Solvatochromic Characterization of Polymers. Effects of Relative Humidity

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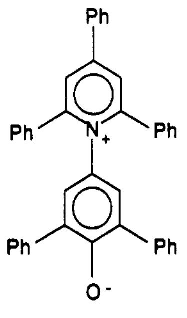
ABSTRACT: This study is concerned with the effects of relative humidity on polymer sorption properties as revealed by changes in hydrogen-bonding acidity and $E_T(30)$ values. Thin films of four polymers containing Reichardt's dye [2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridinio)phenolate] were subjected to varying levels of relative humidity, and the UV–visible spectra of the polymer films were obtained. From these data hydrogen-bonding acidities and $E_T(30)$ values for the polymers were computed. The effect of humidity on these solvatochromic parameters was found to vary greatly, depending on the polymer, indicating that polymer sorption properties (such as solute solubility and membrane permeability) are a function of the humidity to which the polymer is exposed. Kinetic studies of the sorption and desorption of water vapor by films of poly(vinyl acetate) were also conducted, and these studies show that polymer/dye films can give large, reversible, rapid changes in color (visible absorption maximum) with changes in humidity. The possibility of application to sensor technology is discussed.

Much has been done to characterize the physicochemical properties (acidity, basicity, polarity, nucleophilicity, etc.) of small molecules, but considerably less has been done to characterize polymers, especially solid polymers. This is largely because the techniques routinely used to characterize small molecules and liquids are not amenable to characterizing solid polymers. Recently, we have applied the solvatochromic method of Kamlet, Abraham, and Taft (KAT)[1] to determine the solvent dipolarity/polarizabilities, hydrogen-bond acidities, and hydrogen-bond basicities of some important solid polymers by preparing thin films of the polymers containing certain medium-sensitive dyes and obtaining UV–visible absorption spectra of the dyes in these polymeric media.[2,3] Reichardt $E_T(30)$ values,[4,5] another common solvatochromic indicator of solvent polarity, were also determined for the polymers. These solvatochromic parameters have been demonstrated to be effective predictors of sorption properties of small molecules,[1,6,7] and hence they are expected to be of utility in predicting such properties for solid polymers as well.

In our earlier study we observed that the relative humidity of the atmosphere to which the polymer films were exposed often had significant effects on the absorption maxima of the dissolved dyes (and hence on the solvatochromic parameters). Consequently, measurements were made under dry conditions. In practical applications, however, polymers are often used under a variety of conditions requiring exposure to atmospheric moisture. Since we have shown that solvatochromic parameters can vary with atmospheric moisture content, it is apparent that polymer sorption properties (such as solute solubility and membrane permeability) could vary as well.[5]

In our first polymer characterization study we found that, although humidity had little effect on solvent dipolarity/polarizability, π_1^*, and hydrogen-bond basicity, β_1, the hydrogen-bond acidity, α_1, and $E_T(30)$ values of many polymers were affected greatly. This large effect on α_1 and $E_T(30)$ occurs because Reichardt's dye, 1, which is used in determining α_1 and $E_T(30)$, has a basic phenoxide group that readily binds to hydrogen-bonding acids such as water. The other dyes used in solvatochromic characterization (4-nitroanisole, *N,N*-dimethyl-4-nitroaniline, and 4-nitroaniline) are affected only slightly by the presence of small amounts of water in a liquid solvent or solid polymer.[7,8]



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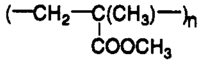
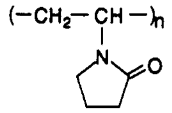
The purpose of the present work is to study, in detail, the effects of relative humidity on the absorption spectrum of Reichardt's dye in some solid polymers and thereby on the hydrogen-bond acidity, α_1, and $E_T(30)$ values of these polymers. Specifically, we examine the effect of relative humidity on the longest wavelength UV–visible absorption band (the solvatochromic band) of Reichardt's dye dissolved in thin films of poly(methyl methacrylate) (PMMA), poly(vinyl acetate) (PVAc), poly(vinyl chloride) (PVC), and poly(vinylpyrrolidone) (PVP). PVAc was studied in the most detail; for this polymer, kinetic studies were carried out on the effects of film thickness and atmospheric flow rate on the sorption and desorption of water by these films. Implications regarding humidity sensors are discussed.



$$(\text{—CH}_2\text{—}\underset{\text{COOCH}_3}{\underset{|}{\text{C}}}(\text{CH}_3)\text{—})_n$$

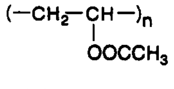
poly(methyl methacrylate)

PMMA



poly(vinyl pyrrolidone)

PVP



$$(\text{—CH}_2\text{—}\underset{\text{OOCCH}_3}{\underset{|}{\text{CH}}}\text{—})_n$$

poly(vinyl acetate)

PVAc

$(\text{—CH}_2\text{—CH(Cl)—})_n$

poly(vinyl chloride)

PVC

Methods and Results

The desired relative humidities were obtained by passing dry nitrogen gas through two bubblers, connected in series,

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Table I
Absorption Maximum of Reichardt's Dye (1), Hydrogen-Bond Acidity (α_1), and $E_T(30)$ Value at Various Relative Humidities for PMMA, PVAc, PVP, and PVC at 25 °C[a]

polymer	RH, %	$\lambda_{max}(1)$, nm	$\nu_{max}(1)$, $\times 10^3$ cm^{-1}	α_1	$E_T(30)$
PMMA	0	636	15.72	0.31	44.95
	8.0	632	15.82	0.33	45.22
	33.0	624	16.03	0.36	45.83
	53.0	618	16.18	0.39	46.26
	75.0	612	16.34	0.41	46.72
	92.0	606	16.50	0.44	47.17
	100	603	16.58	0.45	47.40
PVAc	0	714	14.01	0.04	40.05
	8.0	700	14.29	0.08	40.86
	33.0	676	14.79	0.16	42.28
	53.0	656	15.24	0.24	43.57
	75.0	626	15.97	0.35	45.66
	92.0	612	16.34	0.41	46.72
	100	608	16.45	0.43	47.03
PVP	0	700	14.29	−0.10	40.86
	8.0	670	14.93	0.00	42.68
	33.0	610	16.39	0.23	46.86
	53.0	590	16.95	0.32	48.46
	75.0	588	17.01	0.33	48.63
	92.0	586	17.06	0.34	48.78
	100	586	17.06	0.34	48.78
PVC	0	666	15.02	0.08	42.94
	33.0	658	15.20	0.10	43.46
	100	654	15.29	0.12	43.71

[a] All values are equilibrium values.

filled with saturated aqueous solutions of inorganic salts and thermostated at 25 °C.[9] The humidified nitrogen was then passed over the polymer films in a partially sealed quartz cuvette, and UV–visible spectra were obtained.

The hydrogen-bond acidity, α_1, of each polymer was calculated from the longest wavelength UV–visible absorption maximum of Reichardt's dye (1) and 4-nitroanisole (2) in the polymer film using eq 1.[8] In this equation

$$\alpha_1 = [\nu_{max}(1) + 1.873\nu_{max}(2) - 74.58]/6.24 \qquad (1)$$

and eq 2, wavenumbers (ν_{max}) are in 10^3 cm^{-1}.

The $E_T(30)$ value of each polymer was determined from the longest wavelength absorption maximum of Reichardt's dye using eq 2.[4,5] Here h is Planck's constant, c is the speed of light in vacuum, and N is Avogadro's number.

$$E_T(30) = hcN\nu_{max}(1) = 2.859\nu_{max}(1) \qquad (2)$$

Table I presents the absorption maximum of Reichardt's dye, $\lambda_{max}(1)$ and $\nu_{max}(1)$, dissolved in thin films of the four polymers mentioned above, along with the α_1 and $E_T(30)$ values of the polymers, measured under various known relative humidities. Note that these are *equilibrium* values, i.e., the final values after several hours of exposure to a fixed relative humidity (from a kinetic standpoint, they are infinity values). Figure 1 is a plot of the equilibrium $\lambda_{max}(1)$ values as a function of relative humidity for PMMA, PVAc, and PVP. Because the absorption maximum of Reichardt's dye in PVC showed little variation with relative humidity, $\lambda_{max}(1)$ was determined only at three relative humidities and so no plot is included.

In addition to determining the effect of relative humidity on the equilibrium position of the absorption band of Reichardt's dye in polymers, kinetic studies were also performed to determine the rate at which films of PVAc sorb water vapor from a wet nitrogen atmosphere and desorb water vapor into a dry nitrogen atmosphere and to determine how this process depends on the thickness of the film and the flow rate of nitrogen. The uptake and loss of water by the PVAc films were monitored by observing the shift in position of the absorption maximum of Reichardt's dye in the film as a function of time.

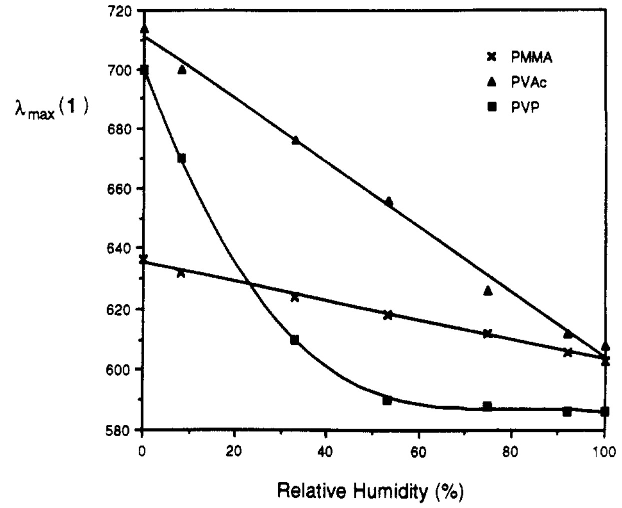

Figure 1. Plot of the equilibrium absorption maximum of Reichardt's dye, $\lambda_{max}(1)$ (nm), as a function of relative humidity in films of PMMA, PVAc, and PVP.

Table II
Absorption Maximum of Reichardt's Dye, $\lambda_{max}(1)$, in a Dried Film (34-μm Thickness) of PVAc as a Function of Time upon Exposure to 100% Relative Humidity (Sorption of Water) and to 0% Relative Humidity (Desorption of Water) at 25 °C[a]

sorption		desorption	
time, min	$\lambda_{max}(1)$, nm	time, min	$\lambda_{max}(1)$, nm
0.00	694	0.00	614
0.08	672	0.08	622
0.17	658	0.17	628
0.25	646	0.25	638
0.33	642	0.33	644
0.42	638	0.42	654
0.58	631	0.50	660
0.83	624	0.83	667
1.17	616	1.08	674
1.67	602	1.42	683
2.33	598	2.00	690
3.00	596	3.33	700
3.67	596	4.17	703

[a] The flow rate of the nitrogen was 100 mL/min for both sorption and desorption.

Table III
Kinetic Data for Sorption and Desorption of Water by Films of PVAc of Varying Thicknesses Containing Reichardt's Dye (1)[a]

thickness, μm	absorption 100% RH		desorption 0% RH	
	k^{λ}, min^{-1}	$t_{1/2}$	k^{λ}, min^{-1}	$t_{1/2}$
130	3.92E−2	17.7	3.07E−2	22.6
71	3.86E−1	1.8	2.03E−1	3.4
85	2.37E−1	2.9	1.44E−1	4.8
34	5.21E0	0.13	1.23E0	0.56

[a] Mean of two or more measurements. Flow rate 100 mL/min.

Table II presents kinetic data for a typical film (34-μm thickness) of PVAc containing Reichardt's dye. Specifically, it shows $\lambda_{max}(1)$ as a function of time upon exposure of this film (dried) to 100% relative humidity (sorption of water), followed by exposure to 0% relative humidity (desorption of water) at 25 °C at a nitrogen flow rate of 100 mL/min. Table III presents kinetic data for four films of PVAc containing Reichardt's dye, with varying thicknesses, for both sorption and desorption of water at a flow rate of 100 mL/min at 25 °C. First-order rate constants

Table IV
Kinetic Data for Absorption and Desorption of Water Vapor by a PVAc Film (71 μm) Containing Reichardt's Dye 1 at Varying Nitrogen Flow Rates

N_2 flow rate, mL/min	absorption 100% RH		desorption 0% RH	
	k^λ, min^{-1}	$t_{1/2}$	k^λ, min^{-1}	$t_{1/2}$
25	4.37E−1	1.6	9.59E−2	7.2
50	2.42E−1	2.9	1.99E−1	3.5
100	3.86E−1	1.8	2.03E−1	3.4
125	2.50E−1	2.8	na	na
150	3.75E−1	1.9	2.37E−1	2.9

for the sorption (k_{1s}) and desorption (k_{1d}) of water were determined for each film. For the 71-μm film, the nitrogen flow rate was varied to determine the effect of flow rate on the rate constants; these results are shown in Table IV.

Discussion

Equilibrium Studies. As seen from Table I, the equilibrium position of the absorption maximum of Reichardt's dye shifts to shorter wavelengths with increasing relative humidity for all four polymers. In most cases this shift is readily apparent with the naked eye; for example, films of PVAc containing Reichardt's dye appear green (λ_{max} 714 nm) under 0% relative humidity and blue (λ_{max} 608 nm) under 100% relative humidity. We estimate the uncertainty in the $\lambda_{max}(1)$ values to be ±2 nm; this relatively large uncertainty results because the band shape near the maximum is broad, making it difficult to discern the maximum.

Note that $\lambda_{max}(1)$ varies greatly with relative humidity in films of PVP and PVAc (shifts > 100 nm), varies moderately in films of PMMA (shift of about 35 nm), and only varies slightly in films of PVC (shift < 15 nm). This indicates that PVP and PVAc sorb more water than do PMMA and PVC or that the sorbed water does not cause a large shift in $\lambda_{max}(1)$ in PMMA and PVC because the nature of the interaction between Reichardt's dye, water, and these polymers is somehow different from that for PVP and PVAc. Note also that for all four polymers, any humidity effects are completely reversible upon exposure to dry nitrogen.

With the exception of PMMA, the polymers, as expected from their structures, show essentially no apparent hydrogen-bond acidity at 0% relative humidity, as indicated by their near-zero α_1 values (Table I). The presence of sorbed water in the polymers, however, causes them to exhibit hydrogen-bond acidity and so they then give nonzero values of α_1. The free hydroxyl group of sorbed water in the polymer acts as a hydrogen-bond donor. It is the hydrogen-bond acidity of this water that causes the shift in the absorption of Reichardt's dye at different relative humidities; the OH group of the water is a hydrogen-bond donor to the basic O^- on the phenoxide ring of the dye.

It is interesting that PMMA retains a significant nonzero α (0.31) even under 0% relative humidity. This probably results from some acidic side groups or acid impurity (methacrylic acid or poly(methacrylic acid)) in the polymer, left over initiator, or possibly even sorbed water that is so strongly bound to the polymer that even exhaustive drying does not remove it (although this possibility seems unlikely in view of the ease with which water is removed from the structurally similar PVAc).

As shown in Table I, the $E_T(30)$ values for all four polymers increase with increasing relative humidity, indicating that the "polarity" of the polymers becomes larger as they sorb water vapor from the atmosphere. This result seems reasonable since the presence of highly polar water molecules in the polymer would be expected to enhance the polarity of the polymer.

From Table I and Figure 1, we see that the equilibrium value of the absorption maximum of Reichardt's dye, $\lambda_{max}(1)$, varies linearly with relative humidity for PMMA, PVAc, and PVC. Because of this linear dependence on relative humidity, it is unlikely that *solvent sorting* between water and 1 is occurring. In liquid solution, solvent sorting takes place when a solute is preferentially solvated by one solvent over another in mixtures of two (or more) solvents; consequently, the immediate environment around the solute molecules consists primarily of one solvent. Thus the solute behaves much as if it were dissolved only in this, preferred, solvent. As a result of solvent sorting, the absorption maximum of a dissolved indicator dye may be essentially the same in the preferred solvent (pure) as in mixtures of the two solvents.[10]

In the case of the polymers and water, if solvent sorting were taking place (where water is the preferred solvent), we would expect $\lambda_{max}(1)$ in each polymer film to vary little from moderate to high relative humidities but to vary significantly from low to moderate relative humidities. In other words, the shift in $\lambda_{max}(1)$ should be greater upon exposure of dry polymer to humidity than upon exposure of polymer already containing sorbed water to water vapor. Since for PMMA, PVAc, and PVC this is not the case (the equilibrium $\lambda_{max}(1)$ values vary linearly from 0% to 100% relative humidity), we conclude that solvent sorting is not occurring.

On the other hand, for PVP (Table I and Figure 1), the dependence of $\lambda_{max}(1)$ on relative humidity is nonlinear; it varies significantly from 0% to 33% relative humidity (shift of 90 nm) but varies much less from 33% to 100% relative humidity (shift of only 24 nm). Hence for this polymer, some solvent sorting probably is taking place. This may occur because PVP, unlike the other three polymers studied here, is water soluble (in fact, at high relative humidities, this polymer becomes soft and tacky because of the presence of sorbed water).

An interesting observation with PVC is that films of this polymer containing Reichardt's dye, which are initially green ($\lambda_{max}(1)$ of 666 nm at 0% relative humidity), slowly fade to a light yellow color over a period of 2 or 3 days. If such a film is then heated under vacuum at 110 °C for a few hours (in an Abderholden drying pistol), it becomes dark violet ($\lambda_{max}(1)$ of 578 nm). The maximum of this dark violet absorption band matches that for Reichardt's dye in poly(vinyl alcohol), 580 nm, determined in our previous polymer study.[2] Apparently, Reichardt's dye, with its bound water of crystallization, may be catalyzing the hydrolysis of the chloride group in PVC to an OH group. The intermediate yellow color of the films probably results from protonation of Reichardt's dye, the acid salts of which are yellow, by the HCl produced from the hydrolysis. Upon heating under vacuum, the film loses HCl and thus the basic form of Reichardt's dye is recovered, imparting a dark violet color to the (partially) hydrolyzed polymer film.

Kinetic Studies. It is of interest to determine how rapidly these effects of humidity are manifested. Of the four polymers studied here, PVAc exhibits the greatest effect of relative humidity on absorption maximum of Reichardt's dye. Unlike PVP, PVAc is not water soluble and thus does not become tacky at high relative humidities; therefore it is the polymer best suited for use in humidity sensors. For these reasons kinetic studies of water sorption and desorption were carried out on films of PVAc.

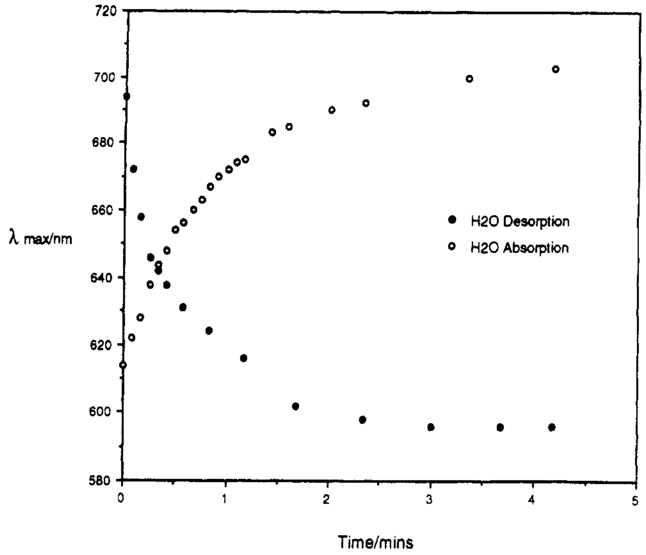

Figure 2. Plot of $\lambda_{max}(1)$ (nm) versus time (min) for a dry film of PVAc (34-μm thickness) containing Reichardt's dye (1) upon exposure to 100% relative humidity (sorption of water) and then to 0% relative humidity (desorption of water) at 25 °C at a flow rate of 100 mL/min.

We see from Table II that, upon exposure to 100% relative humidity, $\lambda_{max}(1)$ for a 34-μm thickness, dry PVAc film shifts from 694 to 596 nm within 3 min. Upon subsequent exposure to 0% relative humidity, $\lambda_{max}(1)$ for this same film shifts back to 703 nm within 4 min (in both cases the nitrogen flow rate was 100 mL/min). Thus desorption of water takes slightly longer than does sorption of water at the same flow rate (see Table III also). From Figure 2, we see that both sorption and desorption of water by the PVAc film follow first-order kinetics (the fit of the data to the first-order rate equation is excellent for both processes). Similar quality was observed when data from other PVAc films were fit to the first-order rate law.

From Table III, we see that the rate constants for both sorption (k_{1s}) and desorption (k_{1d}) of water by the PVAc films become smaller with increasing film thickness. This is expected since it should take longer for water to permeate thicker films. We also note that, in all cases, the rate for desorption is slightly less than that for sorption at the same flow rate.

To determine the effect of the nitrogen flow rate on the kinetics, the flow rate was varied for the 71-μm film, and rate constants for both sorption and desorption were determined. From Table IV, we see that, as the flow rate is increased from 25 to 150 mL/min, there is no steady trend in rate constants (within experimental error), indicating that, within the range examined, there is no effect of flow rate on sorption and desorption rates and that the flows used in this study are sufficiently rapid.

Conclusions

We have demonstrated that relative humidity can have significant effects on the solvatochromic parameters (hydrogen-bond acidities and $E_T(30)$ values) of solid polymers. Since these parameters have been shown to relate to sorption properties of small molecules,[1] they presumably also relate to the sorption properties of the polymers as well. Thus it is apparent that the relative humidity to which a polymer is exposed will affect its sorption properties. On the basis of the results of this study, we conclude that polymer characterization should take into account the relative humidity of the environment to which a polymer may be exposed.

Examples of sorption properties that could vary with humidity include solute solubility and membrane permeability. Additionally, in nonlinear optical applications (such as second-harmonic generation) where thin polymer films containing dyes are employed, the position of the absorption bands of the dye with respect to the laser frequencies can be of critical importance to the efficiency of the nonlinear process.[11] We have seen that as the relative humidity varies, so can the absorption bands of a dissolved dye; thus the efficiency of the nonlinear process may vary drastically with changes in the relative humidity of the atmosphere to which the polymer/dye film is exposed. Clearly, such factors must be taken into account when fabricating devices.

The effects of relative humidity on polymers can also have useful applications, the most obvious being humidity sensors. The large, reversible, linear shift in the absorption maximum of Reichardt's dye in PVAc as a function of relative humidity and the rapid response times of thin films of this polymer (Table III) make it ideal as a humidity sensor. Future work in this area will be devoted to determining the effects of humidity on specific polymer sorption properties and to examining the effects of other common atmospheric "contaminants" on polymer solvatochromic parameters.

Experimental Section

Molecular weights of the commercial polymers were as follows: PMMA, 35 000; PVAc, 102 000; PVP, 360 000; PVC, 100 000. All polymers were purchased from either Aldrich or Scientific Polymer Products. The spin-coating apparatus used in this work was a Headway EC101 photoresist spin coater, made available by Dr. Paul Ashley at NASA, Marshall Space Flight Center. The profilometer, used to determine the thickness of the polymer films, was a Dektak 1012, also provided by Dr. Ashley. The UV-visible spectrometer used was an HP 8452A.

Preparation of Polymer Films. Films of the four polymers containing Reichardt's dye (1) with thicknesses in the range 34–130 μm (Table III) were prepared by coating solutions containing the dye and polymers, prepared as described in our first polymer characterization study,[2] onto quartz slides (dimensions 0.8–0.85-cm width × 2.4–2.5-cm length × 1.0–1.5-mm thickness). For the thicker films spin-coating was not possible; these films were prepared by coating the solution containing the dye and polymer onto the slide and allowing the solvent to evaporate. All polymer films were dried in an Abderholden drying pistol as described in our previous study.[2] Thicknesses were measured by profilometry or, more commonly, with a micrometer screw gauge.

Determination of Equilibrium $\lambda_{max}(1)$ at Various Relative Humidities. To obtain the desired relative humidities, dry nitrogen gas was passed through two bubblers, connected in series, containing saturated aqueous solutions of inorganic salts.[9] The bubblers were thermostated at 25 °C in a water bath. To obtain 8% relative humidity, the nitrogen was bubbled through saturated aqueous KOH; to obtain 33%, saturated $MgCl_2$ was used; for 53%, $Mg(NO_3)_2$ was used; for 75%, NaCl was used; for 92%, KNO_3 was used; and for 100%, pure water was used (the precision in these relative humidities is about ±1%). The flow rate of nitrogen through the bubblers and the cuvette containing the polymer films was 50 mL/min. A flow controller from an old gas chromatograph was used to ensure that the flow rate did not vary.

A quartz cuvette (1-cm path length × 1-cm cross section) containing each polymer film was placed in an Abderholden drying pistol, and the film was dried as described previously.[2] After drying, the cuvette was removed from the drying pistol (under a dry nitrogen atmosphere) and immediately capped with a septum, and a UV-visible spectrum was obtained at 0% relative humidity. Alternatively, we found that the films could be dried by exposure to dry nitrogen (passed through a $CaCl_2$ drying tube) for a couple of hours. This technique is preferred since it involves less risk of damage to the polymer/dye film. A syringe needle, with nitrogen of the desired relative humidity flowing through it, was then inserted through the septum into the cuvette, and UV-visible spectra were again obtained. The nitrogen was kept flowing through the cuvette and spectra obtained over a couple of hours, until the absorption maximum of Reichardt's dye in the polymer film no longer shifted with time. As each polymer film sorbed water vapor from the nitrogen, the absorption maximum of Reichardt's dye shifted to shorter wavelengths. Equilibrium $\lambda_{max}(1)$ values were determined at the seven relative humidities listed above for each polymer (Table I), and the results are shown in Figure 1. In the case of PVC, the effect of relative humidity was so small that only three humidities were studied for this polymer, and so no plot is included.

Determination of α_1 and $E_T(30)$. A thin film (about 10 μm) of each polymer containing 4-nitroanisole (**2**) was prepared by spin-coating, and the absorption maximum was determined at 0% relative humidity as described in our previous study.[2] From that study it was observed that $\lambda_{max}(2)$ in these polymers did not vary by more than 2 nm (our instrument precision) for different relative humidities. Thus $\lambda_{max}(2)$ was only determined at 0% relative humidity for each polymer, and that value was used for the determination of α_1 at all other humidities. The values of $\lambda_{max}(2)$ measured for PMMA, PVAc, PVC, and PVP were 308, 308, 312, and 314 nm, respectively. The values of α_1 for each polymer at the various relative humidities were calculated from the $\nu_{max}(2)$ and equilibrium $\nu_{max}(1)$ values using eq 1. The $E_T(30)$ values were calculated from the equilibrium $\nu_{max}(1)$ values using eq 2. The results are shown in Table I.

Kinetic Studies. Films of PVAc containing Reichardt's dye, with the thicknesses specified earlier, were dried and exposed to nitrogen at 100% relative humidity at 25 °C at a flow rate of 100 mL/min. The kinetics program of the UV-visible spectrometer was used to obtain several spectra in the range 400–800 nm over a period of a few minutes to a couple of hours (depending on the film thickness), until $\lambda_{max}(1)$ reached its equilibrium value at 100% relative humidity. Typical of the kinetic data obtained are those for a 34-μm PVAc film, shown in Table II. The data for each polymer film were fit to the first-order rate equation ($\lambda_{max}(1)$ as a function of time), and the rate constants, k_{1s}, for the sorption of water vapor by the films were determined (using the program Enzfitter);[12] these are shown in Table III. For the 71-μm film, the nitrogen flow rate was varied and the rate constants for sorption were again determined; these results are shown in Table IV.

After $\lambda_{max}(1)$ for each polymer film reached its equilibrium value at 100% relative humidity, kinetic desorption studies were carried out by exposing these same films to nitrogen of 0% relative humidity (passed through a $CaCl_2$ drying tube) and, again, using the kinetics program of the UV-visible spectrometer to obtain several spectra over a period of a few minutes to a couple of hours until $\lambda_{max}(1)$ reached its equilibrium value for 0% relative humidity. As was done for the sorption data, first-order rate constants, k_{1d}, for the desorption of water were determined for each film. The results are shown in Tables II and III.

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Registry No. 1, 10081-39-7; PMMA (homopolymer), 9011-14-7; PVP (homopolymer), 9003-39-8; PVAc (homopolymer), 9003-20-7; PVC (homopolymer), 9002-86-2; H_2O, 7732-18-5.