when the polymer film is more crystalline), consistent with the coverage dependent thermal desorption in Figure 1.

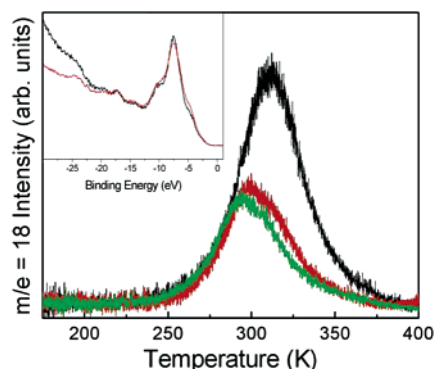
The desorption of water from PMVC appears to be dominated by the diffusion of absorbed water to the surface during thermal desorption. As water exposure is increased, the peak center for the thermal desorption of water from PMVC (Figures 1 and 2) shifts to higher and higher temperatures, which is consistent with water absorbed into the bulk. Reaching large water exposures, 20 L or greater, there is no change in the behavior of the water desorption peak except an increase in temperature, and temperature half-width (Figure 2). No new features appear in the spectra. This is likely a consequence of the strongly bound water species being delayed in leaving the polymer bulk, the further within the film bulk (the farther away from the free surface). When the fwhm increases with water exposure, diffusion into the film bulk is implied. If the water were a non-ice surface species the available sites would decrease as the exposure increased, resulting in a constant fwhm, which is clearly not seen in Figure 2. Again, since the width increases linearly with water exposure, a bulk absorbed species is most likely, not a heterogeneous collection of surface species.

## Two Absorbed States of Water

The fact that there is one stable absorption site does not preclude additional metastable absorption sites. Such metastable states may become occupied at higher water coverages, as indicated in Figure 4. The potential energy curve shows that a weakly bound metastable absorbed phase may exist at the higher water coverages. Indications of this second absorbed water phase are provided by the two features observed in water thermal desorption from PMVC at higher water exposures, such as those taken following 50 L of water exposure to PMVC at 160 K, as seen in Figure 4.

By inserting a greater delay time between water exposure at 160 K and the thermal desorption of water, further evidence for a weakly bound absorbed water species is found. The intensity of the water thermal desorption feature(s) as a function of delay time between the absorption of water and the start of the thermal desorption process is shown in Figure 5. The rapidly decreasing intensity indicates that a considerable fraction of the water absorbed following 15 L of water exposure to PMVC at 160 K is not stable as an absorbed water species at that temperature. The metastable absorbed water quickly desorbs,





**Figure 6.** Thermal desorption (black) and laser assisted thermal desorption spectra for the vector potential **A** parallel (red) and normal (green) to the surface. The spectra are shifted from the thermal desorption peak by approximately 10 K for both light polarizations. All spectra were taken at an exposure of 15 L. The inset shows polarization-dependent ultraviolet photoemission spectra taken from ref 13.

within 10 to 15 min, under ultrahigh vacuum conditions. This effect of delay is indicated in Figure 5.

### UV Laser Assisted Thermal Desorption

In Figure 6, we provide a comparison of three thermal desorption spectra after exposure to 15 L of water. These spectra represent the PMVC sample under no illumination (in Figure 6, the black curve), with the vector potential **A** of the laser parallel to the surface (Figure 6, the red curve) and the vector potential **A** normal to the surface (Figure 6, the green curve) of our sample. Under UV illumination with the vector potential **A** normal to the sample surface we see a shift of 10 K, and desorption occurs at a lower temperature. For UV illumination with the vector potential **A** parallel to the sample surface a similar desorption spectra is obtained.

In comparison to the ferroelectric polymer P(VDF-TrFE 70%:30%),<sup>2</sup> the relatively small enhancement of water thermal desorption due to the UV laser assisted excitations can be explained in several ways. The lifetime of any metastable excited states may be very short, decreasing their effect on the thermal desorption spectra. Alternatively, the strong surface dipoles may not play an important role in holding water in the bulk film for PMVC. In the P(VDF-TrFE)–water system the presence of several phase transitions—surface electronic and structural—may affect the laser assisted desorption process. Photoemission studies of PMVC have provided no indication of any electronic phase transition over a range of temperatures (160–400 K). The use of a UV laser to excite electrons from the graphite substrate into the ferroelectric polymer P(VDF-TrFE 70%:30%) implicated dipole orientation and dipole excitations in water thermal desorption.<sup>2</sup> For PMVC, the ferroelectric transition (if there is any) occurs at a far higher temperature than the 350 K observed for P(VDF-TrFE 70%:30%).<sup>19–20</sup> Furthermore, the local dipoles do not appear to as readily “rotate”.<sup>12</sup>

Because PMVC has a low local symmetry, compared to that of the ferroelectric polymer P(VDF-TrFE 70%:30%),<sup>13</sup> the UV laser light polarization effects are expected to be small. Polarization dependent ultraviolet photoemission spectroscopy of PMVC shows few differences, as reported elsewhere.<sup>2</sup> Similarly the light polarization effects in the UV laser assisted thermal desorption of water from PMVC are also small (as seen in Figure 6). The very slight enhancement seen with the light polarized with **E** along the surface normal may be the result of nothing more than a consequence of boundary conditions (i.e.,

as Fresnel’s equations might suggest). From Fresnel’s equations alone, the reflectivity should be highest and the adsorption lowest with **E** parallel with the surface, in the geometry of our experiment. Unfortunately, for PMVC, poor bulk ordering may reduce any symmetry-dependent excitations.

### Conclusion

In summary, the ferroelectric polymer PMVC is shown to absorb water. The water seen in thermal desorption is shown to diffuse into the bulk of the polymer, and diffusion may play a role in the desorption of absorbed water. Laser assisted thermal desorption shows some effect likely due to metastable excited states of the polymer, but the effect is far less dramatic than observed for the ferroelectric polymer P(VDF-TrFE 70%:30%).<sup>2</sup> Under UV illumination, water desorption occurs at temperatures that are approximately 10 K less than for thermal desorption in the absence of UV illumination.

Unlike the ferroelectric polymer P(VDF-TrFE 70%:30%), there is little difference with changing light polarization in the UV light assisted thermal desorption of water from PMVC. While water desorption from P(VDF-TrFE) is strongly dependent upon the local geometry and the polymer dipole, water desorption from PMVC is largely insensitive to the polymer dipole moment.

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