Solvatochromic Study of Water Sorption in Polymer Films

MASANOBU MATSUGUCHI, YOSHIHIKO SADAOKA, HIROSHI MIZUGUCHI,
KENICHI UMEDA, YOSHIRO SAKAI

Department of Applied Chemistry, Faculty of Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790, Japan

ABSTRACT: A solvatochromic method was used to characterize the water sorption behavior of polymer films. Four different dyes were dissolved in various solid polymers and the relative water vapor pressure in the atmosphere was changed. Evaluated solvatochromic parameters depended not only on the amount of sorbed water but also on the kind of polymer. A linear correlation between the $E_T(30)$ value and Taft's multiparameter was confirmed in both the dried and the water sorbed polymers. The correlation equation was almost identical to that obtained by other researchers in liquid solvents. These results suggest that the dissolved dyes behave as indicators of microenvironmental changes in the solid polymer film. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1681–1691, 1997

Key words: water sorption; solvatochromism

INTRODUCTION

Sorption behavior in various polymer films is currently being investigated because of their theoretical and practical significance. Many of the applications of polymer materials depend wholly or largely on sorption behavior; therefore, the general interaction of water with polymers was reviewed. On the other hand, the water sorption behavior of a polymer, based on its chemical structure, is not properly understood. One of the most important factors affecting water sorption properties is the hydrophilicity of the constituent groups of the polymer. The sorption of water in polymers depends on the intermolecular forces (electrostatic, directional, and inductive forces, as well as hydrogen-bonding forces) between those groups and water molecules. Clarification of the relationship between the chemical structure of the polymer and the sorption behavior from the molecular interaction viewpoint is therefore needed.

In determining the states of gases or vapors sorbed in substances, various techniques have been used. The gravimetric method using a quartz spring has been used as a representative technique. Recently, the quartz crystal microbalance (QCM) technique has been widely used in place of the quartz spring.[1–3] Although the QCM is an instrument for accurately measuring the mass change and is useful for observing the sorption behavior *in situ* in the thin film state, information on the state of sorbed water cannot be obtained directly. Many researchers have also been adopting the measurement of the apparent dielectric constant of sorbed water on metal oxides.[4–9] When water vapor is the sorbate, dielectric measurements are believed to be an effective means of determining the macroscopic state because of their strong polarity. However, the macroscopic dielectric constant does not provide a direct measure of the interactions on a molecular scale as well. Because the polarity and the hydrogen-bond-

ing ability of a polymer can, therefore, only be incompletely specified by its individual physical characteristics, various attempts have been made to obtain such characteristics by such methods as IR, NMR, and DSC, etc.[10]

Recently, Paley et al. extended the well-known solvatochromic method to characterize solid polymers. Thin films of the polymers with dissolved dyes were prepared and the UV/vis absorption spectra of the films were recorded.[11,12] They reported that the obtained solvatochromic parameters of dipolarity/polarizability, hydrogen-bond acidity, and hydrogen-bond basicity showed great potential for clarifying the properties of solid polymers and liquid solvents. This method more accurately reflected a complete picture of the intermolecular forces. Furthermore, Paley and colleagues demonstrated that relative humidity had significant effects on the solvatochromic parameters for the dye dispersed polymer.

The object of this study was to confirm the reliability and usefulness of the solvatochromic method for characterizing the water sorption behavior of a polymer, possibly revealing the water sorption behavior of polymers precisely from the viewpoint of interaction on a molecular scale. For this purpose, the solvatochromic parameters were determined for various kinds of polymers with dispersed dyes. The variation in the measured parameters was examined as a function of the amount of sorbed water in the composite polymers. Furthermore, the correlation between Reichardt's scale of solvent polarity and Taft's multiparameter was examined in dried and water sorbed polymers. The obtained correlation equation was compared with that obtained by other researchers in liquid solvents.[13,14]
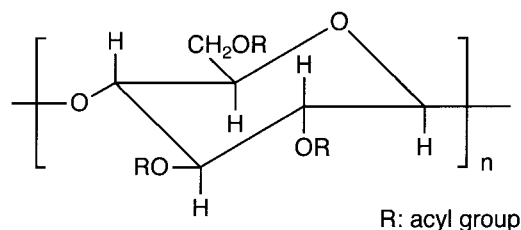
CAB $[C_6H_7O_2(OH)_x(OCOCH_3)_y(OCOC_3H_7)_z]_n$

CA $[C_6H_7O_2(OH)_x(OCOCH_3)_y]_n$

EC $[C_6H_7O_2(OH)_x(OC_2H_5)_y]_n$

CAP $[C_6H_7O_2(OH)_x(OCOCH_3)_y(OCOC_2H_5)_z]_n$

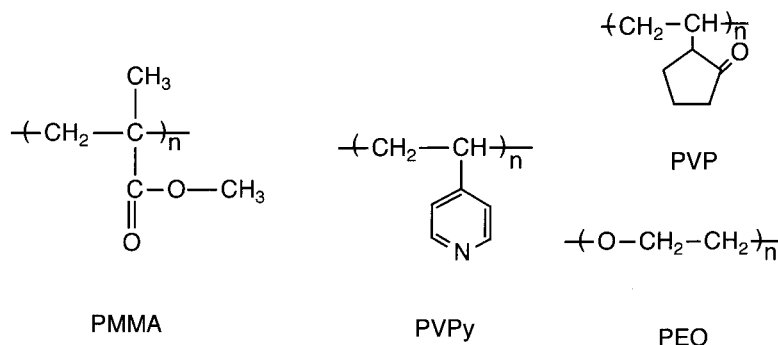|	x^*	y^*	z^*
CAB 17	0.3	2.0	0.7
CAB 38	0.3	1.0	1.7
CAB 50	0.2	0.4	2.4
CA 39	0.8	2.2	
EC	0.5	2.5	
CAP 48	0.5	0.2	2.3
CAP 50	1.0	0.2	1.8

* approx. value

Figure 1   Chemical structure of polymers.

EXPERIMENTAL

Materials

Seven different cellulose derivatives (Kanto Chemical Co., Inc.), poly(N-vinyl-2-pyrrolidone) (PVP, Tokyo Kasei Kogyo Co., Ltd.), poly(4-vinyl-pyridine) (P4VPy, Aldrich Chemical Co., Inc.), poly(methyl methacrylate) (PMMA, Hayashi Pure Chemical Industries, Ltd.), and three different poly(ethylene oxides) (PEO, Aldrich Chemical Co., Inc.) with different molecular weights ($M_w \approx$ 6000, 70,000, and 500,000) were used for the present study. The cellulose derivatives were cellulose acetate (CA), three cellulose acetate butyrates with different butyryl content (CAB), two cellulose acetate propionates with different propionyl content (CAP), and ethyl cellulose (EC). Their chemical structures are shown in Figure 1.

Four dyes, 4-nitro-N,N-dimethylaniline (**1**), 4-nitroaniline (**2**), 4-nitroanisole (**3**), and 2,6-diphenyl-4-(2,4,6-triphenylpyridinio) phenolate (**4**) were used as indicators for the optical measurement. These dyes were purchased from Aldrich and their chemical structures are given in Figure 2.

Preparation of Measuring Device

For the measurement of optical characteristics, the polymers were dissolved in the appropriate solvent (acetone for cellulose derivatives and PMMA, methanol for PVP, and chloroform for PEO). The dyes required to determine the solvatochromic parameters were then dissolved in these solutions at several weight ratios of the polymer and the dye. The composite solution was coated on the inside of a special quartz cell using a syringe as shown in Figure 3. The film was dried at 50°C *in vacuo* in a glass tube oven for 30 min.

A thin film was coated on a quartz crystal in the same way for the measurement of the amount of sorbed water.

Measurement

The optical characteristics were measured using a diode array spectrophotometer (Hewlett–Packard Co., 8452A). The quartz cell was placed in a holder, and the film was dried by passing dry air (dew point is ca. −60°C) into the cell. A UV/vis spectrum at $p/p_0 = 0$ was then obtained. Humid air was prepared by mixing dry and wet air and introducing that mixture into the quartz cell. The UV/vis spectrum at each relative water vapor pressure was then recorded.

The amount of sorbed water was measured using an oscillating QCM based on the variation in oscillating frequency of the QCM with a universal counter (ADVANTEST, TR5822). The principle of the quartz microbalance is given elsewhere.[15] An AT-cut quartz crystal of 4 MHz resonant fre-
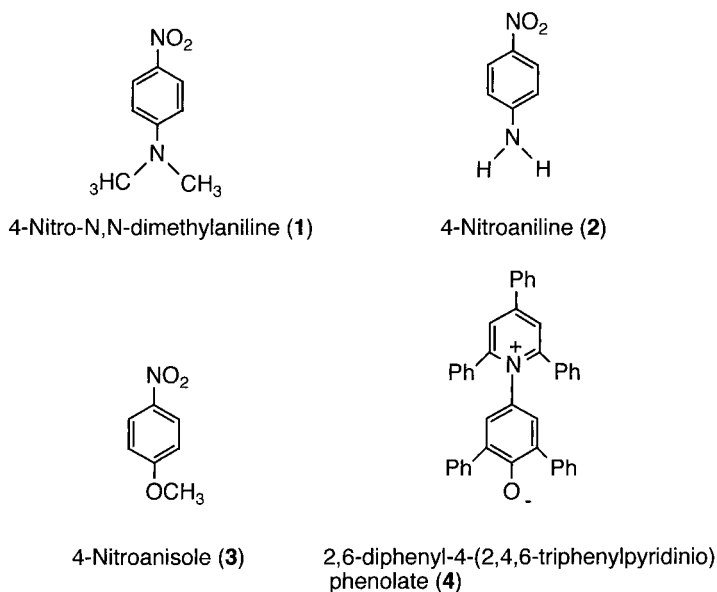

4-Nitro-N,N-dimethylaniline (**1**)

4-Nitroaniline (**2**)

4-Nitroanisole (**3**)

2,6-diphenyl-4-(2,4,6-triphenylpyridinio) phenolate (**4**)

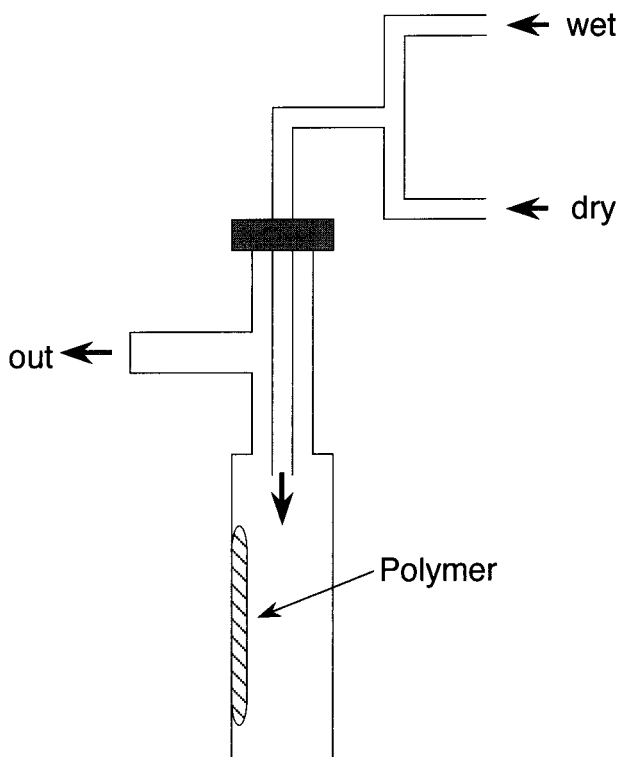**Figure 2**   Chemical structure of four kinds of indicator dye.

Figure 3   The structure of a special quartz cell for optical measurements.

quency was used in this study. The polymer coated crystal was set in a special vessel in which the relative water vapor pressure was thermostatically controlled by mixing dry and wet air.

THEORETICAL BACKGROUND

The absorption spectrum of a substance in solution may be modified by the solvent that causes changes in λ_{max} (the longest wavelength of the absorption maximum), intensity, and shape of the absorption bands. This phenomenon is termed "solvatochromism." Various empirical solvent polarity scales have been developed based on carefully selected and well-understood spectral absorptions.[13,14,16–20] Two of these methods were adopted in this study.

Pyridinium N-phenoxide betaine dye was proposed by Reichardt,[13,16] as a UV/vis spectroscopic indicator of solvent polarity. This dye overcame some of the practical limitations of other solvatochromic dyes because it showed an exceptionally large negative band shift due to a change in the dipole moment by ca. 9 D upon electronic

excitation.[13,16] The longest wavelength intramolecular charge-transfer (CT) absorption band is hypsochromically shifted by 9.73×10^3 cm^{-1} on going from diphenyl ether ($\nu_{max} = 12.35 \times 10^3$ cm^{-1}) to water ($\nu_{max} = 22.08 \times 10^3$ cm^{-1}), where $\nu_{max} = (\lambda_{max})^{-1}$. This is due to stabilization of the highly dipolar electronic ground state of the dye relative to a less dipolar excited state in a polar solvent. It then gives the $E_T(30)$ value as a polarity scale. The $E_T(30)$ value of the polymer is estimated from the longest wavelength absorption maximum of the Reichardt's betaine dye in the polymer:[11]

$$E_T(30)/\text{kcal mol}^{-1} = hc\bar{\nu}N_A$$
$$= 2.8591\bar{\nu}_{max}(\mathbf{4}) \quad (1)$$

where h is Planck's constant, c is the speed of light in a vacuum, and N_A is Avogadro's number. In this equation and all those following, $\bar{\nu}_{max}$ values are given in units of 1000 per centimeter (10^3 cm^{-1}). A high $E_T(30)$ value corresponds to a high solvent polarity. Note that this polarity scale does not mean only van der Waals and Coulombic interactions in the present study. The dye possesses a phenoxide oxygen atom that acts as a highly basic electron-pair donor center and interacts with Brønsted acids and Lewis acids. Therefore, the phenoxide atom binds to hydrogen-bonding acids such as water and thus complicates interpretation of the CT absorption band change.

An alternative method, which uses multiparameter correlation equations, was introduced. The method consists of up to four single empirical parameters.[14,17,18] Each of them measures a certain aspect of the overall solvation capability of a given solvent (e.g., polarizability, dipolarity, Lewis acidity, and Lewis basicity). Kamlet and Taft gave an empirical equation based on a variety of solvent-dependent phenomena (X) that include many reaction rates, equilibria, and spectroscopic properties. If X is the absorption maximum of an indicator dye dissolved in a series of solvents, then

$$X = X_0 + \text{solvent polarity}$$
$$- \text{polarizability effect} + a\alpha + b\beta \quad (2)$$
$$= X_0 + s\pi_1^* + a\alpha + b\beta \quad (3)$$

where X_0 is a constant; π_1^*, α, and β are the solvent scale obtained by selecting the indicators

that are sensitive to dipolarity/polarizability, hydrogen-bond basicity, and hydrogen bond acidity; and s, a, and b are the coefficients, respectively. Paley and colleagues showed that it is possible to determine the above solvatochromic parameters for solid polymers by measuring the UV/vis absorption spectra of a series of four dyes dissolved in polymers.[11,12] Dipolarity/polarizability, π_1^*, is determined from the longest wavelength UV/vis absorption band maximum of 4-nitro-N,N-dimethylaniline (**1**) in the polymer, according to the following empirical equation:

$$\pi_1^* = 8.006 - 0.2841\bar{\nu}_{max}(\mathbf{1}) \qquad (4)$$

Hydrogen bond acidity, α, is determined from the longest wavelength absorption maxima of 4-nitroanisole (**3**, a poor hydrogen bond base) and 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate (Reichardt's betaine, **4** a good hydrogen bond base):

$$\alpha = (\bar{\nu}_{max}(\mathbf{4}) + 1.873\bar{\nu}_{max}(\mathbf{3}) - 74.58)/6.24 \quad (5)$$

Hydrogen bond basicity, β, is determined from the longest wavelength absorption maxima in the polymer of 4-nitroaniline (**2**, a good hydrogen bond acid) and 4-nitro-N,N-dimethylaniline (**1**, a poor hydrogen bond acid)[18]:

$$\beta = (0.984\bar{\nu}_{max}(\mathbf{1}) - \bar{\nu}_{max}(\mathbf{2}) + 3.40)/2.67 \quad (6)$$

RESULTS AND DISCUSSION

The absorption band of Reichardt's betaine dye dispersed in a polymer was influenced by the dye content, particularly at the higher relative water vapor pressure (p/p_0) in the test atmosphere. Therefore, we first measured the water adsorption ability of the dye itself. The dye adsorbed a great deal of water (80.9 mg per gram of the dye at $p/p_0 = 0.84$), and this hydrophilic character affected the absorption spectra of the dye/polymer composites. For other dyes the effect of the dye content on the absorption spectra in a humid atmosphere was small. This was due to the less hydrophilic character of these dyes. However, aggregation of the dye was likely to occur for all dyes when the composite film was exposed to water vapor, particularly in the case of a high dye content. The dye must be dispersed in the polymer on a molecular scale to obtain reliable data. Consequently, find-

Table I λ_{max} of Four Dyes Obtained at 30°C in Dry Air

	λ_{max} (**1**) (nm)	λ_{max} (**2**) (nm)	λ_{max} (**3**) (nm)	λ_{max} (**4**) (nm)
CAB 17	394	364	310	698
CAB 38	397	366	311	655
CAB 50	397	365	310	700
CA 39	396	366	311	638
EC	384	360	306	722
CAP 48	396	367	312	641
CAP 50	397	369	312	617
PMMA	389	362	308	696
PVP	398	385	316	719
P4VPy	404	382	318	716
PEO 500K	394	380	311	673
PEO 70K	394	376	312	664
PEO 6K	393	376	311	649

ing the optimum dye content in the composite film appeared to be important. The absorption spectrum was thus measured as a function of the quantity of the dye dispersed in the polymer. As expected, the lower the content, the lesser the influence on the spectrum. However, the absorption band broadened and λ_{max} could not be assigned precisely at extremely low dye content. The optimum dye contents were determined as follows: the weight ratio of polymer to dye was 100 : 5 for dye **1**, 100 : 5 for dye **2**, 100 : 3 for dye **3**, and 100 : 2.75 for dye **4.** Subsequent examination was carried out on the optimum composite film.

Solvatochromic Parameters in Dry Atmosphere

We measured the UV/vis spectra of composite films in dry air. The λ_{max} obtained for each dye/polymer composite is summarized in Table I. The λ_{max} of the dye was observed to depend on the kind of polymer. In particular, the tendency was remarkable for the pyridinium-N-phenoxide betaine dye (**4**). The solvatochromic parameters were estimated using eqs. (1), (4), (5), and (6) and are listed in Table II (see the column, $p/p_0 = 0$). From these results it seems that CA and CAP are protic, PVP and P4VPy are aprotic, and PEO is an amphiprotic polymer. The trends for each polymer were in good agreement with that of each monomer solvent. Furthermore, the solvatochromic parameters of cellulose derivatives seem to be affected by the content and type of substituent group. These parameters were also depended

Table II   Solvatochromic Parameters Obtained at 30°C

	p/p_0	E_T (30)	π_1^*	α	β
CAB 17	0	40.96	0.795	0.027	0.338
	0.10	41.32	0.800	0.040	0.347
	0.20	41.86	0.803	0.065	0.359
	0.30	42.36	0.808	0.083	0.387
	0.39	42.86	0.812	0.102	0.387
	0.58	43.72	0.823	0.131	0.406
	0.73	44.46	0.832	0.158	0.438
	0.79	44.74	0.835	0.167	0.456
CAB 38	0	43.65	0.850	0.131	0.323
	0.16	44.81	0.850	0.196	0.337
	0.32	45.89	0.853	0.256	0.349
	0.47	46.79	0.857	0.307	0.364
	0.61	47.65	0.862	0.355	0.379
	0.73	48.29	0.868	0.391	0.397
	0.83	48.79	0.873	0.419	0.412
CAB 50	0	40.84	0.850	0.011	0.304
	0.20	41.86	0.852	0.061	0.310
	0.39	42.80	0.855	0.108	0.316
	0.57	43.72	0.861	0.150	0.321
	0.73	44.46	0.868	0.183	0.322
	0.86	45.09	0.875	0.212	0.324
CA 39	0	44.81	0.832	0.211	0.347
	0.11	46.34	0.841	0.284	0.371
	0.21	47.73	0.852	0.353	0.393
	0.39	49.55	0.873	0.443	0.420
	0.57	51.05	0.904	0.493	0.427
	0.71	52.08	0.934	0.536	0.418
	0.82	52.75	0.960	0.558	0.405
EC	0	39.60	0.609	0.086	0.465
	0.17	41.32	0.625	0.173	0.511
	0.31	42.42	0.638	0.225	0.530
	0.52	43.92	0.661	0.297	0.551
	0.67	44.81	0.684	0.334	0.553
	0.77	45.45	0.703	0.364	0.548
	0.83	45.82	0.714	0.378	0.547
CAP 48	0	44.60	0.832	0.172	0.375
	0.10	45.31	0.834	0.208	0.383
	0.21	46.19	0.837	0.251	0.395
	0.33	47.10	0.844	0.299	0.403
	0.43	47.73	0.852	0.332	0.410
	0.63	49.04	0.870	0.396	0.419
	0.79	49.98	0.887	0.443	0.423
CAP 50	0	46.34	0.850	0.266	0.407
	0.08	47.26	0.853	0.314	0.413
	0.16	48.29	0.857	0.369	0.422
	0.24	49.12	0.861	0.413	0.431
	0.32	49.81	0.864	0.448	0.440
	0.47	50.87	0.873	0.502	0.450
	0.62	51.61	0.882	0.537	0.465
	0.75	52.27	0.891	0.568	0.475
PMMA	0	41.08	0.703	0.096	0.407
	0.22	43.45	0.717	0.223	0.419
	0.41	44.46	0.740	0.270	0.418
	0.58	45.38	0.760	0.315	0.425

Table II *Continued*

	p/p_0	E_T (30)	π_1^*	α	β
	0.72	45.96	0.775	0.342	0.431
	0.83	46.49	0.788	0.368	0.440
PVP	0	39.76	0.868	−0.215	0.805
	0.04	40.78	0.907	−0.164	0.809
	0.10	42.36	0.955	−0.088	0.797
	0.39	46.72	1.046	0.100	0.777
	0.56	48.79	1.080	0.180	0.752
	0.71	50.60	1.105	0.250	0.724
	0.83	52.08	1.127	0.309	0.696
P4VPy	0	39.93	0.974	−0.275	0.591
	0.09	41.43	1.005	−0.199	0.602
	0.16	42.04	1.017	−0.171	0.637
	0.28	42.67	1.034	−0.151	0.639
	0.40	43.45	1.043	−0.122	0.653
	0.52	44.12	1.060	−0.100	0.656
	0.63	45.53	1.077	−0.049	0.659
	0.72	46.72	1.127	−0.012	0.642
PEO 500K	0	42.48	0.803	0.081	0.762
	0.07	42.86	0.806	0.071	0.757
	0.15	43.45	0.814	0.104	0.747
	0.26	44.26	0.817	0.119	0.769
	0.38	45.09	0.832	0.166	0.750
	0.49	45.67	0.862	0.198	0.736
	0.59	46.56	0.900	0.248	0.687
	0.66	47.81	0.939	0.318	0.637
PEO 70K	0	43.06	0.801	0.082	0.659
	0.06	43.52	0.808	0.108	0.650
	0.13	43.85	0.814	0.127	0.643
	0.26	44.39	0.823	0.126	0.657
	0.38	45.09	0.843	0.166	0.631
	0.52	45.82	0.886	0.206	0.602
	0.61	46.64	0.914	0.252	0.565
	0.67	47.33	0.939	0.291	0.533
PEO 6K	0	44.05	0.783	0.169	0.683
	0.04	44.39	0.786	0.188	0.678
	0.12	44.67	0.790	0.204	0.673
	0.25	45.09	0.795	0.196	0.666
	0.39	45.53	0.814	0.220	0.643
	0.52	46.04	0.828	0.249	0.676
	0.61	46.72	0.886	0.287	0.602
	0.66	47.18	0.921	0.313	0.556

somewhat on the molecular weight of the polymer (PEO). Further detailed discussion of these results is currently under study and will be presented in the near future. The values obtained in this study for PMMA and PVP were compared with those reported by Paley et al.[11] Comparison of those values showed excellent agreement for PVP, although the values for PMMA were not in accord with reported values. The α value for PMMA is expected to be almost zero, consistent with our result. Paley and coworkers explained the nonzero value for α by the presence of acid groups or acidic impurity in the polymer. Because the dependence of solvatochromic parameters on the polymer species was confirmed, the method was shown to be useful for characterization of the polymer.
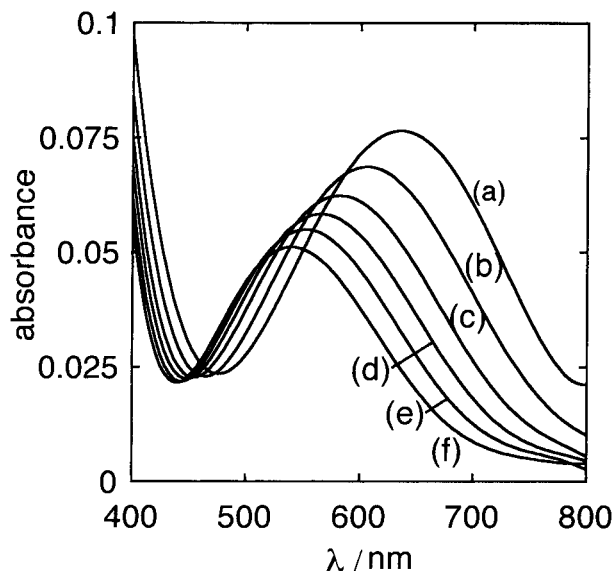
Figure 4 Typical UV/vis spectra for a composite of Reichardt's betaine dye and CA 39: (a) $p/p_0 = 0$, (b) 0.12, (c) 0.3, (d) 0.46, (e) 0.61, and (f) 0.77.

Solvatochromic Parameters in Wet Atmosphere

We examined the effect of relative water vapor pressure (p/p_0) on λ_{max}. In Figure 4 a typical example of the UV/vis absorption spectra observed at various relative water vapor pressures is shown for the composite film of Reichardt's betaine dye and CA 39. The $\lambda_{max}(\mathbf{4})$ was considerably shifted negatively with increasing relative water vapor pressure within the experimental range

studied. This was due to a change in the microenvironment around the dye with an increase in the sorbed water in the film. This result was explained by the stabilization of the highly dipolar electronic ground state of the dye relative to the less dipolar excited state, resulting in an increase in the electronic transition energy. Conversely, the λ_{max} value for other indicator dyes shifted to a longer wavelength with increasing relative water vapor pressure. In the case of these indicator dyes, the sorbed water molecules stabilized the electronic excited states relative to the ground state, and this led to a bathochromic shift. The influence of the sorbed water on the spectrum of indicator dyes **1**, **2**, and **3** was observed to be small.

The solvatochromic parameters (π_1^*, α, β, and $E_T(30)$ were evaluated for all polymers using eqs. (1), (4), (5), and (6) at various relative water vapor pressures and are summarized in Table II. The parameters shifted to a larger value with an increase in the relative water vapor pressure in most cases. β values for EC, PVP, and PEO were lower at higher relative water vapor pressure. We also measured the water sorption ability for the present composite polymers. The changes in the parameters at given sorbed water content with respect to those in dry atmosphere are summarized in Tables III–VI. Here we assume that the total parameter shift is caused by an additive effect due to the polymer matrix and sorbed water. If the water molecules adsorb on the dye molecule and interact with the dye directly, the parameter

Table III π_1^* **Value Change at a Given Amount of Sorbed Water at 30°C**

	π_1^*				
	$W = 10$ (mg g^{-1})	$W = 20$ (mg g^{-1})	$W = 40$ (mg g^{-1})	$W = 60$ (mg g^{-1})	$W = 100$ (mg g^{-1})
CAB 17	0.007	0.016	0.036	—	—
CAB 38	0.004	0.013	—	—	—
CAB 50	0.005	0.018	—	—	—
CA 39	0.009	0.020	0.041	0.072	0.128
EC	0.029	0.052	0.093	—	—
CAP 48	0.005	0.020	0.056	—	—
CAP 50	0.007	0.012	0.032	—	—
PMMA	0.037	0.073	—	—	—
PVP	—	0.039	—	—	0.096
P4VPy	0.024	0.040	0.062	0.071	0.099
PEO 500K	0.027	0.066	0.105	0.123	—
PEO 70K	0.056	0.102	—	—	—
PEO 6K	0.041	—	—	—	—

Table IV α Value Change at a Given Amount of Sorbed Water at 30°C

	α				
	$W = 10$ (mg g^{-1})	$W = 20$ (mg g^{-1})	$W = 40$ (mg g^{-1})	$W = 60$ (mg g^{-1})	$W = 100$ (mg g^{-1})
CAB 17	0.038	0.076	0.105	—	—
CAB 38	0.126	0.224	—	—	—
CAB 50	0.097	0.172	—	—	—
CA 39	0.073	0.142	0.232	0.282	0.347
EC	0.139	0.210	0.277	—	—
CAP 48	0.080	0.160	0.271	—	—
CAP 50	0.104	0.182	0.271	—	—
PMMA	0.174	0.246	—	—	—
PVP	—	0.050	—	—	0.213
P4VPy	0.055	0.085	0.126	0.154	0.211
PEO 500K	0.079	0.126	0.182	0.213	—
PEO 70K	0.097	0.153	—	—	—
PEO 6K	0.072	—	—	—	—

change with the amount of adsorbed water would be identical for all polymers. In practice, however, the difference depends not only on the amount of sorbed water but also on the kind of polymer species. In other words, the difference in the properties of the polymer matrix and the state of sorbed water in each polymer were reflected in the solvatochromic parameter. More detailed discussion of the sorption behavior of the individual polymers will be presented in the near future along with results of gravimetric, dielectric, and spectroscopic measurements.

Correlation of Reichardt's $E_T(30)$ with Taft's Multiparameter

Many researchers have confirmed that the $E_T(30)$ parameter correlates with Taft's multiparameter in liquid solvents.[13,14] We examined the relationship between the Reichardt's polarity scale $[E_T(30)]$ and

Table V β Value Change at a Given Amount of Sorbed Water at 30°C

	β				
	$W = 10$ (mg g^{-1})	$W = 20$ (mg g^{-1})	$W = 40$ (mg g^{-1})	$W = 60$ (mg g^{-1})	$W = 100$ (mg g^{-1})
CAB 17	0.022	0.049	0.100	—	—
CAB 38	0.026	0.056	—	—	—
CAB 50	0.013	0.019	—	—	—
CA 39	0.025	0.046	0.073	0.080	0.058
EC	0.066	0.087	0.083	—	—
CAP 48	0.021	0.035	0.049	—	—
CAP 50	0.015	0.033	0.059	—	—
PMMA	0.011	0.025	—	—	—
PVP	—	0.004	—	—	0.030
P4VPy	0.008	0.021	0.046	0.050	0.067
PEO 500K	−0.011	−0.036	−0.086	−0.108	—
PEO 70K	−0.038	−0.081	—	—	—
PEO 6K	−0.017	—	—	—	—

Table VI E_T **Value Change at a Given Amount of Sorbed Water at 30°C**

	E_T				
	$W = 10$ (mg g^{-1})	$W = 20$ (mg g^{-1})	$W = 40$ (mg g^{-1})	$W = 60$ (mg g^{-1})	$W = 100$ (mg g^{-1})
CAB 17	0.36	1.90	3.50	—	—
CAB 38	2.24	4.00	—	—	—
CAB 50	2.32	3.98	—	—	—
CA 39	1.53	2.92	4.74	6.24	7.94
EC	2.82	4.32	5.86	—	—
CAP 48	1.59	3.13	5.38	—	—
CAP 50	1.96	3.47	5.27	—	—
PMMA	3.39	4.88	—	—	—
PVP	—	1.02	—	—	4.49
P4VPy	1.17	1.96	2.86	3.58	5.26
PEO 500K	2.53	3.36	4.34	4.91	—
PEO 70K	2.26	3.26	—	—	—
PEO 6K	1.84	—	—	—	—

Taft's multiparameters (π_1^*, α, and β) for the present dye/polymer composite systems. The multiple-parameter least-square correlations obtained are

$$E_T(30) = 15.52\pi_1^* + 14.49\alpha + 28.80$$

$$(n = 13, r = 0.957) \quad (7)$$

for a dry film, and

$$E_T(30) = 15.72\pi_1^* + 16.16\alpha + 28.70$$

$$(n = 87, r = 0.983) \quad (8)$$

for a wet film, where n equals the number of data points and r is a correlation coefficient. The contribution of β was negligible. The correlation coefficients, r, of eqs. (7) and (8) are excellent and satisfactory, respectively. These equations clearly show that $E_T(30)$ values represent a combination of nonspecific (π_1^*) and specific (α) water–polymer interactions. In addition, both correlations had similar coefficients. This linear relationship shows that the observed parameter reflects the microscopic environment in the wet film as well as that in the dry film.

To further confirm the reliability of the solvatochromic method as a tool to elucidate the polymer–water interaction, a study of whether the indicator dyes in the polymer behave in the same way as those in the solvent was required. For this purpose, the relationships obtained above were compared with those reported for a liquid system.

Although correlation equations for a liquid solvent depend on the kind of solvent used and had a slightly different coefficient for each experimental condition, we adopted the one reported by Reichardt.[13] The relationship may be expressed as

$$E_T(30) = 13.68(\pi_1^* - 3.45\delta) + 14.51\alpha + 30.8$$
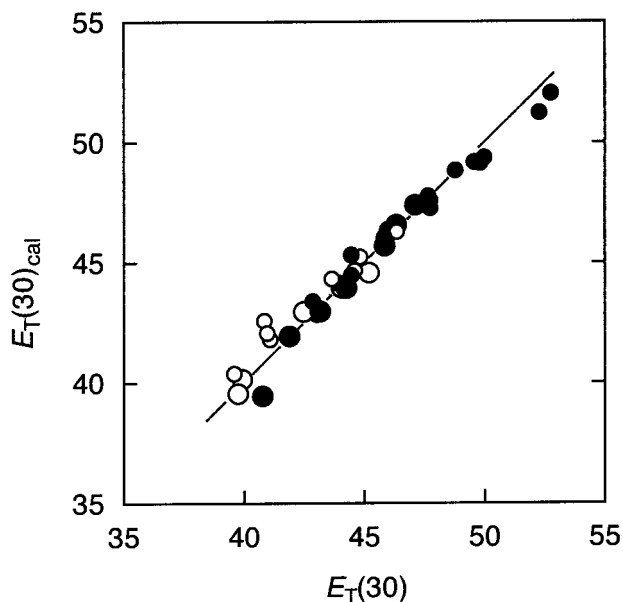
$$(n = 100, r = 0.984) \quad (9)$$

Figure 5   Plot of $E_T(30)$ against $E_T(30)_{cal}$ for all dye/polymer composite films: (○) dry air and (●) wet air.

where δ is a polarizability correction term for the solvent, aromatic ($\delta = 1.0$), polyhalogenated aliphatic ($\delta = 0.5$), or neither ($\delta = 0.0$). It is clear that the coefficient of eq. (9) is in good agreement with that of eqs. (7) or (8). The $E_T(30)$ values calculated using eq. (9) and data from Table II were defined as $E_T(30)_{cal}$. The relationship between the experimentally obtained $E_T(30)$ and $E_T(30)_{cal}$ is illustrated in Figure 5. A linear relationship was obtained. This is important because the behavior of the indicator dye in the solid polymer and the water sorbed polymer was similar to that in a liquid solvent. These solvatochromic parameters were useful for describing the microscopic environmental changes in the water sorbed polymer.

CONCLUSION

We confirmed that the solvatochromic parameters reflect the nature of a polymer in terms of the chemical structure and molecular weight. The solvatochromic parameters were also affected by the relative water vapor pressure in the atmosphere. Variation in the parameters with relative humidity depend not only on the water content of the composite film but also on the kind of polymer. The correlation between $E_T(30)$ and Taft's parameters was examined. The $E_T(30)$ parameter correlated linearly with Taft's multiparameter in the dried and water sorbed polymers, and the relationship was in good agreement with published work on liquid solvents. The solvatochromic method seems to be effective for distinguishing the different water–polymer interactions (dielectric, hydrogen-bond accepting, or hydrogen-bond donating) using different solvatochromic indicators.

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