

# Diffusion of Water into a Photopolymer Film

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## SYNOPSIS

Sorption of water vapor into thin films of a crosslinked dimethacrylate UV-cured polymer was measured by means of a quartz crystal microbalance apparatus. The diffusion coefficient and solubility were obtained. An upper limit to the water vapor diffusion coefficient, namely, the diffusion coefficient for liquid water in intimate contact with the sample, was measured for reference purposes by both gravimetric and infrared spectral techniques. A water uptake value for thick films was obtained gravimetrically as a reference for the thin film value. Measurement of the diffusion coefficient allows the determination of the length of time that the photopolymer could act as an effective water vapor barrier.

## INTRODUCTION

Polymers have been used for a variety of products in the packaging industry.<sup>1,2</sup> Because polymers absorb fluids, sorption parameters are important factors in determining whether a certain polymer layer can be used for a specific application and operating conditions. UV-curable polymers, often referred to as photopolymers or "2P" materials, have recently been used in optical storage devices<sup>3</sup> for the grooved layer necessary for data tracking and for the protective topcoat-encapsulating layer. Optical disks are expected to survive under a wide range of environmental conditions that could affect the physical, chemical, and optical properties of a disk assembly. For example, water in a disk package may prove to be detrimental to the long-term performance of the optical disk, causing certain key interfaces to fall apart because of poor adhesion. Transmission of water causes corrosion of the metallic storage medium and the components of the disk assembly. Furthermore, the absorbed water can act as a plasticizer in the polymer grooving layer, causing changes in mechanical properties that could affect servo tracking signals.

In this work, water sorption properties of a sample photopolymer were investigated to quantify the suitability of such materials for optical storage-encapsulating purposes.

## EXPERIMENTAL

### Measurement Techniques

Sorption of water vapor by the photopolymer was monitored by means of a quartz crystal microbalance (QCM) apparatus that has been previously described.<sup>4</sup> It is analogous to a system constructed by Bonner and Cheng<sup>5,6</sup> for high-pressure and high-temperature measurements. The instrument uses only milligram quantities of polymer and is very precise since the oscillation frequency of the crystal can be measured to a high degree of precision. Samples are, however, limited to thicknesses of a few micrometers, and the overall accuracy is limited by the measurement of such sample thicknesses. The crystal is housed inside a vacuum system that contains controlled amounts of water vapor at controlled temperatures. Changes in mass are measured by monitoring the change in frequency of the coated quartz crystal as the coating picks up water vapor.

The relationship between frequency of a quartz crystal and added mass for small loads is given by the Sauerbrey equation,<sup>7,8</sup> which for AT-cut crystals reduces to eq. (1):

$$\frac{\Delta m}{A} = -4.43 \times 10^{-7} \frac{\Delta \nu}{\nu_0^2}, \quad (1)$$

where  $\nu_0$  is the initial frequency of the crystal in MHz,  $\Delta \nu$  is the change in frequency in Hz, and  $\Delta m/A$  is the change in mass per unit area ( $g/cm^2$ ). Coated crystals were mounted in the QCM chamber

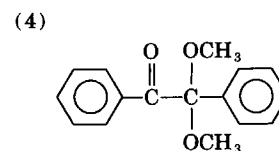
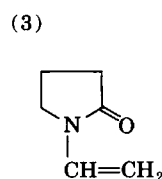
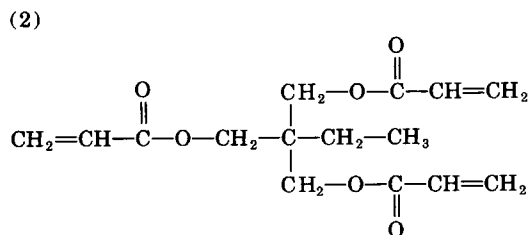
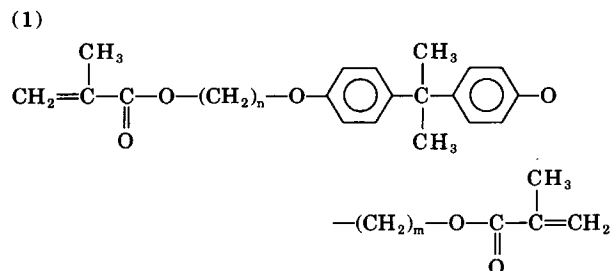
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and heated to 105°C at 10<sup>-7</sup> torr or below overnight before the sorption experiments. The frequency of the baked sample after cooling was used as the initial value. The sorption/desorption experiments were done at 21°C and 19 torr (the vapor pressure of water). Sorption and desorption curves were in good agreement. Sorption experiments were used to determine the maximum solubility of water in the polymer. After a sample had been saturated, a desorption experiment was performed to measure the diffusion coefficient. Desorption runs were used for diffusion coefficients because the pressure change in the chamber was much closer to a step function than it could be during a sorption run. The use of desorption data were justified by the evidence that diffusion of water in this material is Fickian (see below). Room temperature sorption isotherms were measured also by allowing pressures of water vapor from 0–19 torr in 1-torr increments into the chamber and measuring the mass change at each pressure.

The gravimetric and infrared measurements were performed as follows. After preconditioning, the films were immediately weighed on a Mettler AE163 microbalance and infrared spectra were taken with an IBM IR44 FTIR spectrophotometer to determine baseline values for the H<sub>2</sub>O absorption peaks. The films then were placed into containers of deionized H<sub>2</sub>O to soak. At specified time intervals (up to 75 h), the films were carefully withdrawn from the liquid, dried between sheets of lintless blotting paper, and then measured for weight gain and IR absorption. At the completion of each series of tests, the film was again placed in the vacuum oven for 24 h and then reweighed to determine if there had been any measurable change in its starting weight after the soaking process. Within experimental error, the films showed no change in starting weight.

### Materials

A crosslinked methacrylate film was made with the following composition<sup>9</sup>: (1) 60% ethoxylated bisphenol-A based dimethacrylate, (2) 19% trifunctional acrylate, (3) 19% monofunctional reactive diluent, and (4) 2% photoinitiator.



The relative concentration of components shown in Scheme 1 is such that the photoinitiated polymerization of the mixture occurs in three dimensions to give a polymer of high molecular weight and very high crosslink density. Dynamic mechanical analysis of the photopolymer shows a glass transition temperature of about 170°C, with only a gradual change in modulus above that point, a characteristic of highly crosslinked materials.

### Sample Preparation

Samples of photopolymer were prepared for the QCM experiments as follows. An Inficon 6 MHz plano-convex quartz crystal equipped with gold electrodes was used for each experiment. A small drop of the photopolymer liquid was placed at the center of the crystal and covered with a piece of plastic wrap. A glass lens with the same radius of curvature as the quartz crystal was placed on top to mold the liquid polymer so that it evenly covered the curved crystal surface. This mold was removed, leaving the plastic wrap in place, and the polymer was cured and postbaked as described above. Prepared in this manner, photopolymer films conformed to the convex shape of the quartz crystals so that shrinkage during curing did not affect their oscillation.

Film thickness was measured by profilometry both before and after the sorption QCM experiments. The technique requires that the polymer coatings be less than 3 μm thick so that the frequency will be linearly dependent upon the mass.

To make a large piece of photopolymer film, a quantity of the liquid photopolymer formulation sufficient to yield a film of approximately 9 cm diameter and between 10 and 100 μm in thickness (approximately 0.3 mL) was placed between two clean glass plates. The film was exposed for 120 sec using an

OIA exposure tool fitted with a medium-pressure mercury arc lamp having an intensity of 15.2 mW/cm<sup>2</sup> at 365 nm. The film was peeled from the glass plates, transferred to aluminum foil, and placed in an oven. The oven was nitrogen flushed, then heated to 180°C for 1.5 h, maintaining a nitrogen blanket during the heating of the films. Thinner films of 1 cm diameter were made for the infrared measurements, where thickness uniformity over the entire film was not critical because of the small spot size of the infrared beam. Film thickness was measured by profilometry.

The 2P films were preconditioned prior to the measurements of weight gain and IR absorption. The preconditioning consisted of protecting each film between sheets of aluminum foil and placing the films into a vacuum oven for 24 h at 80°C and 100 μm Hg. Preconditioning the film resulted in a reproducible baseline weight and IR spectrum for each film.

## RESULTS

### Vapor Sorption

The most mathematically tractable penetrant/polymer systems are those that exhibit Fickian diffusion. The experimental criterion for Fickian diffusion is that plots of mass uptake divided by ultimate

mass uptake ( $t = \infty$ ) vs. square root of time divided by film thickness are linear up to at least half of the ultimate uptake, and that such curves obtained with samples of different thickness lie on top of each other within experimental error. Figure 1 shows three such curves obtained from QCM experiments superimposed. Clearly, diffusion of water vapor into this photopolymer is Fickian. The diffusion coefficient can thus be assumed to be a true diffusion constant, and its measurement becomes meaningful.

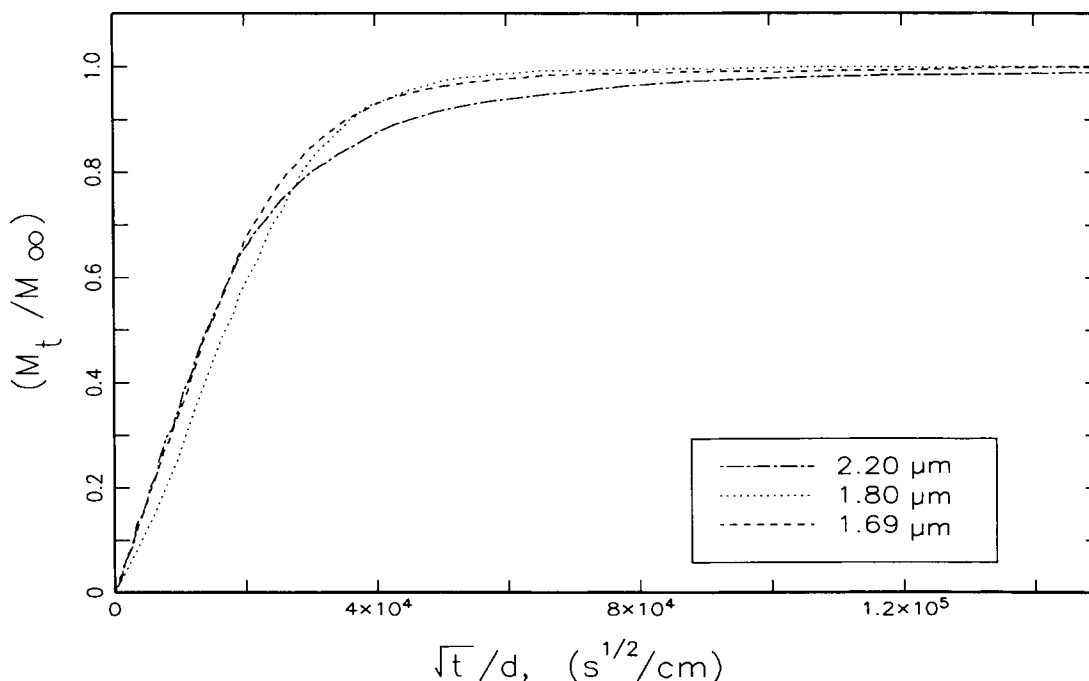
Fickian sorption is described by Fick's second law of diffusion (where  $x$  is depth into a sample and  $C$  is concentration of permeant),

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}, \quad (2)$$

which can be solved<sup>10,11</sup> by using the appropriate boundary conditions. For the initial phase of sorption ( $M_t/M_\infty < 0.4$ ), the solution can be expressed in the following simplified form for diffusion from both sides of the film<sup>12,13</sup>:

$$\frac{M_t}{M_\infty} = \frac{4}{d} \left[ \frac{Dt}{\pi} \right]^{1/2}, \quad (3)$$

where  $M_\infty$  is the uptake at equilibrium,  $M_t$  is the uptake at a given time,  $t$  = time, and  $d$  = film thick-



**Figure 1** Normalized weight gain of three thicknesses of photopolymer films exposed to water vapor in the QCM apparatus. The curve overlap implies that diffusion is Fickian.

ness. The slope of  $M_t/M_\infty$  at  $< 0.4$  vs.  $\sqrt{\text{time}}/\text{thickness}$  can be used to calculate the diffusion coefficient (diffusion through both sides of the film)

$$D = \frac{\pi}{16} (\text{slope})^2 \quad (4)$$

or through one side of the film (due to a factor of  $2d$  squared):

$$D = \frac{\pi}{4} (\text{slope})^2 \quad (5)$$

The solubility for any given sample at a given pressure of water vapor is determined simply by measuring the ultimate uptake, but the solubility coefficient can be determined accurately only by taking a sorption isotherm and determining whether it has a constant slope; if so, the slope equals  $S$ . The diffusion coefficient  $D$  is determined from the initial slope of an uptake curve when replotted vs. the square root of time. The product of these two quantities is, of course, the permeability.

Sorption isotherms for the photopolymer were measured with the QCM, and an example is shown in Figure 2. The solubility coefficient is the slope of this curve,  $3.1 \pm 0.5 \text{ mg/cm}^3$  per torr water vapor pressure. This photopolymer obeys Henry's Law: The sorption isotherm is very close to a straight line. The small deviation from linearity corresponds to a slight tendency towards Flory-Huggins sorption

behavior, indicating either a small preference for water molecules to bind to each other rather than the polymer or a minor degree of swelling of the polymer as sorption proceeds.

The QCM method yields water uptake values expressed as mass per unit volume of polymer. To convert these numbers to weight percent units, the density of the polymer must be determined. The density of this photopolymer was determined with a density gradient column to be  $1.224 \text{ g/cm}^3$ . The vapor pressure of water at  $25^\circ\text{C}$  is 23.8 torr, so the maximum uptake at STP would be 6.0 wt %. Our experiments were performed at  $21^\circ\text{C}$ , so the maximum uptake observed was  $5.4 \pm 0.3 \text{ wt } \%$ , commensurate with the lower vapor pressure. The diffusion coefficient determined from the slope of the desorption curves (Fig. 1) was  $8.2 \pm 0.2 \times 10^{-10} \text{ cm}^2/\text{s}$ .

### Immersion

Diffusion coefficients for liquid water sorption into thick photopolymer films were determined both gravimetrically and spectroscopically. Figure 3 is a plot of normalized water uptake, measured gravimetrically, for three film thicknesses. Because the curves overlap within experimental error, diffusion must be Fickian for liquid water in thicker samples, as well as for water vapor in the thinner ones measured with the QCM method. The diffusion coefficient obtained from these data was  $3.6 \pm 1.2 \times 10^{-9} \text{ cm}^2/\text{s}$ . The average uptake of water at equilibrium as measured gravimetrically was  $3.0 \pm 0.1 \text{ wt } \%$ .

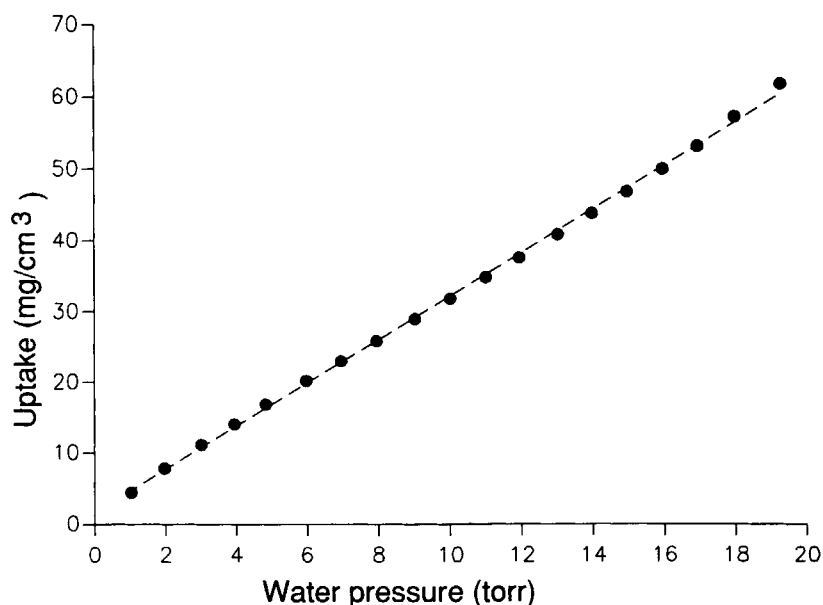
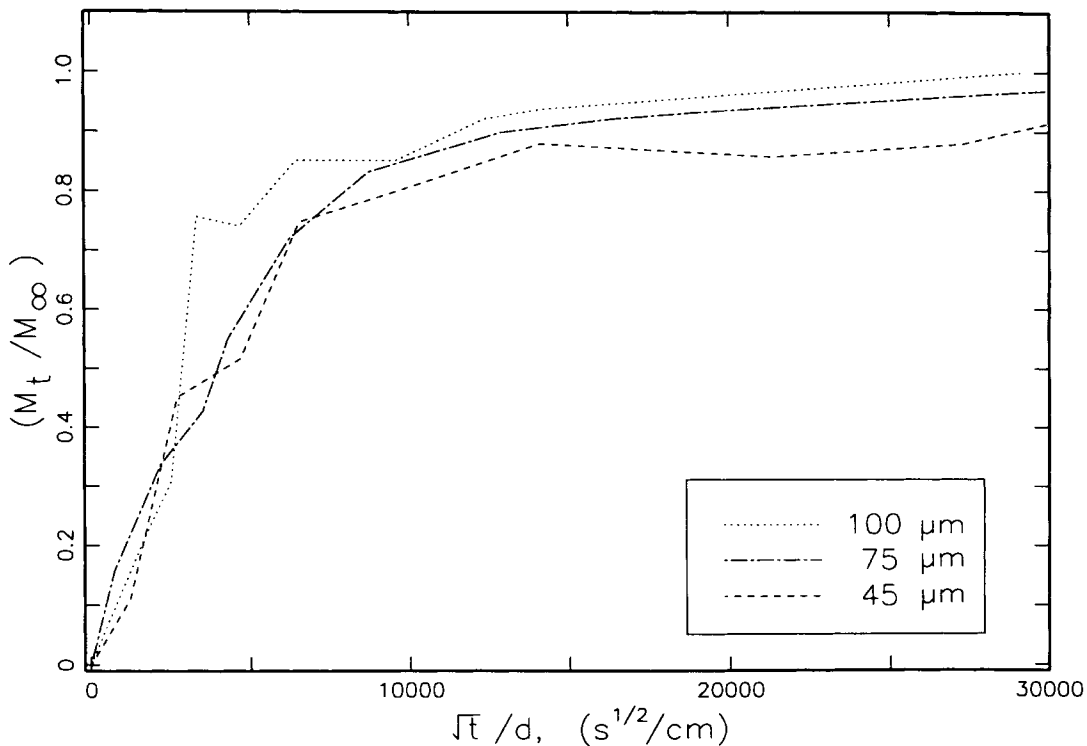
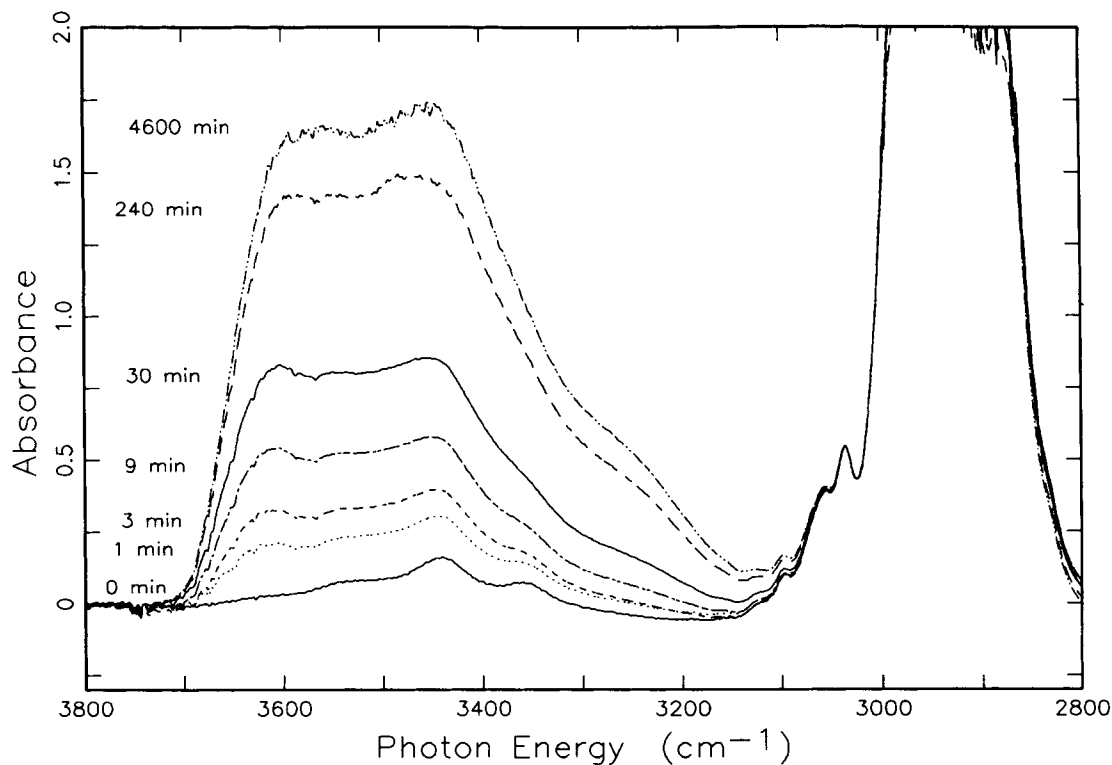


Figure 2 Water vapor sorption isotherm for a thin film of the photopolymer.



**Figure 3** Normalized weight gain of three photopolymer films in liquid water, measured gravimetrically.



**Figure 4** A plot of infrared absorbance vs. wavelength for a 100- $\mu\text{m}$  film immersed in  $\text{H}_2\text{O}$  for various times. The area under the peak is proportional to the concentration of water in the film.

In the infrared experiments, spectra taken in transmission were converted to absorbance units and normalized to the  $3,063\text{ cm}^{-1}$  peak to remove variations in sample thickness due to spot location. The  $3,063\text{ cm}^{-1}$  peak represents an aromatic C—H vibration in the material that is not affected by water sorption. The  $\text{H}_2\text{O}$  absorbance peak is broad so the area under the absorbance curve was integrated from  $3,720\text{--}3,145\text{ cm}^{-1}$ . Figure 4 illustrates how a  $100\text{-}\mu\text{m}$  film absorbed water as a function of time. Spectroscopic data confirmed again that diffusion is Fickian; the diffusion coefficient calculated from the data was  $3.5 \pm 0.9 \times 10^{-9}\text{ cm}^2/\text{s}$ , equal to the gravimetric number within experimental error.

## DISCUSSION

The QCM value for total water uptake is larger than the gravimetric value, and the difference is greater than the standard deviation across the sample set for each technique. Two explanations for the discrepancy immediately suggest themselves. First, the gravimetric results might be too low because the last data points might still not be at equilibrium due to the thicknesses of the samples. This explanation is unlikely given the apparent equilibrium behavior observed in Figure 3. The second explanation is that the thicker films actually absorbed relatively smaller amounts of water than did the thinner films. This explanation makes physical sense because it has been shown<sup>14</sup> that thin films exhibit substantially more in-plane orientation of their polymer chains than do thick films so that packing is disrupted in the vertical direction and there is more free volume available for sorption. Our results are consistent with this phenomenon, although the effect is expected to be greater for linear polymers than for crosslinked materials such as the photopolymer investigated here.

The diffusion coefficient for liquid water sorption is indeed an upper limit for the water vapor diffusion coefficient, as one might expect. The water vapor value was about 23% of the upper limit. Clearly, if a semiinfinite medium of permeant molecules is in contact with the polymer, sorption will occur more quickly than if the permeant molecules must first find the polymer surface. The measured diffusion coefficient allows an estimation of the length of time during which an optical disk or any other object could be shielded from water vapor by this photopolymer. When a permeable film is exposed to permeant on one side, there is a measurable time lag before substantial amounts of permeant appear on the other side. The time lag  $t$  can be shown<sup>15</sup> to be

$$t = \frac{d^2}{6D} \quad (6)$$

Therefore, for any desired length of time, a thickness can be determined based on the diffusion coefficient for which the material will keep water vapor out for that length of time. If an optical storage medium were to be protected from water only by this photopolymer, and if it were intended to last for 10 years, the required thickness would be 1.25 cm (10 years is approximately  $3.16 \times 10^8\text{ s}$ ). This thickness is much greater than any grooved tracking layer should be so any metallic storage medium would have to be encapsulated by something besides the grooved layer. On the other hand, 1.25 cm is a reasonable value for the radial extent of a disk beyond the edge of the medium. For preventing permeation of water vapor in from the edge of a disk, the photopolymer alone would suffice.

## CONCLUSIONS

The diacrylate crosslinked polymer takes up between 3 and 5%  $\text{H}_2\text{O}$  by weight at  $23^\circ\text{C}$ . The thicker films absorb less water, presumably due to the fully three-dimensional chain packing that occurs in thicker films. Quartz crystal microbalance measurements show that the solubility coefficient is  $3.1 \pm 0.5\text{ mg/cm}^3$  per torr water vapor pressure. The polymer obeys Henry's Law. The diffusion coefficient for water vapor sorption in the photopolymer is  $8.2 \times 10^{-10}\text{ cm}^2/\text{s}$ ; for liquid water sorption, the value is  $3.6 \times 10^{-9}\text{ cm}^2/\text{s}$ . The data suggest that one could not prevent water from permeating a film of this photopolymer under ambient conditions for long periods of time unless the polymer thickness were on the order of 1 cm. The diffusion coefficients measured here are similar to those for many other polymers so for rigorous water vapor exclusion purposes rather specialized polymers or other materials would be preferable.

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