Solvatochromism. A New Method for Polymer Characterization

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ABSTRACT: The solvatochromic method of Kamlet, Abraham, and Taft (KAT) has been used extensively for characterizing solvents, solutes, and solvent-solute interactions. Here we extend this method to characterize solid polymers as solvent phases by preparing thin films of the polymers with dissolved dyes and measuring the UV-visible absorption spectra of the films. The resulting solvatochromic measures of dipolarity/polarizability, hydrogen-bond acidity and hydrogen-bond basicity show great potential for determining solubility and sorption properties of polymers with gaseous, liquid, and solid solutes, as well as with bulk liquid solvents. Additionally, the solvatochromic parameters can be used to predict optical properties of molecules dissolved in polymers (e.g., for nonlinear optical applications). This particular application is illustrated by predicting the absorption maximum of an important nonlinear optical dye dispersed in various polymers. The $E_T(30)$ solvatochromic scale of solvent polarity developed by Reichardt is also applied to the polymers, and the results are compared to those obtained by the KAT method.

Introduction

The solubility and sorption properties of solid and liquid polymers are of great interest. For example, the ability of solutes to diffuse in and out of polymers and the compatibility of polymer additives (e.g., UV inhibitors and plasticizers) are of considerable importance especially when considering industrial applications (e.g., packaging, lifetime expectancy, tensile strength, etc.). Similarly, the optical properties of dyes dissolved in polymers are of interest for a variety of applications including nonlinear optics.[1] In contrast to the tremendous volume of work that has been done on characterizing liquid solvents, much less has been done to characterize the properties (polarity, acidity, basicity, etc.) of solid polymers as solvent phases. This is probably due in part to difficulties of handling macromolecules that are not encountered with small molecules, e.g., measuring UV-visible spectra in solid polymers. Over the past decade Kamlet, Abraham, Taft, and co-workers have developed a solvatochromic method for characterizing a variety of properties (including those discussed above) that are dependent on solute-solvent interactions for liquid solvents.[2] In the present work we have applied this method to the characterization of solid polymers.

The KAT approach describes solvent-solute interactions in terms of four phenomena: (1) the ability of a species to act as a hydrogen bond acid; (2) the ability of a species to act as a hydrogen bond base; (3) the dipolarity/polarizability of a species; and (4) the size of a species. A mathematical expression is given to this theory through the Kamlet-Taft solvatochromic equation, which is an empirical equation based on a variety of solvent-dependent phenomena (including the shifting of the absorption maxima of certain dyes in different solvents—hence the term solvatochromic), eq 1.[2]

$$\mathrm{SP} = \mathrm{SP}_o + A(\delta_H^2)_1 V_2 + B\pi_1^*\pi_2^* + C\alpha_1\beta_2^H + D\beta_1\alpha_2^H \tag{1}$$

In this equation, SP is some solvent-dependent property; SP_0 is a constant; δ_H is the Hildebrand solubility parameter and is a measure of the energy required to form a cavity in the solvent phase; the cavity size is taken as some volume parameter, V, of the solute[3] or a combination of volume and dispersion forces of the solute;[4-7] π_1^* and π_2^* are the solvent and solute parameters, respectively, that measure dipolarity/polarizability; α_1 and α_2^H are the solvent and solute parameters, respectively, that measure hydrogen bond acidity; β_1 and β_2^H are solvent and solute parameters, respectively, that measure hydrogen bond basicity; and A–D are constants, the magnitude and sign of which are dependent on the particular solution property being studied and not on the individual solvents or solutes. By convention subscript 1 in the solvatochromic equations applies to the solvent and subscript 2 to the solute.

For processes involving the SP of a single solute in a series of solvents, the solute parameters are constant and can be subsumed into A–D to give the coefficients l, s, b, and a in eq 2.

$$\mathrm{SP} = \mathrm{SP}_o + l(\delta_H^2)_1 + s\pi_1^* + b\beta_1 + a\alpha_1 \tag{2}$$

For a process involving the SP of a series of solutes in a single solvent, the solvent parameter is constant and can be subsumed into A–D to give the coefficients m, s', b', and a' in eq 3.

$$\mathrm{SP} = \mathrm{SP}_o + mV_2 + s'\pi_2^* + b'\beta_2^H + a'\alpha_2^H \tag{3}$$

If the SP in eq 2 is the absorption maximum of an indicator dye dissolved in a series of solvents, then the cavity term, $l(\delta_H^2)_1$, drops out, because in the process of excitation from the ground to the excited state, the size of the cavity does not change (according to the Frank-Condon principle), and thus l is equal to zero, eq 4.

$$\mathrm{SP} = \mathrm{SP}_o + s\pi_1^* + b\beta_1 + a\alpha_1 \tag{4}$$

This is the equation that Kamlet and his co-workers used originally to construct the solvent scales π_1^*, β_1, and α_1, by selection of indicators that are sensitive to dipolarity/polarizability, hydrogen bond basicity, and hydrogen bond acidity. In practice, it has been shown that these solvatochromic equations are capable of correlating, predicting, and elucidating hundreds of physicochemical properties and reactivity parameters of many diverse types. Physicochemical, biological, toxicological, and pharmacological properties that depend on interaction between solute and solvent phases have all been shown to correlate well via such equations and a compilation of references to 1985 has been published by Kamlet and Taft.[8] Included in more

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recent work are solvent effects on rotational isomerism and rate constants for several chemical processes.[2,9]

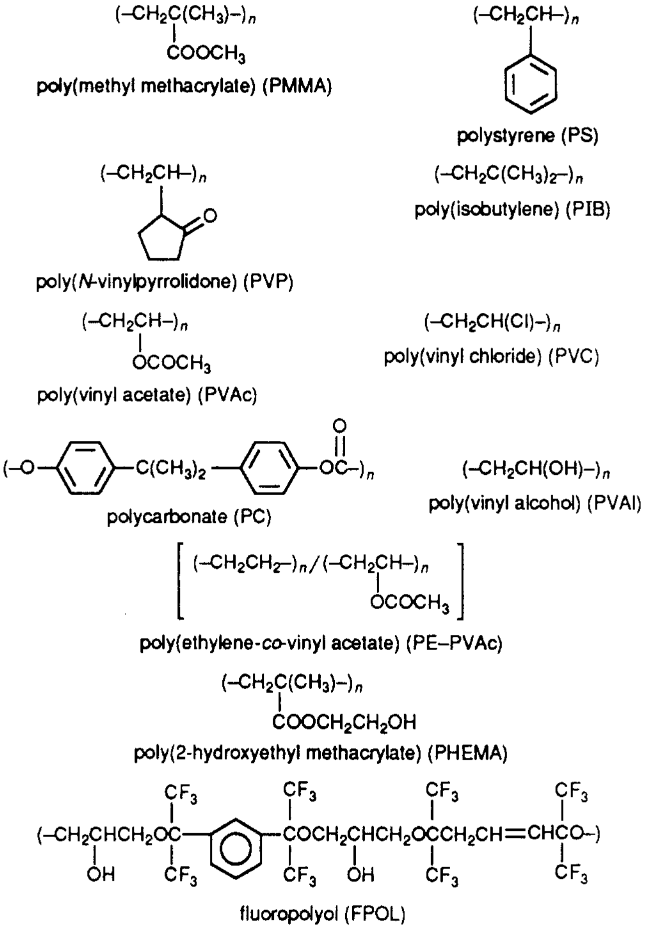
Recently, interest has been shown in applying this methodology to characterize polymer solvent phases by means of eq 3.[4,7,10-12] In this work, retention data from gas–liquid chromatography were used to evaluate polymeric stationary phases by chromatography of a series of solutes (of known solvatochromic parameters) for a variety of polymers. The retention data were shown to be well correlated by the solute solvatochromic parameters. The resulting coefficients (m, s', b', and a') provide an accurate description of the specific processes involved, and these coefficients can be used to compare the properties of a series of polymer stationary phases. However, this approach does not provide the solvent parameters (π_1*, α_1, and β_1 from eq 4) that are of general utility for predicting a variety of solvent-dependent processes.

No previous work on direct measurement of the solvatochromic parameters of solid polymers has been done. In the most closely related work, Carr and co-workers have measured π_1* for a series of liquid, polymeric siloxanes (OV type gas chromatography stationary phases) by dissolving the appropriate dyes directly in the viscous liquids; although these workers did not do so, β_1 can be calculated from these spectra.[13] Solution of the dyes required up to 5 days. Also, Drickamer and co-workers have recently studied the effect of high pressure on the solvatochromism of Reichardt's betaine dissolved in poly(methyl methacrylate) and polystyrene by spin-coating thin films of these polymers containing this dye.[14] They did not, however, determine any solvatochromic parameters.

The goal of the present work is to measure directly α_1, β_1, and π_1* for 11 solid polymers (listed below), chosen to provide a range of solvent properties, by measuring the UV–visible absorption spectra of a series of dyes (described below) dissolved in the polymers. These measurements were made possible by dissolving the dyes and polymers in a suitable solvent and spin-coating polymer–dye films onto quartz slides, which were then subjected to UV–visible analysis. This approach permits determination of the solvatochromic parameters of any polymer that can be dissolved in a volatile solvent, that is sufficiently translucent as a thin film to permit measurement of UV–visible absorption spectra, and in which the indicator dyes are soluble. Because Reichardt's dye was used in the measurements, we have also determined the polymer $E_T(30)$ values, another commonly used indicator of solvent polarity.[15] Additionally, we have examined the extent to which liquid monomeric solvents act as models for the solid polymeric solvents.

Lastly, we have examined one application of the solvatochromic parameters for polymers. The parameters can be used to predict the absorption maxima of dyes in polymer films. We have illustrated this latter application by predicting the absorption maximum of the nonlinear optical material *N*,*N*-dimethyl-3-acetamido-4-nitroaniline, DAN,[16] in several polymers (Chart I).

Chart I
Polymer Structures



Methods and Results

As the KAT solvatochromic method has developed, there has been much discussion of the best ways to determine the solvatochromic parameters. Recently Abraham, McGill, and co-workers have carefully examined this issue.[17,18] In the present work we have adopted the recommendations of this study. In particular, we have used the aniline indicators 4-nitro-*N*,*N*-dimethylaniline (1) and 4-nitroaniline (2), rather than the phenol indicators 4-nitroanisole (3) and 4-nitrophenol, for determining π_1* and β_1. More generally, we agree that it is desirable that solvatochromic parameters be determined through a common reference process rather than by averaging data from a variety of solvent-dependent processes. This single-process approach removes an objection to the averaging approach, which is that the parameters change as new processes are entered into the averaging procedure.

Dipolarity/polarizability, π_1*, is determined from the longest wavelength UV–visible absorption band maximum (the solvatochromic band) of 4-nitro-*N*,*N*-dimethylaniline (1) in the polymer, eq 5.[18] In this equation, and all

$$\pi_1^* = 8.006 - 0.2841\nu_{\max}(1) \qquad (5)$$

those following, $\nu_{\max}$ values are given in units of 10^3 cm^{-1}.

Hydrogen bond basicity, β_1, 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), eq 6.[18]

$$\beta_1 = [0.984\nu_{\max}(1) - \nu_{\max}(2) + 3.40]/2.67 \qquad (6)$$

Hydrogen bond acidity, α_1, is determined from the longest wavelength absorption maxima of 4-nitroanisole (3) (a poor hydrogen bond base) and Reichardt's betaine, 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate (4) (a good hydrogen bond base), eq 7.[19]

$$\alpha_1 = [\nu_{\max}(4) + 1.873\nu_{\max}(3) - 74.58]/6.24 \qquad (7)$$

The $E_T(30)$ value of the polymer is computed from the longest wavelength absorption maximum of Reichardt's

Table I
Absorption Maxima for Dyes in Polymers (λ_{max} in nm)[a]

	1	2	3	4	PNP[b]
PS	386	348	310	678	306
PVP	400	386	314	700	418
PIB	362	328	298	718	292
PHEMA	404	376	314	520	318
PVC	398	358	312	666	312
PC	392	358	310	710	312
PMMA	392	364	308	650	312
PVAc	392	366	308	714	312
PE–PVAc	380	360	304	688	306
PVal	412	386	316	580	408
FPOL	394	367	308	524	312

[a] All values were measured under 0% relative humidity. [b] PNP, 4-nitrophenol, can be used along with 4-nitroanisole (**3**) to calculate π_1^* and β_1 using oxygen indicators instead of the nitrogen indicators (**1** and **2**). Generally, however, these give incompatible results with the nitrogen indicators.[4,17,18]

Table II
Absorption Maxima for Dyes in Dried Liquid Solvent Models (λ_{max} in nm)

	1	2	3	4	PNP[a]
ethylbenzene	376	342	310	*b*	304
1-methyl-2-pyrrolidone	400	386	314	680	418
n-hexane	352	320	290	*b*	284
ethylene glycol monoacetate	394	368	310	532	312
1,3-dichlorobutane	388	378	308	672	304
ethyl acetate	382	356	304	754	304
methyl acetate	384	356	304	738	306
ethylene glycol	404	382	314	510	394
1,3-butanediol	396	380	310	544	402

[a] Footnote *a*, Table I. [b] These values were not determinable experimentally because Reichardt's dye (**4**) is not sufficiently soluble in these solvents.

Table III
Solvatochromic Parameters for Some Polymers and Model Solvents

polymer/solvent model	π_1^*	β_1	α_1	$E_T(30)$
PS/ethylbenzene	0.65/0.46	0.06/0.12	0.08/(0.00)[a]	42.2/33.9[b]
PVP/methylpyrrolidone	0.91/0.91	0.78/0.78	−0.12/−0.05	40.8/42.0
PIB/*n*-hexane	0.16/−0.06	0.04/0.04	0.33/(0.00)[a]	39.8/30.9[c]
PHEMA/ethylene glycol monoacetate	0.98/0.80	0.43/0.45	0.67/0.74	55.0/53.7
PVC/1,3-dichlorobutane	0.87/0.68	0.07/0.01	0.06/0.18	42.9/42.5
PC/---[d]	0.76/---	0.21/---	−0.03/---	40.3/---
PMMA/methyl acetate	0.76/0.61	0.38/0.35	0.24/0.09	44.0/38.7
PVAc/ethyl acetate	0.76/0.57	0.44/0.40	0.02/0.03	40.0/37.9
PE–PVAc (60:40)/---[d]	0.54/---	0.57/---	0.23/---	41.6/---
PVAl/1,3-butanediol	1.11/0.84	0.52/0.72	0.29/0.66	49.3/52.6
FPOL/---[d]	0.80/---	0.42/---	0.84/---	54.4/---

[a] Not determinable experimentally because the required indicator dye, Reichardt's dye (**4**), is not sufficiently soluble in these solvents. This is probably due to their lack of hydrogen bond acidity, and so we assume a zero value of α_1. [b] Literature value for toluene.[15] [c] Reference 15, p 365. [d] No suitable model available.

Table IV
Solvatochromic Data for DAN[16] in Various Liquid Solvents (Dried)[a]

solvent	λ_{max}, nm	ν_{max}, $\times 10^3$ cm^{-1}	π_1^*	β_1	α_1	$E_T(30)$
5. benzene	348	28.74	0.59	0.10	0.00	34.3
6. chlorobenzene	352	28.41	0.71	0.07	0.00	36.8
7. chloroform	352	28.41	0.58	0.00	0.44	39.1
8. pyridine	382	26.18	0.87	0.64	0.00	40.5
9. acetone	368	27.17	0.71	0.48	0.08	42.2
10. acetonitrile	372	26.88	0.75	0.37	0.19	45.6
11. dimethyl sulfoxide	398	25.13	1.00	0.76	0.00	45.1
12. 1,4-dioxane	352	28.41	0.55	0.37	0.00	36.0
13. methyl acetate	358	27.93	0.60	0.42	0.00	40.0
14. butyl acetate	354	28.25	0.50	0.45	0.00	38.5
15. nitromethane	380	26.32	0.85	0.25	0.22	46.3
16. 2-butanone	368	27.17	0.67	0.48	0.06	41.3
17. ethyl ether	343	29.15	0.27	0.47	0.00	34.5
18. ethanol	370	27.03	0.54	0.77	0.83	51.9
19. methanol	372	26.88	0.60	0.62	0.93	55.4
20. water	404	24.75	1.09	0.18	1.17	63.1
21. tetrahydrofuran	360	27.78	0.58	0.55	0.00	37.4
22. 1,1,1,3,3,3-hexafluoro-2-propanol	380	26.32	0.65	0.00	1.96	65.3
23. 2,2,2-trifluoroethanol	376	26.60	0.73	0.00	1.51	59.8
24. hexamethylphosphoramide	398	25.13	0.87	1.05	0.00	40.9

[a] The solvatochromic parameters are literature values.[15,18,23]

dye in the polymer, eq 8.[15] Here h is Planck's constant,

$$E_T(30) = hcN\nu_{max}(4) = 2.859\nu_{max}(4) \qquad (8)$$

c is the speed of light in a vacuum, and N is Avogadro's number.

Table I presents the UV–visible absorption data for thin films (about 10–15-μm thickness) of the 4 dyes **1**–**4** dissolved in the 11 polymers. Because spectra for several of the films were found to be highly dependent on atmospheric moisture, samples were dried under vacuum and heat in the presence of a desiccant (P_2O_5). Small temperature effects on the spectra were also noted, but they were shown to be inconsequential over the ambient temperature range of the laboratory.

Table II presents the UV–visible absorption data for dyes **1**–**4** dissolved in a series of liquid solvents that were chosen as models for the polymers. The models were chosen such that the structure of the model was as close as possible to the repeat unit of the polymer. Table III presents the calculated solvatochromic parameters for the 11 polymers and the related model compounds.

Table IV presents the absorption maxima of DAN in various liquid solvents with known α_1, β_1, π_1^*, and $E_T(30)$ values. Figures 1 and 2 are plots of the observed absorption maxima versus those calculated by the KAT and $E_T(30)$ methods, respectively. Table V lists the observed and calculated (using both methods) absorption maxima for DAN in various polymers.

Discussion

Comparison of Polymers with Monomeric Models. Examination of Table III shows that the solvatochromic parameters generally follow the trends that one would expect from experience with small molecules. For example, PVP has basic sites (significant β_1), PHEMA has acidic sites (significant α_1), FPOL has the highest α_1 of any of the polymers studied, and PS has a higher dipolarity/polarizability than PIB.

These qualitative trends are readily revealed by comparison with the solvatochromic parameters of the monomeric models. In most cases the monomeric liquid solvents serve as good models for the polymeric solid solvents. Of the 34 model solvatochromic parameters (π_1^*, β_1, and α_1) in Table III, only four differed from the polymer values by more than 0.2 (these are α_1 and π_1^* for PIB and PVAl).

It is interesting to note the low α_1 value for PVAl of 0.29 relative to the higher values of its model (1,3-butanediol has an α_1 of 0.66) and PHEMA and its model (ethylene glycol monoacetate), Table III, and relative to small-molecule alcohols (e.g., methanol has an α_1 of 0.93 and ethanol has a value of 0.83). Possibly this is the result of intermolecular hydrogen bonding in PVAl that reduces the effective hydrogen-bonding acidity of the polymer. A possible mechanism is as follows. As a solute approaches

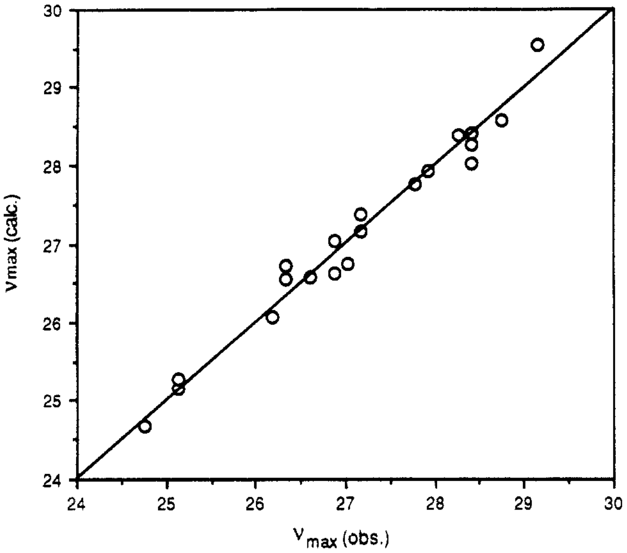


Figure 1. Plot of observed absorption maxima (ν_{max} in 10^3 cm^{-1}) versus those calculated by the KAT method (eq 9) for DAN[16] in liquid solvents.

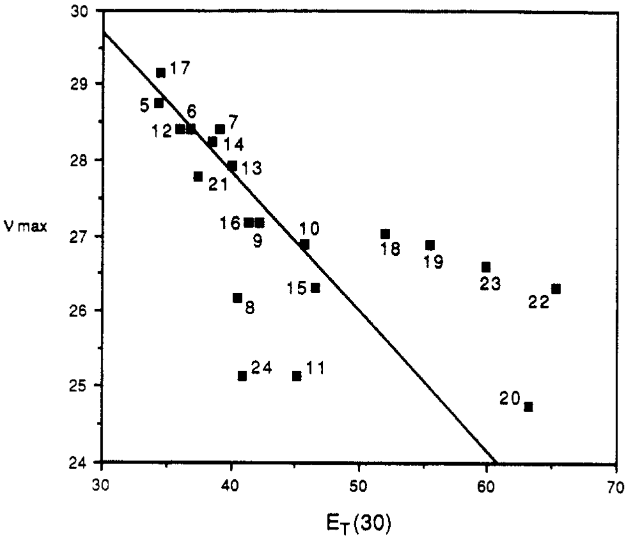


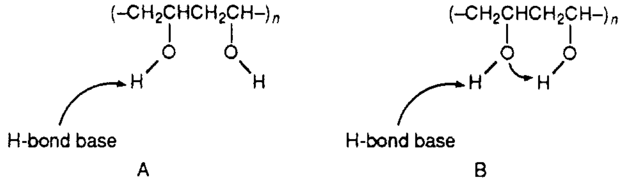
Figure 2. Plot of absorption maxima (ν_{max} in 10^3 cm^{-1}) versus E_T(30) for DAN[16] in liquid solvents.

Table V
Observed and Calculated Absorption Maxima for DAN[16] in Various Polymers

	obs value		calc by KAT (eq 9)		calc by E_T(30) (eq 12)	
polymer	ν_{max} $\times10^3$ cm^{-1}	λ_{max}, nm	ν_{max}, $\times10^3$ cm^{-1}	λ_{max}, nm	ν_{max}, $\times10^3$ cm^{-1}	λ_{max}, nm
PS	28.25	354	28.28	354	27.26	367
PVP	25.13	398	25.71	389	27.54	363
PHEMA	25.77	388	25.25	396	24.70	405
PVC	27.32	366	27.12	369	27.12	369
PMMA	27.17	368	26.92	371	26.90	372
PE–PVAc	27.93	358	27.71	361	27.38	365
PVAl	25.13	400	24.77	404	25.84	387

the chains of PVAl that are connected by intermolecular hydrogen bonds, it disturbs the hydrogen bond connecting the two hydroxyls on opposite chains and is left to interact with only one hydroxyl (A, Chart II), which acts as a solute hydrogen bond acid site (solute values of hydrogen bond acidity, $\alpha_2{}^H$, for hydroxylic molecules are typically about 0.3). This would not be expected to be the case if there was intramolecular hydrogen bonding in the PVAl chain at the solute site, because the solute interaction at the hydrogen bond acid site on the PVAl chain would not disrupt all intramolecular hydrogen bonds connected to the hydroxyl that the solute is interacting with (B); if this was the case, the polymer would exhibit a higher α_1 value than observed, closer to the solvent model 1,3-butanediol.

Chart II
Solute Base–Polymer Hydrogen Bond Interactions for PVAl



Similarly, the E_T(30) values for the solid polymers are generally within 10% of the values for the liquid models. The exceptions are PS, PIB, and PMMA, for which the E_T(30) values are somewhat higher than those for the models. This is discussed in the next section.

Thus it appears that carefully chosen liquid monomeric solvents can often provide reasonable estimates for the solvatochromic parameters of many polymers. On the other hand, it is important to note that good models do not exist for many complex polymers, such as fluoropolyol, which are made up of large complex monomers or widely differing comonomers.

Effects of Moisture and Other Impurities. The UV–visible absorptions for the polymer films were obtained for samples that were carefully dried because absorption maxima for several of the films (especially those containing Reichardt's dye) were very sensitive to atmospheric moisture. For example, the maximum for Reichardt's dye in PVAc shifted slowly (over a period of a few hours) from 714 nm (α_1 = 0.02) when dry to around 640 nm (α_1 = 0.28) upon exposure to ambient laboratory air. Similarly, Reichardt's dye in PMMA, PVP, and PC gave large shifts upon exposure to ambient air. The other dyes and films showed this effect to a smaller extent (shifts of <20 nm).

Apparently many of the films are highly permeable to water, and the water is sorbed by hydrogen bonding to basic sites in the polymer framework. These hydrogen-bonded water molecules then become acidic sites, which bind to the basic –O$^-$ site on Reichardt's dye, with the result that the polymer exhibits an enhanced α_1 (with an increased selectivity toward hydrogen bond basic solutes). We observed that this acidity-enhancing effect of atmospheric humidity could be reversed by repeating the drying procedure. Clearly, polymer characterization should be done under the atmospheric conditions to which the polymer will be exposed.[20]

Although α_1 changed significantly upon exposure of these polymers to water, β_1 and $\pi_1{}^*$ did not. Presumably this results because the dyes **1**–**3** are less sensitive to moisture than Reichardt's dye, and thus an insufficient amount of water is taken up by the polymer films to significantly alter their basicity and dipolarity/polarizability. However, it is important to note that other atmospheric contaminants can also dissolve in the polymer films and that these contaminants could possibly alter these other parameters as well. A more detailed study of the effects of humidity on the polymer films is currently underway, and the results will be described in a forthcoming publication.

Interestingly, PMMA, PE–PVAc, and PIB retain significant α_1 values even after exhaustive drying, although values near zero were expected. We suspect that the nonzero values for α_1 derive from some acid functionality associated with the polymer that is unrelated to dissolved water and that is unrelated to any property of the small model solvents, all of which give the expected near-zero values of α_1. Possibly there are acid groups in the polymer, or there could be some small acidic impurity in the polymer. These same factors could account for the larger than expected $E_T(30)$ values of PS, PIB, and PMMA. This result shows the power of the solvatochromic approach to reveal the true character of polymers, and again the danger of relying on monomeric models is revealed.

This result also points out an important difference between polymer and monomer characterizaton. Small molecules can be effectively purified, and one would expect all purified samples of any particular small molecule to have identical solvatochromic parameters. On the other hand, many polymers can be prepared by a variety of processes involving different initiators, reaction conditions, molecular weights, end groups, etc. As a consequence, it may turn out that there will be small, but possibly significant, differences between the solvatochromic parameters for what is supposedly the same polymer obtained from different sources. It would be erroneous to view this possible result as a weakness of solvatochromic characterization of polymers, since the method would, in fact, be revealing real differences between the materials that could well have important consequences for certain applications.

Use of the KAT Solvatochromic Parameters. As noted in the Introduction, the solvatochromic parameters and eq 1 can be used to predict a variety of polymer properties including solubility and permeability of solutes in polymers and miscibility of pairs of polymers. These phenomena will be considered in a later publication. Here we illustrate the utility of the parameters by applying eq 4, along with the α_1, β_1, and π_1^* values from Table III, to predict the absorption maxima of an important optical dye, *N*,*N*-dimethyl-3-acetamido-4-nitroaniline, DAN,[16] in several of the polymers we have characterized. This application is important for nonlinear optics, in particular, where polymer films containing nonlinear dyes are employed. The position of the absorption bands of a dye is of critical importance for the efficiency of some nonlinear processes (e.g., frequency doubling of laser radiation).[21] The types of dyes used are often highly solvatochromic; i.e., the position of their absorption bands is very sensitive to the solvent (liquid or solid polymer) in which they are placed. Clearly the ability to predict the position of the absorption bands of a particular dye in a certain polymer would be of great value. This goal can be attained in a logical fashion by taking advantage of the solvatochromic parameters of the polymers and dyes.

The first step in applying this concept is to characterize the solvatochromic parameters of the dye as a solute in a series of liquid solvents, i.e., to determine *a*, *b*, and *s* in eq 4, where SP is now the ν_{max} of DAN in each solvent. The absorption maximum of the solvatochromic band (the longest wavelength band) of DAN was determined in 20 liquid solvents with wide-ranging properties for which π_1^*, β_1, and α_1 are known (Table IV). The data were fit by multiple linear regression to eq 4 to determine the coefficients *a*, *b*, and *s*. The regression fit obtained is given by eq 9 and shown in Figure 1. The standard deviation

$$\begin{array}{lcccccccl} \nu_{max} & = & 31.870 & - & 5.231\pi_1^* & - & 1.941\beta_1 & - & 0.977\alpha_1 \quad (9) \\ \text{std dev} & & 0.214 & & 0.293 & & 0.203 & & 0.100 \\ \text{t test} & & 1.00 & & 1.00 & & 1.00 & & 1.00 \end{array}$$

$$n = 20 \quad r = 0.986 \quad \text{std dev} = 230\ \text{cm}^{-1}$$

of 230 cm^{-1} means that values of λ_{max} are predicted within about 3 nm, which is close to the instrument precision of ±2 nm. Note that eq 9 shows a significant dependence of the absorption maximum of DAN on both α_1 and β_1, as expected from the presence of both acidic and basic sites in the molecule. The strongest dependence, however, is clearly on π_1^*.

Table VI
Observed and Calculated λ_{max} (nm) for DAN in PHEMA, PVP, and Their Small-Molecule Solvent Models

solvent	λ_{obs}	λ_{calc} (eq 9)	λ_{calc} (eq 10)
PVP	398	389	
1-methyl-2-pyrrolidone	394	390	
PHEMA	388	396	386
ethylene glycol monoacetate	374	383	373

This equation, along with the values of π_1^*, β_1, and α_1 determined for the polymers, was used to calculate the values of ν_{max} (and λ_{max}) for DAN in several polymers, and the results were then compared to the experimentally observed values (Table V). For all polymers except PVP and PHEMA, the agreement between the calculated and observed values of λ_{max} was excellent; they agreed within 4 nm. In the cases of PVP and PHEMA, however, the agreement was not as good; the calculated value for PVP was 9 nm below the experimental value and that for PHEMA was 8 nm above the experimental value (see Table VI). In other words, the calculated energy gap between ground and excited states of DAN is wider than expected in PVP and narrower than expected in PHEMA.

The discrepency for PHEMA can be explained by assuming that site sorting is operating for this bifunctional polymer. The solvatochromic shifts of DAN in different solvents (as revealed in their UV–vis spectra) are primarily the result of excited-state interactions (note the negative coefficients in eq 9). Thus if we assume that site sorting is operating so that DAN interacts with PHEMA at the basic ester site only, the α_1 term will drop out of eq 9, and the ground–excited-state energy gap will widen, eq 10. Using this equation, we calculate a λ_{max} for DAN of 386

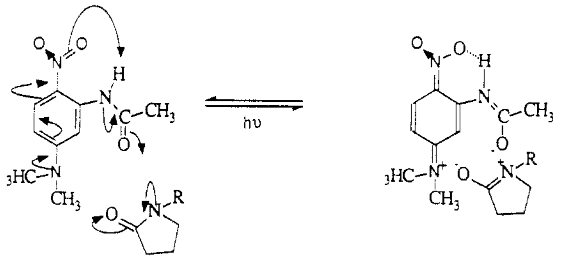
$$\nu_{max} = 31.870 - 5.231\pi_1^* - 1.941\beta_1 \qquad (10)$$

nm, which is very close to the observed value of 388 nm. On the other hand, if we assume that DAN interacts at the acidic hydroxyl site of the polymer, but not at a basic site, then the term in eq 9 for β_1 drops out, and λ_{max} is calculated to be 383 nm, 5 nm below the observed value. Thus, if we assume site sorting, with DAN being solvated only by the basic ester site of PHEMA, the calculated λ_{max} agrees well with experiment. Another possibility is that the hydroxyl in PHEMA acts toward DAN as a solute hydrogen bond acid/base site (cf. PVAl); if the solute α_2^H and β_2^H for ethanol (0.33 and 0.41, respectively) are substituted for the PHEMA α_1 and β_1 values in eq 9, then λ_{max} is calculated to be 390 nm, which is also very close to the observed λ_{max}. The model solvent for PHEMA, ethylene glycol monoacetate, exhibits similar behavior (see Table VI).

In the case of PVP (and its model, 1-methyl-2-pyrrolidone), the situation is reversed; i.e., the calculated λ_{max} is too short, and the calculated energy gap is too wide. We suggest that there is a special interaction that occurs between PVP or its model and the excited state of the DAN molecule that is not observed in other classes of common solvents. This might occur from the mechanism suggested in Scheme I in which there is a synergistic movement of charge density between the two molecules, giving rise to stabilization of the excited state.

E_T(30) Model. There is a large body of work showing that the Reichardt $E_T(30)$ solvatochromic scale of solvent

Scheme I
Proposed Mechanism for Charge Transfer between DAN and PVP



polarity (from eq 8) is effective at correlating a variety of solvent-dependent phenomena.[15] Thus, it is of interest, in analogy with the preceding section, to determine the ability of this model to predict the absorptions of DAN in polymer films.

The first step in this process is to determine the relationship between ν_{max} for DAN and $E_T(30)$, Table IV and Figure 2. As can be seen, the correlation is a poor one, with strong hydrogen bond bases giving a negative deviation and strong hydrogen bond acids giving a positive deviation from a line drawn through the more "normal" solvents. Least-squares regression of all the data gives eq 11, while regression of the "normal" solvents gives eq 12. These results indicate that the $E_T(30)$ scale is in general of less value than the more complex KAT solvatochromic model for predicting dye absorptions in liquid or solid solvents. However, once the empirical information of Figure 2 is in hand, it appears that *qualitative* predictions from $E_T(30)$ are possible because of the regularity of the deviations in Figure 2. Thus, one would expect that eq 12 (the "normal" solvent correlation) will accurately predict absorptions of DAN in polymers that do not contain strong hydrogen bond acid or hydrogen bond base groups. On the other hand, polymers with significant β_1 should give an observed λ_{max} that is smaller than that predicted, while polymers with significant α_1 should give an observed λ_{max} that is greater than that predicted.

ν_{max}	=	$-0.082E_T(30)$	+	30.74	(11)
std dev		0.025		1.13	
t test		0.996		1.00	

$r = 0.626$ std dev = 1010 cm^{-1}

ν_{max}	=	$-0.200E_T(30)$	+	35.70	(12)
std dev		0.020		0.878	
t test		1.00		1.00	

$r = 0.958$ std dev = 261 cm^{-1}

The predicted absorptions shown in Table V indicate that this qualitative prediction is correct in five of the seven examples studied. Among the polymers with low values of α_1 and β_1, the values for PVC, PMMA, and PE–PVAc are excellent while those for PS and PVAl are in error by more than 10 nm. As predicted, the observed λ_{max} for the high β_1 polymer PVP is too small and the observed λ_{max} for the high α_1 polymer PHEMA is too large.

Limitations. As noted above, it is important when making the solvatochromic measurements to control factors such as humidity and temperature (if wide ranges are expected). In addition to these restrictions, we have noted three other limitations of the KAT solvatochromic methodology.

First, the dyes must be soluble in the polymer. Otherwise aggregates of dye molecules are formed whose UV–visible spectra reveal nothing about properties of the polymers.

Second, the polymer and dye must be soluble in some volatile solvent to permit coating of the polymer onto the slides. It should be pointed out that spin coating is not essential to produce the polymer films; films of satisfactory quality can be obtained by simply coating the solutions of the polymers onto the slides and allowing the solvent to evaporate. Spin coating, however, has the advantage that it produces films of better quality and reproducibility and it gives greater control over thickness. Alternatively, we have attempted to prepare thin films from monomers by dissolving dyes in the monomers and initiating polymerization. Not surprisingly, this process usually destroys the chemical integrity of the dye molecules (this is especially the case with Reichardt's dye). Thus it appears, at this point, that direct application of the solvatochromic method to polymers is restricted to those polymers that are capable of solution in solvents that also dissolve dye molecules 1–4. A possible extension of the method, which we have not examined, would be to diffuse dyes into swollen, but insoluble, polymer matrices.

Third, as with liquid solvents, the method may be limited in its application to polymers with several different functional groups because of site-sorting or solvent-sorting interactions. Elucidating these types of interactions will be the subject of future work in our laboratory.

Conclusions

In summary, we have shown that it is possible to determine the KAT parameters π_1^*, β_1, and α_1 and the Reichardt $E_T(30)$ values for solid polymers by measuring the UV–visible absorption spectra of a series of four dyes dissolved in the polymers. The parameters obtained make chemical sense in that they are similar to those found for liquid solvent models. The parameters are also quite sensitive to the presence of water in the polymers, thus demonstrating that polymer solubility and sorption properties will in many cases be dependent upon the composition of the atmosphere to which the polymers are exposed. Although we have not conducted the experiments, we expect that this applies as well to atmospheric constituents other than water.

The polymer solvatochromic parameters should prove useful in predicting and understanding the solubility and sorption properties for interaction of polymers with gaseous, liquid, and solid solutes and with bulk liquid solvents. The usefulness of the polymer KAT solvatochromic parameters for predicting the absorption maxima of dyes dissolved in polymers has been demonstrated. The $E_T(30)$ model is of limited utility for the particular applications considered here.

Experimental Section

All polymers and solvents were purchased from either Aldrich or Scientific Polymer Products and used without further purification (except where noted), with the exception of fluoropolyol, which was supplied by Dr. Jay Grate at the Naval Research Laboratory in Washington, DC. 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 Solutions. Polymer solutions were prepared by dissolving a weighed amount of the pure solid polymer in the indicated solvent (Table VII). The dyes required to determine the solvatochromic parameters were then dissolved in these solutions to give 10 mL of each polymer/dye solution. *N*,*N*-Dimethyl-4-nitroaniline (**1**) was dissolved at a concentration of 0.02 M (0.025 g in 10 mL), 4-nitroaniline (**2**) at 0.01 M (0.017 g

Table VII
Solvents and Concentrations Used for Polymer Solutions

polymer	mol wt	g of polym in 100 mL of solv	solvent
PS[a]	250 000	20	2-butanone
PVP[b]	360 000	20	methanol
PIB[b]	420 000	15	chloroform
PHEMA[b]	300 000	30	methanol
PVC[a]	100 000	10	2-butanone
PC[a]	20 000–25 000	15	1,2-dichloroethane
PMMA[a]	35 000	20	acetone
PVAc[b]	102 000	20	acetone
PE-PVAc (60:40)[a]	100 000	20	dichloromethane
PVAl[a]	11 000–31 000	5	water[c]
FPOL	unknown	5	chloroform

[a] Purchased from Aldrich. [b] Purchased from Scientific Polymer Products. [c] Reichardt's dye (4) is not soluble in water, so a warm solution of 2:1 (v/v) ethylene glycol/10% aqueous (w/v) PVAl was used to dissolve this dye.

in 10 mL), 4-nitroanisole (**3**) at 0.02 M (0.030 g in 10 mL), Reichardt's dye (**4**) at 0.01 M (0.055 g in 10 mL), and 4-nitrophenol at 0.02 M (0.025 g in 10 mL). In the case of Reichardt's dye, stirring overnight or gentle heating was sometimes necessary to achieve complete solution. In the case of poly(vinyl alcohol) (PVAl), the dyes **1–3** and 4-nitrophenol were found to be sufficiently soluble only in warm water; thus coating of the slides had to be done with warm solutions. Reichardt's dye (**4**) was insoluble even in hot water, so in this case the slides were coated with a warm solution of the dye in 2:1 (v/v) ethylene glycol/10% (w/v) aqueous PVAl.

Spin Coating. Polymer films with a thickness of about 10–15 μm were desired, except for those containing Reichardt's dye, which, because it is more weakly absorbing than the other dyes, required films of about 20–30-μm thickness. To optimize the spin-coating conditions (polymer concentration, spinning rate), films of the polymers containing no dye were first prepared. The concentrations of the polymer solutions are listed in Table VII. Once the conditions had been worked out, three films of each polymer containing dye were prepared on quartz slides with dimensions 0.8–0.85 cm in width and 2.4–2.5 cm in length and 1.0–1.5 mm thickness. In the case of fluoropolyol (FPOL), there was insufficient material to permit spin coating, so these films were prepared by simply coating the slides with the solutions and allowing the solvent (chloroform) to evaporate, leaving films that were about 2 μm thick. The concentrations of the dyes were increased accordingly to give measurable absorbances. This same technique was also used for PVAl because spin coating from hot solutions presented difficulty; in this case the films obtained were about 10–15 μm thick (hence, the dye concentrations did not have to be altered). The PVAl slides containing Reichardt's dye were baked at 120 °C for 1 h to evaporate ethylene glycol.

Drying of Polymer Films. It is critical that solvent or water contamination of the films does not occur. All films were exhaustively dried under vacuum and heat (110 °C, refluxing toluene) for 30 min in an Abderholden drying pistol with P_2O_5 as the drying agent. In the case of the films of Reichardt's dye in poly(vinyl chloride) and polycarbonate, no heat was applied because it caused an apparent reaction between the dye and polymers (evident by fading of the dye in the films). Also, in the case of the ethylene-vinyl acetate copolymer (PE-PVAc), no heat was used except for the film containing Reichardt's dye because the other dyes showed absorption bands that became much weaker after drying with heat. Possibly the interaction between the dyes and the polymer is so weak that under vacuum and heat the dyes can volatilize out of the polymer films.

Determination of UV-Vis Spectra. The slides coated with the polymer films were placed in a 1-cm path length quartz cuvette, and UV-vis spectra were obtained in the range 250–800 nm by using an empty cuvette as the reference. The concentrations of the dyes, specified above, were chosen to give absorbances in the range 0.2–2.0 (based on the known solution values of the extinction coefficients). A spectrum was obtained on each polymer film before it was dried to make sure the absorption was in the preferred range. The film was then left in the cuvette, the cuvette was placed in an Abderholden drying pistol and the film was dried as described above. After drying, the Abderholden was filled with dry N_2 (passed through a $CaCl_2$ drying tube); the cuvette was removed immediately and capped with a septum, and the UV-vis spectrum was again obtained. The values of π_1^*, β_1, and α_1 were then calculated from eqs 5–7, and the values of $E_T(30)$ were calculated from eq 8. The results are shown in Tables I and III.

Determination of π_1^*, β_1, and α_1 for Liquid Solvent Models. For the solvents chosen as models for the polymers, values of π_1^*, β_1, and α_1 were determined by using the same dyes that were used to characterize the polymers. Solutions of each dye were prepared and dried over molecular sieves, UV-vis spectra were obtained, and π_1^*, β_1, α_1, and $E_T(30)$ were calculated using eqs 5–8. In the case of ethylene glycol monoacetate, the solvent was placed over solid $NaHCO_3$ for 12 h to remove any trace of acetic acid. The results are shown in Tables II and III.

Drying of dye solutions (in a sealed cuvette for about 3 h) with activated molecular sieves (3 or 4 Å, baked at 300 °C) is complicated by adsorption of dyes onto the sieves, with the result that dye absorptions are gradually reduced during drying. It is useful during this process to observe the *position* of the absorption band (i.e., λ_{max}). If λ_{max} shifts to a different wavelength as the absorbance decreases, then water is still being removed. In contrast, if λ_{max} remains unchanged as the absorbance decreases, then one is simply observing the process of dye being adsorbed onto the sieves.

Characterization of DAN. Solutions of DAN were prepared in 20 solvents and dried over molecular sieves (except for water and HFIP), UV-vis spectra were obtained (Table IV), and the values of s, a, and b were determined by a multiple linear regression fit of the data (ν_{max} of the longest wavelength band) to eq 4. The ν_{max} values of DAN in each solvent were also correlated by means of a single linear regression with the $E_T(30)$ values of the solvents, eqs 11 and 12 and Figure 2.

DAN spectra show three distinct absorption bands in the region 250–800 nm. It is important when obtaining spectra to avoid those solvents in which the long-wavelength solvatochromic band overlaps appreciably with the adjacent band (weak but present in all solvents), since in these cases the solvatochromic band may be obscurred or λ_{max} shifted by an indeterminant amount. For example, this was the case with DAN in hexane, cyclohexane, and dichloromethane, and these solvents were therefore not included in the correlation.

Thin films of DAN in PS, PVP, PHEMA, PVC, PMMA, PE-PVAc, and PVAl were prepared and dried, and UV-vis spectra were obtained for these films as described above. The values of ν_{max} and λ_{max} for DAN in each polymer were then calculated using eqs 9 and 12, and the results compared to the experimental values (see Table V and Discussion).

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Registry No. **1**, 100-23-2; **2**, 100-01-6; **3**, 100-17-4; **4**, 10081-39-7; DAN, 129195-09-1; PMMA, 9011-14-7; PS, 9003-53-6; PVP, 9003-39-8; PIB, 9003-27-4; PVAc, 9003-20-7; PVC, 9002-86-2; PC (SRU), 25037-45-0; PC (copolymer), 24936-68-3; PVAl, 9002-89-5; PE–PVAc, 24937-78-8; PHEMA, 25249-16-5; ethylbenzene, 100-41-4; methylpyrrolidone, 30207-69-3; *n*-hexane, 110-54-3; ethylene glycol, 542-59-6; 1,3-dichlorobutane, 1190-22-3; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; 1,3-butanediol, 107-88-0.