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Isomerization Behavior of Azobenzene Chromophores Attached to the Side Chain of Organic Polymer in Organic−Inorganic Polymer Hybrids

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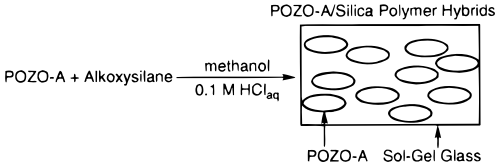
ABSTRACT: Isomerization behavior of azobenzene chromophores in organic−inorganic polymer hybrids was investigated. Polymer hybrids were prepared from azobenzene-modified poly(2-methyl-2-oxazoline) (POZO-A) and methyltrimethoxysilane (MeTMOS) or tetramethoxysilane (TMOS). Isomerization behavior in polymer hybrids was compared with that in DMSO solution or in films of POZO-A. Two kinds of model compounds were synthesized, and their isomerization behaviors were also examined. Photoinduced trans-to-cis isomerization took place in all samples. The cis isomer ratios in the photostationary state were found to be smaller in solid films than in solution. Especially, model compound having a triethoxysilyl group showed a markedly small cis isomer ratio. Thermal cis-to-trans isomerization was investigated kinetically. A distinct deviation from the first-order kinetics was observed in solid films.

Introduction

Increasing attention has been paid to photochemistry and photophysics of chromophores in amorphous solid matrices such as polymers and sol−gel glasses from both scientific and practical points of view.[1−13] Light-induced changes of the structure or the conformation of organic chromophores in glassy solids can be affected by various factors such as polarity and viscosity of the local environment and free volume distribution around the chromophores. Generally the change of the structure or the conformation also induces the change in electronic absorption of the chromophores, and if the absorption changes reversibly in the visible region, it is called photochromic.[14] Investigation of the photochromic behaviors in solid matrixes affords valid information concerning the local environment around the chromophores. Azobenzene chromophores photoisomerize from a thermally more stable trans form to a less stable cis one by ultraviolet light, and the reverse process takes place thermally and/or by visible light irradiation.[1−3,15] Kinetic studies of this reversible isomerization have been carried out for azobenzene moieties doped in or covalently incorporated into both organic polymers and sol−gel glasses.[16−26]

We have investigated organic−inorganic polymer hybrids, in which organic polymers are dispersed in a silica gel matrix at the molecular level.[27,28] They are prepared by the sol−gel reaction of alkoxysilanes in the presence of organic polymers. In the previous report of this study,[29] we have prepared the organic−inorganic polymer hybrids from azobenzene-modified poly(2-methyl-2-oxazoline) (POZO-A) and tetramethoxysilane (TMOS) or methyltrimethoxysilane (MeTMOS) (Scheme 1). Transparent and homogeneous polymer hybrids could be obtained over a wide range of polymer-to-silicate ratios. The present paper describes the behavior of the trans-to-cis isomerization and the kinetics of the thermal cis-to-trans isomerization of azobenzene chromophores in the polymer hybrids. They are compared with those in dilute polymer solution or in polymer film, as well as model compounds doped in sol−gel glass.

Scheme 1



Experimental Section

Materials. Preparation of poly(2-methyl-2-oxazoline) (POZO) and partial hydrolysis of amide groups of POZO were reported previously.[30] *p*-Phenylazobenzoic acid was prepared by the reaction of *p*-aminobenzoic acid with nitrosobenzene in glacial acetic acid according to the literature.[31] *p*-Phenylazobenzoyl chloride was prepared by the treatment of *p*-phenylazobenzoic acid with thionyl chloride in the presence of anhydrous sodium carbonate according to the literature.[31] Spectroscopic grade DMSO and 0.1 M HCl$_{aq}$ were used as received. The following reagents were stored under nitrogen atmosphere. Acetonitrile was dried and distilled from CaH$_2$. 1,8-Diazabicyclo[5.4.0]-undec-7-ene (DBU) was distilled under reduced pressure. Dichloromethane and diethylamine were dried and distilled from CaH$_2$. 3-(Aminopropyl)triethoxysilane was distilled under reduced pressure. Methanol was dried and distilled from magnesium methoxide. Ethanol was dried and distilled from magnesium ethoxide. Tetramethoxysilane (TMOS), methyltrimethoxysilane (MeTMOS), tetraethoxysilane (TEOS), and methyltriethoxysilane (MeTEOS) were distilled. Ethylene glycol was distilled from MgSO$_4$ under reduced pressure.

Measurements. ^{1}H NMR spectra were recorded on 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. Electronic absorption spectra were obtained on a JASCO V-530 spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a DSC200, Seiko Instruments Inc., with a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

Preparation of Azobenzene-Modified Poly(2-methyl-2-oxazoline) (POZO-A). In a typical procedure, 1.7 mol % hydrolyzed POZO (4.44 g, 0.89 mmol equiv NH) was dissolved in acetonitrile (30 mL) under nitrogen atmosphere, and DBU (0.20 mL, 1.34 mmol) was added to trap HCl gas. To this solution was added *p*-phenylazobenzoyl chloride (330 mg, 1.35 mmol), and the resulting mixture was stirred overnight at

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room temperature. The polymer was isolated by reprecipitation from acetonitrile into diethyl ether for two times. Further purification was performed by dialysis with distilled water in order to remove remaining DBU·HCl salt. POZO-A was obtained after freeze-drying with benzene. Yield was 3.76 g (82%). Degree of modification was calculated from ^{1}H NMR and absorption spectra to be 1.2 mol %.

Preparation of *N*,*N*-Diethyl-*p*-phenylazobenzamide (MC-1). A 128 mg (0.52 mmol) sample of *p*-phenylazobenzoyl chloride was dissolved in 10 mL of dry dichloromethane under nitrogen atmosphere. The solution was cooled to 0 °C, and 0.12 mL (1.16 mmol) of diethylamine was added dropwise. The reaction mixture was stirred for 2 h at room temperature. The mixture was poured into water, and the organic layer was washed with water and saturated $NaCl_{aq}$. After evaporation of dichloromethane, a crude product was obtained (144 mg). The crude product was applied to a silica column chromatography, using ethyl acetate/hexane (1/2, v/v) as an eluting solvent. The first fraction containing product was concentrated by evaporation and dried under reduced pressure. MC-1 was obtained as an orange viscous liquid. Yield was 139 mg (0.50 mmol, 95%). ^{1}H NMR ($CDCl_3$): δ 1.14 and 1.25 (broad peaks, 6H, CH_3), 3.29 and 3.57 (broad peaks, 4H, CH_2), 6.81−6.89 (m, 4H, aromatic H of cis isomer), 7.13−7.35 (m, 5H, aromatic H of cis isomer), 7.48−7.57 (m, 5H, aromatic H of trans isomer), 7.91−7.95 (m, 4H, aromatic H of trans isomer). ^{13}C NMR ($CDCl_3$): δ 12.76 (br), 14.02 (br), 39.19 (br), 43.07 (br), 122.73, 122.79, 127.04, 128.93, 131.16, 139.34, 152.33, 152.51, 170.26. IR (neat): 1630 cm^{-1} (ν_{CO}). Anal. Calcd C, 72.57; H, 6.81; N, 14.94. Found: C, 72.36; H, 6.78; N, 14.97. UV/vis (DMSO): $\lambda_{max}^{trans} = 328$ nm ($\epsilon = 2.38 \times 10^4$ M^{-1} cm^{-1}), 447 nm ($\epsilon = 670$ M^{-1} cm^{-1}). $\lambda_{max}^{cis} = 435$ nm ($\epsilon = 1.37 \times 10^3$ M^{-1} cm^{-1}).

Preparation of *N*-3-Triethoxysilylpropyl-*p*-phenylazobenzamide (MC-2). A 126 mg (0.51 mmol) sample of *p*-phenylazobenzoyl chloride was dissolved in 10 mL of dry dichloromethane under nitrogen. The solution was cooled to 0 °C, and then 0.25 mL (1.07 mmol) of 3-(aminopropyl)triethoxysilane was added. The reaction mixture was stirred for 2 h at room temperature. After evaporation of the solvent, crude product was applied to a silica column chromatography, using ethyl acetate/hexane (1/2, v/v) as an eluting solvent. The first fraction containing product was concentrated by evaporation and dried under reduced pressure. MC-2 was obtained as an orange solid. Yield was 180.5 mg (0.42 mmol, 82%). Mp 107 °C. ^{1}H NMR ($CDCl_3$): δ 0.74 (t, 2H, $J = 7.76$ Hz, CH_2Si), 1.23 (t, $J = 6.93$ Hz, 9H, CH_3), 1.80 (m, 2H, $C-CH_2-C$), 3.51 (m, 2H, CH_2N), 3.84 (q, $J = 6.93$ Hz, 6H, $SiO-CH_2$), 6.64 (broad s, 1H, NH), 7.50−7.56 (m, 3H, aromatic), 7.91−7.98 (m, 6H, aromatic). ^{13}C NMR ($CDCl_3$): δ 7.84, 18.22, 22.79, 42.27, 58.47, 122.77, 122.98, 127.84, 129.08, 131.43, 136.68, 152.49, 154.03, 166.70. IR (neat): 3300 (ν_{NH}), 1632 (ν_{CO}), 1545 (δ_{NH}), 1079 (ν_{SiO}). Anal. Calcd C, 61.51; H, 7.27; N, 9.78. Found: C, 61.25; H, 7.34; N, 9.80.

Preparation of Organic−Inorganic Polymer Hybrids from POZO-A. A typical procedure is as follows. POZO-A and alkoxysilane were dissolved into methanol (10 times in volume to alkoxysilane). A drop of aqueous HCl (0.1 M) was added to the solution, and the mixture was stirred for 30 min. Then the mixture was placed in a polypropylene mold covered with thin paper towel and left in air at room temperature. After a few days solvents were removed by evaporation, and POZO-A/silica gel polymer hybrid was obtained as a glassy material.

Preparation of Film Samples for Isomerization Study. Samples for isomerization study were prepared by casting the reaction mixture on quartz substrates (10 mm × 45 mm). The surface of the substrates has to be very clean to obtain good homogeneous wetting. The plates were immersed for 24 h in a neutral detergent solution and then ultrasonically agitated in concentrated HNO_3 for 10 min, washed well with distilled water and then methanol, dried, and kept in a desiccator. In cases of the polymer hybrids using TMOS, ethylene glycol (quarter volume to alcohol solvent) was added to the reaction mixture before casting to avoid cracking. The films were kept at room temperature for 24 h and then heated at 120 °C for 12 h to complete the sol−gel reaction. Sol−gel films with model compounds were prepared in the same way. The concentration of the chromophore was set to be comparable to that of the polymer hybrid film. The thickness of the films was ca. 100 μm.

Table 1. Absorption Maximum Wavelength and Cis Fraction in the Photostationary State for All Samples

	λ_{max} (nm)	% cis
MC-1 (in DMSO)	328	90
POZO-A[a] (in DMSO)	330	85
POZO-A[a] (film)	330	63
POZO-A/MeTMOS[a,b] (film)	330	63
POZO-A/TMOS[a,b] (film)	329	58
MC-2/MeTEOS (film)	323	54
MC-2/POZO/TEOS (film)	327	50

[a] POZO-A: $M_n = 8500$, degree of modification = 1.2 mol % (calculated from ^{1}H NMR spectrum). [b] POZO-A/alkoxysilane = 1/10 (w/w).

POZO-A film was also prepared on a quartz substrate by casting a methanol solution of POZO-A. It was kept at room temperature for 24 h and then heated at 70 °C in vacuo for 7 h to remove residual solvent.

Measurements of Photoisomerization and Thermal Isomerization Processes. A sample was irradiated with ultraviolet light at room temperature to induce the trans-to-cis photoisomerization of azobenzene chromophores. As a ultraviolet light source, 450 W high-pressure mercury lamp (Ushio UM-452) was used with a Pyrex cooler and a glass filter (Toshiba UV-D33S) to cut off the wavelengths below 300 nm and visible region. The reaction was followed by absorption spectra. To follow the cis-to-trans reverse isomerization process, the sample was equilibrated with ultraviolet light beforehand. Then it was placed in a temperature-controlled box for thermal cis-to-trans reverse isomerization process. The reaction was also followed by absorption spectra.

Results and Discussion

POZO-A/Silica Polymer Hybrids. The synthesis and characterization of POZO-A are described in detail in a previous paper.[29] Polymer hybrids were prepared via the acid-catalyzed sol−gel reaction of TMOS or MeTMOS in the presence of POZO-A. As reported in a previous paper,[29] the polymer hybrids from POZO-A were found to be transparent and homogeneous over a wide range of POZO-A/alkoxysilane ratios and degrees of modification of POZO-A. The glass transition temperature, T_g, which is defined as the midpoint of the glass transition in DSC thermograms, of POZO-A was observed at 78 °C. T_g of the POZO-A/MeTMOS (1/10) polymer hybrid was found at 82 °C, indicating that the segment mobility of organic polymer in the polymer hybrids from trifunctional alkoxysilane (MeTMOS) is comparable to that of polymer itself. On the contrary, no well-defined glass transition was observed for the POZO-A/TMOS (1/10) polymer hybrid. This result suggests a good dispersion of the organic polymer chains in the silica gel network.[32,33]

Photochemical Trans-to-Cis Isomerization. To examine the isomerization behavior of azobenzene chromophores in the polymer hybrids, photochemical trans-to-cis isomerization and thermal cis-to-trans reverse isomerization were investigated and compared with a solution or a film of POZO-A as well as model compounds in sol−gel glasses. All samples studied are listed in Table 1 with absorption maximum wavelengths (λ_{max}). Absorption spectra of each sample in thermal equilibrium (dotted lines) are shown in Figure 2. It was found that the shape of absorption and λ_{max} of all the samples were almost the same. Therefore, it can be

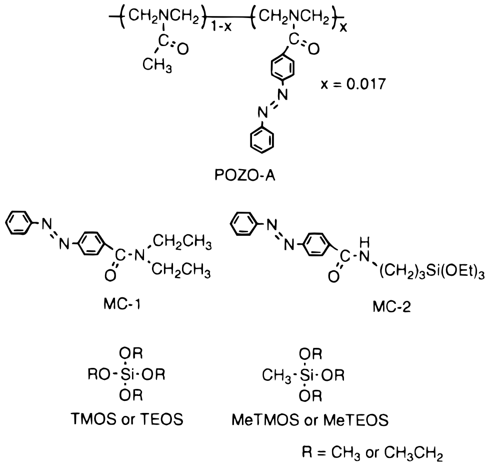

Figure 1. Chemical structures of POZO-A, model compounds, and alkoxysilanes.

concluded that the difference of the electronic interaction between the azobenzene chromophores and the surroundings can be ignored.

The photoisomerization of azobenzene chromophores from the trans form to the cis one was induced by the irradiation of ultraviolet light with wavelengths between 300 and 400 nm from a high-pressure mercury lamp through a Pyrex cooler and a glass filter. A photostationary state was achieved within 20 min in all the samples. Absorption spectra in the photostationary state (broken lines) are also shown in Figure 2. The fraction of cis isomers was calculated from the absorbance (A) at λ_{max} for the $\pi-\pi^*$ absorption of the trans isomer at time t according to the equation[23]

$$[\mathrm{cis}]_t/[\mathrm{trans}]_0 = (1 - A/A_0)/(1 - \epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{trans}}) \qquad (1)$$

where $[\mathrm{cis}]_t$ is the concentration of the cis isomer at time t, $[\mathrm{trans}]_0$ is the initial concentration of the trans isomer, A_0 is the initial absorbance at λ_{max}, and $\epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{trans}}$ is the ratio of the molar absorption coefficients of the cis and trans isomers at λ_{max}. The $\epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{trans}}$ value in the present study was determined from the absorption spectra and ^{1}H NMR spectra of MC-1 in DMSO solution in the initial state and in the photostationary state.[29]

Cis fractions in the photostationary state calculated for other samples are also summarized in Table 1. First, it is noticed that the cis fractions of film samples turned out to be smaller than those in solution, indicating the inhibition of the photoisomerization due to a relatively small free volume in the solid matrices compared with that in solution. The same phenomena were found in other systems.[26] Moreover, the photoisomerization was hindered rather more strongly in the samples using TMOS and TEOS than those with MeTMOS and MeTEOS. This might reflect the rigidity of the silica matrices. Tetrafunctional alkoxysilanes generate more rigid silica matrices than trifunctional ones. Movement of the azobenzene chromophores directly attached to the silica matrices (MC-2) seems to be more restricted than those in the polymer hybrids, even in the presence of the additional organic polymer. This might suggest that the introduction of the chromophore on the polymer chain brought about some differences of the local environment for the chromophores in the polymer hybrids.

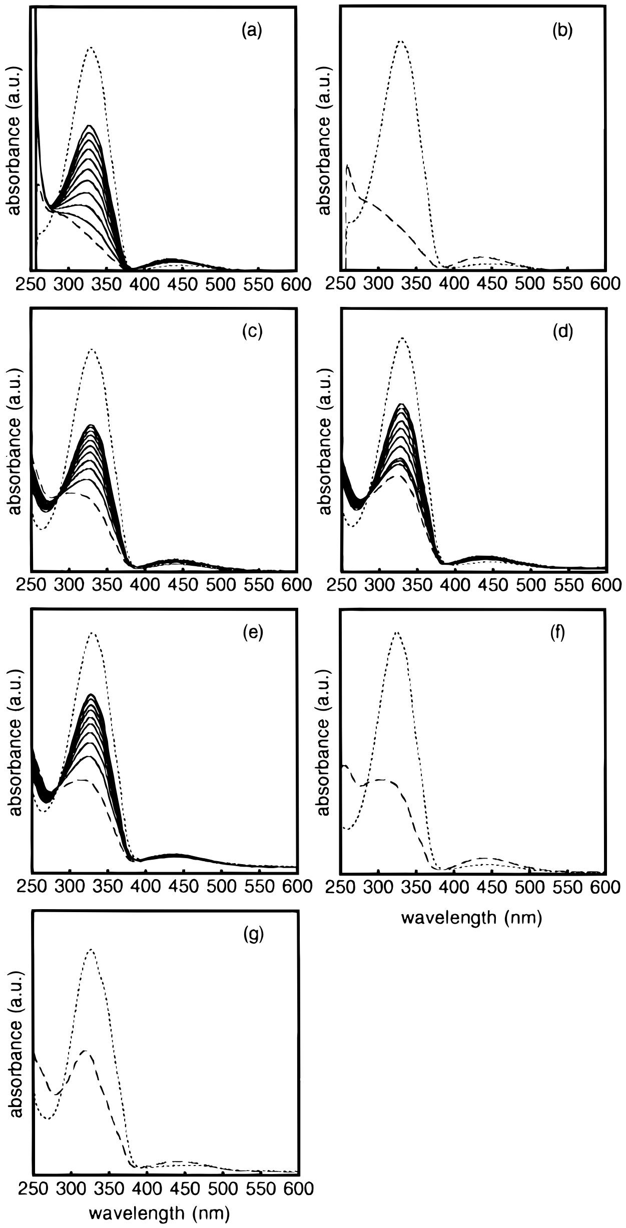

Figure 2. Electronic absorption spectra of (a) MC-1 in DMSO, (b) POZO-A in DMSO, (c) POZO-A film, (d) POZO-A/MeTMOS, (e) POZO-A/TMOS, (f) MC-2/MeTEOS, and (g) MC-2/POZO/TEOS. Dotted lines are in thermal equilibrium, and broken lines are in photostationary state. Solid lines show the change of the absorption during the thermal cis-to-trans isomerization at 60 °C (every 30 min).

Kinetics of Thermal Cis-to-Trans Reverse Isomerization. The thermodynamically unstable cis isomer isomerizes thermally to the more stable trans form. Solid lines in Figure 2 are the changes of absorption during the thermal cis-to-trans isomerization at 60 °C (every 30 min). Absorbance of the $\pi-\pi^*$ band of the trans isomer around 330 nm increased progressively with time, and finally the initial absorption was recovered. The kinetics of the thermal cis-to-trans isomerization were analyzed according to the equation

$$\ln\{[\mathrm{cis}]_0/[\mathrm{cis}]_t\} = kt \qquad (2)$$

where $[\mathrm{cis}]_0$ and $[\mathrm{cis}]_t$ were the concentration of the cis isomer in the photostationary state (time $t = 0$) and at time t (min), respectively, which were calculated from eq 1, and k is the first-order rate constant for the thermal cis-to-trans isomerization.

Table 2. Fraction of the Fast Process (α) and Kinetic Parameters of Thermal Cis-to-Trans Isomerization

	60 °C			85 °C		
	α	k_{fast} (10^{-2} min^{-1})	k_{slow} (10^{-3} min^{-1})	α	k_{fast} (10^{-1} min^{-1})	k_{slow} (10^{-2} min^{-1})
MC-1 (DMSO)	0		2.9			
POZO-A	0.15	2.5	1.9	0.14	2.1	2.6
POZO-A/MeTMOS (1/10)	0.12	6.2	2.6	0.11	2.1	2.6
POZO-A/TMOS (1/10)	0.17	3.4	2.6	0.11	2.0	2.8

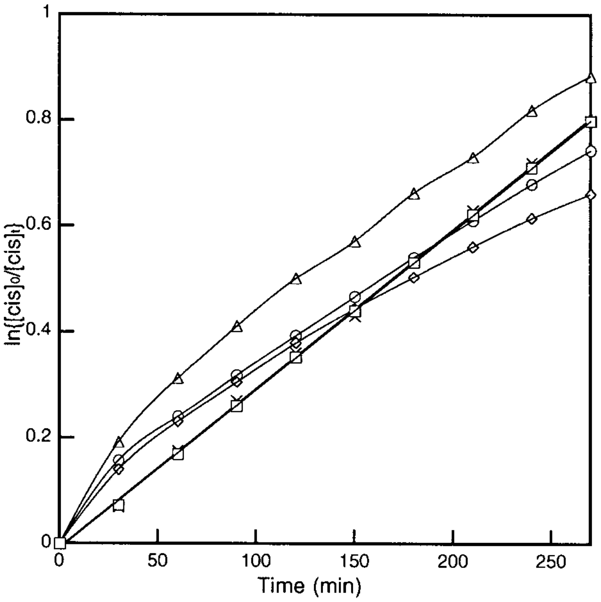

Figure 3. First-order plots for the thermal cis-to-trans isomerization at 60 °C: square, MC-1 in DMSO; cross, POZO-A in DMSO; diamond, POZO-A film; circle, POZO-A/MeTMOS polymer hybrid; triangle, POZO-A/TMOS polymer hybrid.

The first-order plots for the thermal cis-to-trans isomerization at 60 °C in the polymer hybrids are shown in Figure 3 with those of POZO-A and MC-1 in DMSO solution and in POZO-A film. The isomerization in solution was found to follow first-order kinetics, and the rates were almost the same between MC-1 and POZO-A. On the other hand, deviation from first-order kinetics was observed in solid film samples. In the early stage of the reaction the isomerization in films proceeded faster than in solutions. It gradually decelerated, and finally the rates became slower than those in solutions. The existence of such anomalously fast components for thermal reverse isomerization has been found often in solid matrices,[16,18b,c,19c,20b,21c,22,23] and attributed to the trapping of some of cis isomer in a strained conformation during UV irradiation. Such strained-cis species can return more easily to the trans form than the relaxed-cis species. Nonmonoexponential decay kinetics of unimolecular reactions in amorphous polymers have been described by many kinetic models.[6] One of the simplest models introduces a sum of two or more exponential terms to fit the decay kinetics.[34] The biexponential equation[25]

$$[\mathrm{cis}]_t/[\mathrm{cis}]_0 = \alpha \exp(-k_{\mathrm{fast}}t) + (1 - \alpha) \exp(-k_{\mathrm{slow}}t) \quad (3)$$

where α is the fraction of the fast species and k_{fast} and k_{slow} are the rate constants for the fast and slow processes, respectively, fitted the experimental data quite well. Table 2 summarizes the fitting parameters. The relative rate constant for the fast process (k_{fast}) appears to differ from k_{slow} by 1 order of magnitude, and the fraction of the fast process (α) was about 15%. These values are comparable with the previous studies.[20b,22a] The same analysis was carried out for the thermal cis-to-trans isomerization at 85 °C (Table 2). At both temperatures, the difference in the kinetic parameters among POZO-A, POZO-A/MeTMOS, and POZO-A/TMOS was not so large. Recently, we have found that a solvatochromic chromophore in the polymer hybrids was relatively insensitive to the polarity of silica matrices,[35] which might be due to the presence of organic polymer between the chromophore and the silica matrices. The result of the kinetic study of the cis-to-trans isomerization of the azobenzene chromophore in the polymer hybrids seems to indicate the same situation. Further studies on thermal cis-to-trans isomerization for polymer hybrids with different polymer/silicate ratios as well as MC-2/silica samples are in progress to clarify the effect of organic polymer for the isomerization behavior of azobenzene in the polymer hybrids.

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