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# Solvatochromic Characterization of Organic−Inorganic Polymer Hybrids with Pyridinium *N*-Phenolate Betaine Dyes

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ABSTRACT: We have estimated the local polarity in organic−inorganic polymer hybrids by employing solvatochromic pyridinium *N*-phenolate betaine dyes. Solvatochromic polymer was prepared by introducing Reichardt's betaine dye in the side chain of poly(2-methyl-2-oxazoline), and the model compound for the dye unit was also prepared. Polymer hybrids were prepared from these compounds and mixtures of various proportions of tetramethoxysilane (TMOS) and methyltrimethoxysilane (MeTMOS). The electronic absorption spectra were measured by the diffuse reflectance method. It was found that the local polarity in the polymer hybrids was affected by both the TMOS:MeTMOS ratio and the presence of the organic polymer. In addition, it was suggested that the dye molecules are preferentially surrounded by the organic polymer rather than the siloxane network in the polymer hybrids.

## Introduction

Sol−gel-derived organic−inorganic nanocomposites have received a great amount of scientific and technological interests during the past 2 decades.[1−5] Ambient processing condition of the sol−gel technique enables one to construct nanocomposites of organic and inorganic components.[6] Several types of preparation methods have been proposed for the organic−inorganic nanocomposites. Organically modified silica gels (ormocers) were prepared by the sol−gel reaction of alkoxysilanes having organic residues (e.g., methyltrimethoxysilane or phenyltrimethoxysilane).[7,8] Alkoxysilanes having a polymerizable functional group such as a methacryl group can polymerize with both organic monomers such as methyl methacrylate (MMA) and inorganic precursors, resulting in a hybrid material where organic polymer and inorganic network are linked covalently.[7,8] Impregnation of MMA to the porous silica gel and subsequent radical polymerization of MMA afford another kind of organic−inorganic composite matrix.[9] Organic polymers coexist in the sol−gel reaction of alkoxysilanes to construct organic−inorganic hybrid matrixes.[10,11]

It is of great interest to utilize these nanocomposites as host media for numerous organic, organometallic, and biological molecules.[12−17] This approach has been applied extensively for the design and synthesis of a wide range of novel materials in the fields of photonics (solid-state dye lasers,[18−20] nonlinear optics,[21−23] optical storage,[24] optical switches[25]), sensors,[26,27] and biological catalysts.[28] Probing the microenvironment of the entrapped molecules in the nanocomposites is another area of interest.[15,29−35] The nature of the local environment around the entrapped molecule is usually decisive in achieving the desired property. It is necessary to understand the microenvironment around the doped molecules to predict and design the property of the molecules and the resulting property of the materials.

Solvatochromic techniques for characterizing the local polarity around the dye have been developed.[36−38] The techniques are based on the solvent-dependent shifts of absorption band of a dye used as a probe for the solvation properties of a given medium. Polarity is one of the most important properties of such materials, as the property of the doped molecule are intrinsically affected by their surroundings. Here, "solvent polarity" is the overall solvation capability of the solvents.[37] Reichardt's betaine dye (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate) is a well-known solvatochromic dye and is frequently used to determine the polarity of the medium experimentally.[36,37] It exhibits a quite large negative solvatochromism, and the polarity of the medium is estimated by the molar electronic transition energy of a dye, $E_T$, as defined by eq 1.

$$E_T\ (\text{kcal mol}^{-1}) = hcN_A\nu_{\max} = 28\,591/\lambda_{\max}\ (\text{nm}) \quad (1)$$

Here $h$ is Plank's constant, $c$ is the speed of light in a vacuum, $N_A$ is Avogadro's number, and $\nu_{\max}$ and $\lambda_{\max}$ are the frequency and the wavelength, respectively, of the absorption maximum of the intramolecular charge-transfer band of the dye. A high $E_T$ value corresponds to high solvent polarity. The $E_T$ value for Reichardt's betaine dye has been utilized as an empirical scale for solvent polarity and called the $E_T(30)$ scale. This scale was also utilized to investigate the polarity of solid matrixes such as organic polymers or sol−gel glass.[32,39]

We have been investigating the organic−inorganic polymer hybrids, which are the molecular composite materials of organic polymers and a three-dimensional siloxane network.[10,11] They are prepared by the sol−gel reaction of alkoxysilanes in the presence of organic polymers such as poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone). The hydrogen-bonding interactions between amide groups of the organic polymers and silanol groups remaining in the siloxane network prevent the aggregation of the organic polymer during the sol−gel reaction and induce the molecular-level homogeneity.

In the present study, the local polarity of the microenvironment in the organic−inorganic polymer hybrids was investigated by utilizing the solvatochromic method. The solvatochromic polymer was prepared by incorporating Reichardt's betaine dye in the side chain of poly(2-methyl-2-oxazoline) (**9** in Scheme 1), and the model compound for the dye unit was also synthesized

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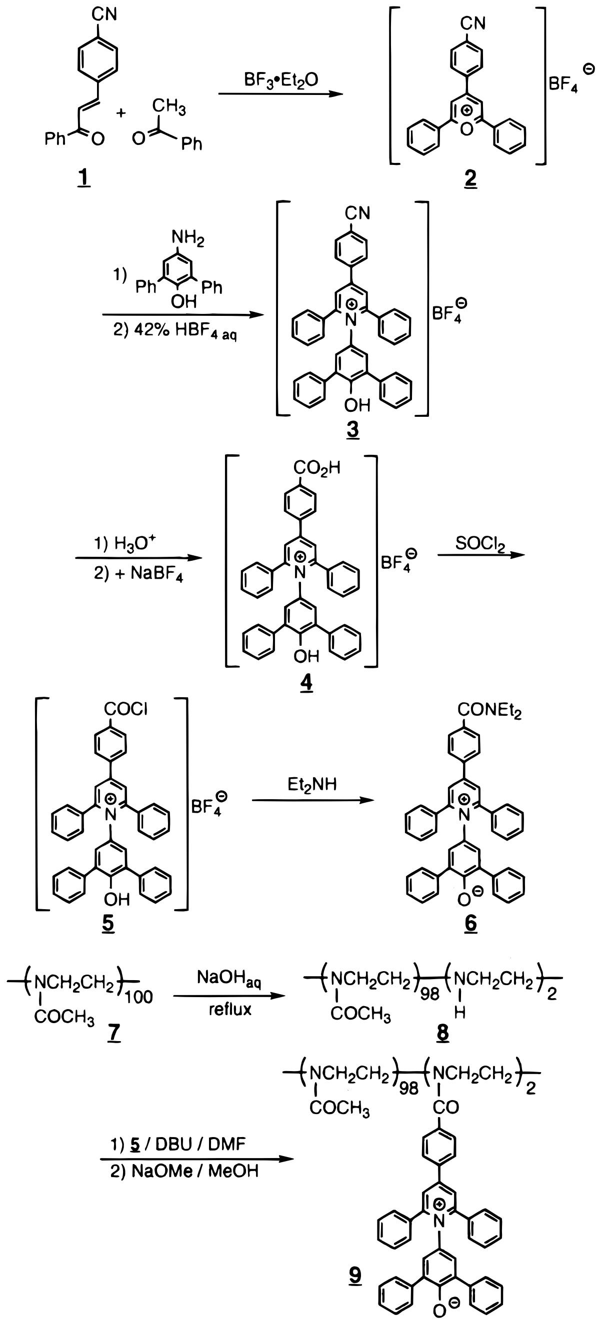
**Scheme 1. Synthesis of 9 and 6**



(**6** in Scheme 1). They coexist in the sol−gel reaction of TMOS and MeTMOS. The local polarity was estimated and compared with each other.

## Experimental Section

**Materials.** Preparation of poly(2-methyl-2-oxazoline) (**7**) and partial hydrolysis of amide groups of **7** to obtain **8** were reported previously.[40] Distilled reagents were stored under nitrogen atmosphere. Acetophenone and boron trifluoride diethyl etherate were distilled under reduced pressure. Chloroform was dried and distilled from CaH$_2$. Acetone was dried and distilled from K$_2$CO$_3$. Diethylamine was distilled. DMF was dried and distilled from MgSO$_4$ under reduced pressure. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was distilled under reduced pressure. 4-Cyanobenzaldehyde, 4-amino-2,6-diphenylphenol, 42% aqueous tetrafluoroboric acid, sodium tetrafluoroborate, concentrated aqueous hydrochloric acid, glacial acetic acid, thionyl chloride, and sodium methoxide were used as received. Tetramethoxysilane (TMOS) and methyltrimethoxysilane (MeTMOS) were distilled.

**Measurements.** $^1$H NMR spectra were recorded on a 270 MHz JEOL-JNM-GX270 NMR spectrometer. $^{13}$C NMR spectra were recorded on a 67.5 MHz JEOL-JNM-GX270 NMR spectrometer. IR spectra were obtained on a Perkin-Elmer 1600 infrared spectrometer. UV/vis/NIR absorption spectra of solutions and films were obtained on a JASCO V-530 spectrophotometer. Diffuse reflectance UV/vis/NIR absorption spectra of polymer hybrids were obtained on a Perkin-Elmer UV/vis/NIR spectrometer Lambda 19 with an attached Labsphere RSA-PE−19 reflectance spectroscopy accessory. Thermogravimetric analysis (TGA) was performed on a Shimadzu TG-30, TGC-30 with the heating rate of 10 °C min$^{-1}$ up to 950 °C under air. Nitrogen adsorption porosimetry was conducted on a BEL Japan Inc. The powdered polymer hybrid was calcined at 600 °C in air for 24 h to remove organic components. The resulting porous silica was then dried at 200 °C for 2 h under reduced pressure before the porosimetry measurement. The surface area was calculated with the Brunauer−Emmett−Teller (BET) equation in the range of 0.05−0.30 ($p/p_0$), and the pore size distribution was calculated by the Barrett−Joyner−Halenda (BJH) method.

**3-(4-Cyanophenyl)-1-phenyl-2-propen-1-one (1).** Compound **1** was prepared according to the literature.[41] Yield after recrystallization from ethanol was 75%.

**4-(4-Cyanophenyl)-2,6-diphenylpyrylium tetrafluoroborate (2).** To a solution of **1** (9.54 g, 40.9 mmol) and acetophenone (2.45 g, 20.4 mmol)[42] in chloroform (50 mL) was added BF$_3$·OEt$_2$ (21 mL) under nitrogen atmosphere. The mixture was stirred at 60 °C for 50 h. Diethyl ether (50 mL) was added, and the precipitate was filtered and dried. The crude product was recrystallized from methanol to give 2.96 g (35%) of **2** as a yellow crystal. $^1$H NMR, IR, and melting point (mp) were in agreement with the data in the literature.[41] $^{13}$C NMR (acetone-$d_6$): 118.06, 118.64, 118.82, 130.46, 130.59, 131.50, 131.72, 134.83, 137.02, 138.58, 166.20, 177.35.

**4-(4-Cyanophenyl)-1-(4-hydroxy-3,5-diphenylphenyl)-2,6-diphenylpyridinium tetrafluoroborate (3).** Compound **3** was prepared according to the literature.[41] Yield after recrystallization from 2-propanol was 76%.

**4-(4-Carboxyphenyl)-1-(4-hydroxy-3,5-diphenylphenyl)-2,6-diphenylpyridinium tetrafluoroborate (4).** The procedure in the literature[41] was slightly modified. Compound **3** (1.14 g, 1.71 mmol) in a mixture of concentrated hydrochloric acid (100 mL), glacial acetic acid (60 mL), and water (33 mL) was refluxed for 90 min. After the solution was cooled to room temperature, 30% aqueous NaBF$_4$ (75 mL) was added and left overnight in a refrigerator. The precipitate was filtered, washed well with water, recrystallized from water−methanol, and dried at 60 °C under reduced pressure. Compound **4** was obtained as a yellow crystal (76%). $^1$H NMR, IR, and mp were in agreement with the data in the literature.[41]

**2,6-Diphenyl-4-{[4-(4-*N*,*N*-diethylcarbamoylphenyl)-2,6-diphenyl]-*N*-pyridino} phenolate (6).** Compound **4** (144 mg, 0.21 mmol) was refluxed with thionyl chloride (5 mL) for 30 min, and then excess thionyl chloride was removed by evaporation. Acyl chloride **5** was used in the next step without further purification. Compound **5** was dissolved in dried acetone (5 mL) under nitrogen atmosphere, and diethylamine (74 mg, 1.0 mmol) was added dropwise with stirring. The resulting deep purple mixture was stirred at room temperature for 30 min before the solvent was removed by evaporation. The remaining solid was washed well with water and dried at 80 °C under reduced pressure. Dye molecule **6** was obtained as a deep green solid. Yield: 100 mg (0.15 mmol, 75%). $^1$H NMR (CD$_3$OD): $\delta$ 1.15 and 1.28 (broad peaks, 6H, CH$_3$), 3.33 and 3.58 (broad peaks, 4H, CH$_2$), 6.82 (s, 2H, 3,5-positions of phenolate), 7.08−7.58 (m, 20H, Ph), 7.63 and 8.21 (AB system, $J_{AB}$ = 8.3 Hz, 4H, aromatic protons of 4-carbamoylphenyl ring), 8.47 (s, 2H, aromatic protons of pyridinium ring). $^{13}$C NMR (CD$_3$OD): $\delta$ 13.84 and 15.19 (CH$_3$), 41.73 and 45.69 (CH$_2$), 127.82, 128.02, 128.34, 128.63, 129.48, 129.57, 130.41, 130.73, 131.27, 131.78, 132.01, 133.59, 136.18, 137.24, 141.41, 142.36, 157.15, 159.63, 162.11, 172.98 (CO). IR (KBr): 1618 cm$^{-1}$ ($\nu_{CO}$). Elem. Anal.: calcd C 80.69, H 5.89, N 4.30; found: C 80.69, H 5.68, N 4.30.

**Reichardt's Dye-Modified Poly(2-methyl-2-oxazoline) (9).** Compound **4** (146 mg, 0.21 mmol) was refluxed with thionyl chloride (5 mL) for 30 min, and then excess thionyl chloride was removed by evaporation. Acyl chloride **5** was used in the next step without further purification. Acyl chloride **5** and 2 mol %-hydrolyzed poly(2-methyl-2-oxazoline) (**8**, 470 mg, 0.10 mmol NH) were dissolved in DMF (10 mL) under nitrogen atmosphere, and DBU (15 mg, 0.10 mmol) was added to trap HCl gas. The mixture was stirred at room temperature overnight. The polymer was isolated by reprecipitation into diethyl ether and further purified by reprecipitation from methanol into diethyl ether (two times). The resulting precursor polymer was dissolved in methanol (10 mL), and sodium methoxide (18 mg, 0.3 mmol) in methanol (5 mL) was added. The solution turned deep purple and was stirred for 10 min. The polymer was isolated by reprecipitation from methanol into diethyl ether (four times) and freeze-dried with benzene. Yield: 443 mg (92%). Quantitative introduction of the chromophore on the polymer chain and complete conversion to phenolate by the treatment with sodium methoxide was confirmed by $^1$H NMR as well as electronic absorption spectroscopies. In the $^1$H NMR spectrum of **9** in $CD_3OD$, the methylene protons next to secondary amine groups in **8** disappeared, and peaks of aromatic protons corresponding to the chromophore appeared in the same position of **6**. Solvatochromic behavior of **9** in various solvents is discussed later.

**Preparation of Polymer Hybrids and Sol−Gel Glasses from Solvatochromic Compounds.** In a typical experiment, a mixture of 100 mg of **9**, 0.20 mL of TMOS, 0.19 mL of MeTMOS (molar ratio of 5:5), and 2 mL of methanol was sonicated for 10 min and then 0.17 mL of water was added, followed by sonication for an additional 10 min. The mixture was placed in a polypropylene mold covered with a paper towel and left in air at room temperature for 5 days and then at 60 °C for 2 days. The obtained solid was ground in a mortar, and the resulting powder was heated at 120 °C for 12 h to complete the sol−gel reaction. The polymer hybrids from **6** and polyoxazoline **7** were prepared in the same way as above, but employing 100 mg of polyoxazoline **7** and 13.6 mg of **6** instead of **9**. The **6**-doped sol−gel glasses were prepared similarly, but without polymer.

**Electronic Absorption Spectra.** All of the solvents for measurement of absorption spectra were dried and distilled in traditional methods according to the literature.[43] The concentration of the dye was set to be ca. $3 \times 10^{-4}$ M to acquire absorbances of the intramolecular charge-transfer band ≈ 1. A film of **9** was prepared by casting methanol solution onto a quartz substrate, followed by drying in vacuo at 110 °C for 3 h. A film of **6**-doped polyoxazoline was prepared by casting methanol solution (3 mg of **6** and 100 mg of polymer in 0.5 mL of methanol) onto a quartz substrate followed by drying in vacuo at 110 °C for 3 h. The spectra of the films were obtained by using a clean quartz substrate of the same thickness as the reference. The diffuse reflectance absorption spectra of the powdered polymer hybrids were obtained by using $MgO_2$ powder as the reference. The powders of polymer hybrids were dried in vacuo at 120 °C just before the measurement.

## Results and Discussion

Solvatochromic compounds **6** and **9** were prepared according to Scheme 1. The degree of introduction of the dye into the polymer was calculated to be 2 mol % from the $^1$H NMR spectrum, which was in good agreement with the degree of hydrolysis of the precursor **8**. Quantitative introduction of the chromophore on the polymer chain was also confirmed by the disappearance of methylene protons adjacent to secondary amine group in **9**. Aromatic peaks of **9** corresponded well with those of **6**, indicating that the betaine dye was actually formed in the side chain of the polymer.

**Table 1. $E_T$ Values[a] of 6, 9, and Reichardt's Dye in Various Solvents**

| solvent | 6 | 9 | Reichardt's dye[b] |
|---|---|---|---|
| water | | 61.2 | 63.1 |
| methanol | 53.8 | 54.7 | 55.4 |
| ethanol | 50.6 | | 51.9 |
| 2-propanol | 46.8 | 48.2 | 48.4 |
| acetonitrile | 44.3 | | 45.6 |
| DMSO | 43.9 | | 45.1 |
| DMF | 42.2 | 43.5 | 43.2 |
| DMAc | 41.6 | | 42.9 |
| acetone | 41.7 | | 42.2 |
| $ClCH_2CH_2Cl$ | 40.0 | | 41.3 |
| $CH_2Cl_2$ | 39.1 | | 40.7 |
| chloroform | 38.8 | | 39.1 |
| THF | 36.6 | | 37.4 |

[a] In kilocalories per mole. [b] From Reichardt.[37]

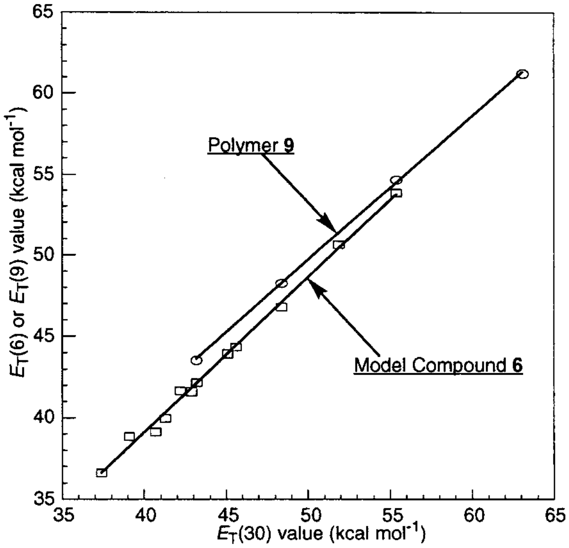


**Figure 1.** Correlations between the $E_T$ values of **6** or **9** and those of Reichardt's dye[37] in various solvents.

The electronic absorption spectra of **6** were observed in various solvents. The absorption maximum wavelength ($\lambda_{max}$) of the intramolecular charge-transfer band shifted from 781 nm (in THF) to 531 nm (in methanol). The polarity parameter $E_T$ values in each solvents are listed in Table 1. Table 1 also includes $E_T$ values of **9** and Reichardt's dye.[37] Because of the low solubility of **9** especially in nonpolar solvents, only four solvents were examined for **9**. Linear correlations between $E_T$ values of Reichardt's dye and those of **6** or **9** were found to be excellent (Figure 1).

$$E_T(\mathbf{6}) = 0.908 + 0.954E_T(30); \quad \text{correlation coefficient } |r| = 0.998$$

$$E_T(\mathbf{9}) = 5.042 + 0.892E_T(30); \quad \text{correlation coefficient } |r| = 1.000$$

The slopes of the correlation functions indicate slightly lower but comparable solvatochromic sensitivities of these compounds with Reichardt's dye.

The organic−inorganic polymer hybrids were prepared from **9** with mixtures of various proportions of TMOS and MeTMOS (Table 2). No acid catalyst was used in this study since the protonated phenol form of the chromophore showed no solvatochromism. The polymer hybrids from **6**, the polyoxazoline **7** and TMOS/MeTMOS mixture, and the **6**-doped TMOS/MeTMOS sol−gel glasses were also prepared. Transparent and homogeneous polymer hybrids were obtained with the

**Table 2. Results of Preparation and $E_T$ Values of Polymer Hybrids and Sol−Gel Glasses from 9 and 6**

| | **9** | | | **6** + polyoxazoline | | **6** | Reichardt's dye[b] |
|---|---|---|---|---|---|---|---|
| TMOS:MeTMOS (molar ratio) | appearance | ceram. yield[a] (%) | $E_T$(**9**) (kcal mol$^{-1}$) | ceram. yield[a] (%) | $E_T$(**6**) (kcal mol$^{-1}$) | $E_T$(**6**) (kcal mol$^{-1}$) | $E_T$(30) (kcal mol$^{-1}$) |
| 5:5 | transparent | 98 | 47.1 | 83 | 45.9 | 50.5 | 47.0 |
| 6:4 | transparent | 97 | 47.4 | 88 | 46.1 | 53.6 | 49.3 |
| 7:3 | transparent | 98 | 47.8 | 88 | 46.4 | 53.8 | 50.2 |
| 8:2 | transparent | 101 | 48.5 | 90 | 46.9 | 56.2 | 54.1 |

[a] Ceramics yields = (weight percent of ceramics in polymer hybrids observed by TGA)/(calculated value of weight percent of ceramics). [b] From Rottman et al.[32]

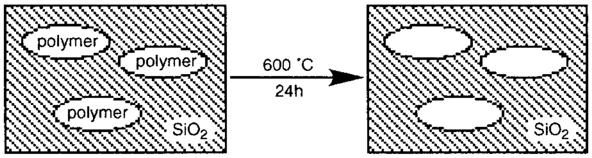
**Table 3. Porosity of Calcined Polymer Hybrids[a]**

| TMOS:MeTMOS (molar ratio) | $S_{BET}$[b] (m$^2$ g$^{-1}$) | $R_{peak}$[c] (nm) |
|---|---|---|
| 8:2 | 222 | 1.8 |
| 7:3 | 218 | 1.9 |
| 6:4 | 205 | 1.8 |
| 5:5 | 179 | 1.8 |

[a] The porous silica was obtained by charring the polymer hybrid at 600 °C for 24 h. [b] Surface area calculated by BET method. [c] Pore radius calculated by BJH method from desorption branch.

molar ratio of TMOS:MeTMOS from 8:2 to 5:5. The quantitative progress of the sol−gel reaction of TMOS and MeTMOS was confirmed by TGA of the obtained polymer hybrids. The dispersity of organic polymers in the polymer hybrids was evaluated by nitrogen adsorption porosimetry. The polymer hybrids were calcined at 600 °C for 24 h to achieve complete removal of organic components (Scheme 2). The siloxane lattice is so rigid that it would not be affected at this temperature. Therefore, the size of the remaining pores was expected to be comparable to the size of the domain of organic polymer. Surface areas as well as pore radii evaluated by nitrogen adsorption porosimetry are listed in Table 3. All of the porous silica gels prepared from the polymer hybrids had a surface area of ca. 200 m$^2$ g$^{-1}$ and the sharp pore size distributions that peaked at 1.8−1.9 nm. These results suggest the nanolevel dispersion of the organic polymer in the polymer hybrids.

**Scheme 2. Formation of Porous Silica from the Polymer Hybrid by Calcination**



The electronic absorption spectra of the polymer hybrids and the sol−gel glasses were observed by diffuse reflectance absorption spectroscopy. Representative spectra for **9**/TMOS/MeTMOS and **6**/**7**/TMOS/MeTMOS were shown in Figure 2. The absorption bands in the polymer hybrids were found to be somewhat broader than those in methanol solution, indicating the heterogeneity of matrix in the solid polymer hybrid compared with the solution phase. However, as suggested from the results of nitrogen adsorption porosimetry, the organic polymers were dispersed in the range of a few nanometers. The polarity of the matrixes could be estimated from the maximum wavelength of the absorption. The $E_T$ values are collected in Table 2. It was found that the $E_T$ values became larger with higher TMOS ratios in all cases and were linearly correlated with the relative amounts of TMOS (Figure 3). The linear correlations ($|r| > 0.985$) denote a homogeneous polymerization of TMOS and MeTMOS.

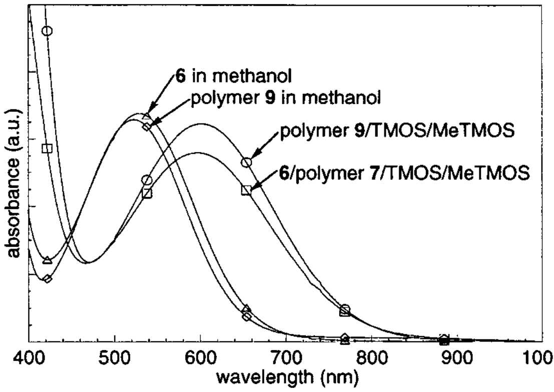


**Figure 2.** Absorption spectra for the following: circle, **9**/TMOS:MeTMOS(7:3) polymer hybrid; square, **6**/**7**/TMOS:MeTMOS-(7:3) polymer hybrid; diamond, **9** in methanol; and triangle, **6** in methanol.

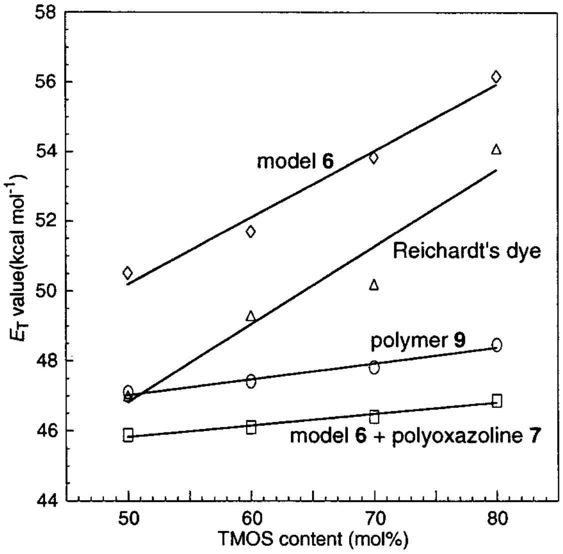


**Figure 3.** Matrix polarity as a function of the molar percent of TMOS: diamonds, **6**-doped sol−gel glasses; triangles, Reichardt's dye-doped sol−gel glasses;[32] circles, **9**/TMOS:MeTMOS(7:3) polymer hybrid; and squares, **6**/**7**/TMOS:MeTMOS(7:3) polymer hybrid.

Moreover, it is noticed that there is a remarkable difference between the polymer hybrids and the sol−gel glasses, in other words, between the samples containing organic polymer and those without polymer. In the polymer hybrids, the change of $E_T$ values with different TMOS:MeTMOS ratios and, consequently, the slopes of the correlation functions in Figure 2 diminished compared with those of the sol−gel glasses. The **6**-doped sol−gel glasses exhibited almost the same change toward TMOS:MeTMOS ratio as Reichardt's dye-doped ones. On the contrary, the polymer hybrids from **9** and those from polyoxazoline **7** and **6** appeared to show smaller changes of $^1/_5$ or $^1/_6$. As mentioned

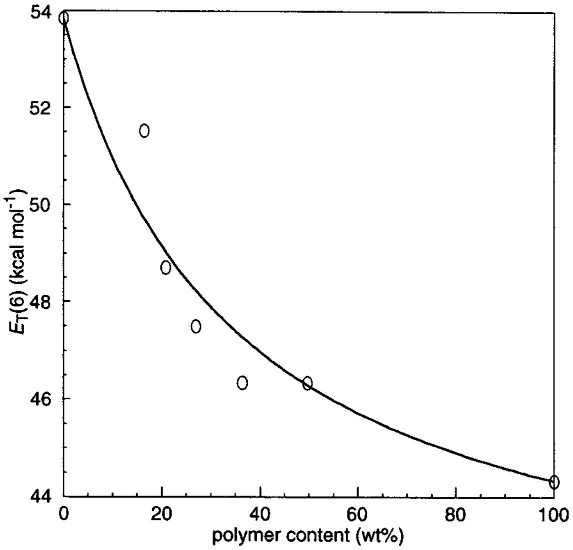


**Figure 4.** Matrix polarity of **6**/**7**/TMOS:MeTMOS(7:3) polymer hybrids as a function of polymer content in weight percent.

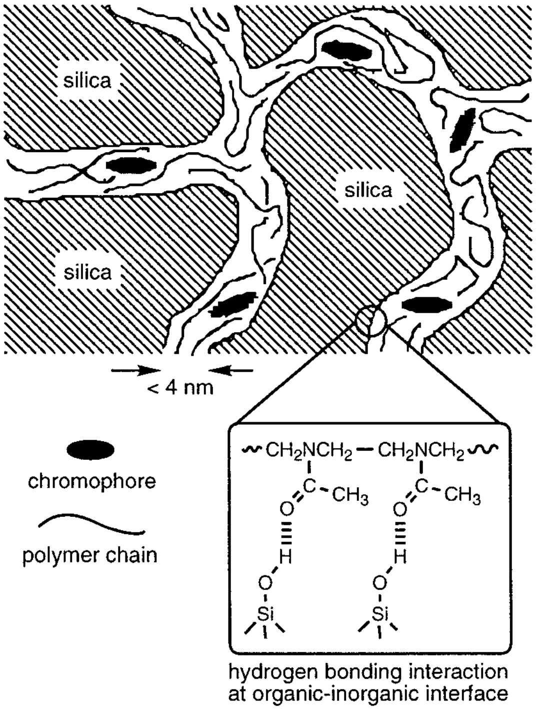


**Figure 5.** Illustration representing the dispersion of the chromophore in a polymer hybrid.

above, the solvatochromic sensitivities of **6** and **9** are comparable to that of Reichardt's dye in solution (Figure 1), and indeed **6** doped in the sol–gel glasses showed a large difference in $E_T$ values with different TMOS:MeTMOS ratios. Therefore, the decline of solvatochromic changes in the polymer hybrids should be attributed to the presence of the organic polymer in the solid state. The solvatochromic dye seems to experience a more polymer-like environment but is substantially influenced by the sol–gel matrix.[30] To verify this circumstance, **6**-doped polymer hybrids with different polymer/silicate ratios (TMOS:MeTMOS = 7:3) were prepared, and those absorption spectra were measured. In Figure 4, the obtained $E_T$ values are plotted against the polymer content (wt %) determined from TGA measurements. It again suggests that the microenvironment around **6** composed of a larger amount of organic polymer than did the bulk composition. This kind of phenomena is frequently observed in binary solvent mixtures and described as "preferential solvation".[36,44] Figure 5 presents a simple illustration consistent with the microenvironment felt by the solvatochromic dye in the polymer hybrids. At present, it is not clear whether the concentration fluctuation of organic polymer exists in the polymer hybrids and the doped dye molecule is located in the polymer-rich environment or if the doping of the dye molecule induces the concentration fluctuation. It can also be pointed out that the slopes of the linear correlation lines for the polymer hybrids in Figure 3 are almost the same. This indicates that the polarity of the microenvironments around the dye are apparently equivalent independently of the existence of a chemical bond between the dye and the polymer.

## Summary

The polarity of the microenvironment in the organic–inorganic polymer hybrids was characterized with the solvatochromic pyridinium *N*-phenolate betaine dyes. The values of the solvatochromic parameter $E_T$ for the polymer hybrids were found to correlate linearly with TMOS:MeTMOS ratio. It seems that the solvatochromic dyes are preferably surrounded by the organic polymer rather than the siloxane network in the polymer hybrids. Furthermore, the polarity of the microenvironments around the dye molecule are apparently equivalent whether the dye is chemically connected to the organic polymer or not. These results suggest the possibility of more precise control of the property of the dye molecule doped in the polymer hybrids by controlling the microenvironment around the dye.

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