tion that extraordinary care must be taken when critical bonds are made that rely on epoxies. Accurate weighing of the resin and curing agent must be done. This should then be followed by a mixing process that has been tested to give uniform distribution of the epoxy components. Unless these precautions are taken, the joints that are formed will obviously be subject to attack and weakening by a variety of chemical agents.

Conclusions

The diglycidyl ether of bisphenol A was cured with triethylenetetramine at several concentrations of amine. The ratio of hardener -NH group to epoxy group spanned the range from a large deficiency (50%) to a large excess (120%). Infrared spectra indicate that even with a large excess of amine, a small amount of unreacted epoxy was present. Density measurements on the cured epoxy showed that the density went through a maximum when the amine concentration was near 90% of the theoretical amount.

Seven solvents, including water, methanol, acetone, isopropyl alcohol, ethyl acetate, 1,2-dichloroethane, and toluene, were used in sorption experiments with the various amine/epoxy ratio polymers. The most sensitive mixture of all solvents, except water and isopropyl alcohol, was the 50% amine material. This result was rationalized on the basis that the polymer containing a large deficiency of amine formed a less tightly cross-linked network (it had the lowest T_g), thereby providing more free volume and easier means of ingress. Water sorption was insensitive to the amount of curing agent used suggesting that association of the water to the cured epoxy, by hydrogen bonding, was not important.

Acknowledgment. The authors thanks Arturo Hale and Donald Dahringer for helpful discussions.

Registry No. (DGEBPA)(TETA) (copolymer), 73310-55-1; H_2O, 7732-18-5; MeOH, 67-56-1; H_3CCOCH_3, 67-64-1; $Cl(CH_2)_2Cl$, 107-06-2; PhMe, 108-88-3; $HOCH(CH_3)_2$, 67-63-0; H_3CCO_2Et, 141-78-6.

Photoisomerization of an Azobenzene in Sol–Gel Glass Films

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Received April 28, 1992. Revised Manuscript Received August 3, 1992

Sol–gel films of tetraethyl orthosilicate (TEOS) doped with 4-methoxy-4′-(2-hydroxyethoxy)azobenzene (MHAB) were prepared under various conditions. The trans–cis photoisomerization and the thermally induced cis–trans reversion of MHAB in the sol–gel films were studied and compared with that in poly(methyl methacrylate) (PMMA) film or in solution. An increased absorption between the π–π^* and the n–π^* absorption bands observed in sol–gel films doped with MHAB was attributed to hydrogen bond between the azo group and silanol groups. The cis fraction in the photostationary state in sol–gel films was much smaller than in PMMA. This suggests that the sol–gel matrix is more rigid than PMMA. The rigidity of the matrix in the sol–gel glass depends on the water concentration during its preparation.

Introduction

The sol–gel process is now a well-accepted technique for the preparation of various inorganic oxide glasses at low temperature without melting.[1-5] Such inorganic matrices are prepared by condensation–polymerization of a suitable metal alkoxide. For instance, the sol–gel process of TEOS can be described by

$$\text{hydrolysis}\quad Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH$$

$$\text{condensation}\quad Si(OH)_4 \rightarrow SiO_2 + 2H_2O$$

Therefore, the overall reaction is

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH$$

The sol–gel process consists of two main steps. In the first step, metal alkoxides hydrolyze at a low temperature to form a microporous glass with a large surface area. In the second step the porous glass is annealed at an elevated temperature in order to fill the pores. This results in a shrunken, nonporous glass. The porous glass obtained in the first stage is the precursor for the second stage and determines not only the properties of the final glass but also the annealing conditions. The porous glass is of particular interest because of its ability to trap organic photoactive molecules in the inorganic matrices.

Avnir et al. showed that organic molecules can be embedded in silica glasses by the sol–gel process[6-10] and the resulting materials may be used in such photochemical applications[11,12] as solid-state dye laser, nonlinear optical materials, and optical sensors. However, detailed information on the microscopic environment of organic molecules embedded in a matrix of silica gel glass by the sol–gel process has not been fully clarified since little is known about the mobility of organic molecules in the silica cage and about the interaction between the silica cage and the guest molecules.

Zink et al. have reported the preparation of silica and aluminosilicate gels doped with bipyridyltriscarbonylchlororhenium(I) and studied the changes in rigidity of sols

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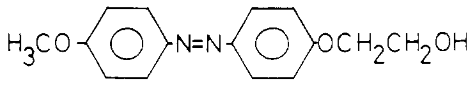

MHAB

Figure 1. Structure of 4-methoxy-4′-(2-hydroxyethoxy)azobenzene (MHAB).

and gels.[13] They have also studied the changes in aluminosilicate glass properties during aging and drying by monitoring photochromism of spiropyrans.[14]

On the other hand, many studies have been dealt with the photochemical trans-to-cis isomerization and thermal cis-to-trans isomerization of azobenzene chromophores in polymer solids.[15-20] The distribution of local free volume in polymers has been characterized by using these photochromic probe molecules.[18,19] Hence, incorporation of molecularly dispersed azobenzene chromophores in the sol–gel glass matrices is a useful method for studying the characteristics of reactions in the silica cage, since the reaction rates of photoexcited molecules are expected to reflect the rigidity of the matrix.

In this paper, we studied the photoinduced trans-to-cis isomerization under steady-state irradiation at 365 nm and the thermal cis-to-trans isomerization of an azobenzene derivative in sol–gel films prepared under varying conditions in order to estimate the rigidity of the sol–gel glass matrix compared with a polymer matrix.

Experimental Section

Materials. MHAB was synthesized from 4-hydroxy-4′-methoxyazobenzene by the Williamson method (Figure 1). The product was purified by repeated recrystallization from a toluene/hexane (9:1) mixture. TEOS purchased from Tokyo Kasei Kogyo Co. was used without further purification. Ethanol, ether, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and water were of spectroscopic grade. Poly(methyl methacrylate) (PMMA, $M_n = 1.0 \times 10^5$, $T_g = 105$ °C) was obtained from Wako Pure Chemical Co.

Sample Preparation. Sol–gel films were prepared on quartz substrates. To obtain good homogeneous wetting of the substrate surface, it has to be clean. The substrates were immersed for 24 h in a neutral detergent solution and then agitated ultrasonically in concentrated HNO_3 for 10 min, washed with distilled water, and dried at 120 °C for 60 min.

Various techniques to prepare sol–gel films have been reported.[2,21-23] We selected the dip-coating technique. A quartz substrate was immersed into a metal alkoxide solution and pulled up vertically at a rate of 3.33 mm/s and allowed to stand for 1 min, followed by heating at 60 °C for 2 h, or at 110 °C for 15 h. Three coating solutions with different ratios of TEOS:water were prepared (solution A: $[H_2O]/[Si(OC_2H_5)_4] = 2$; solution B: $[H_2O]/[Si(OC_2H_5)_4] = 1$; solution C: $[H_2O]/[Si(OC_2H_5)_4] = 4$). The thin film coating from solution A was obtained as follows: A mixture of 7.50 g (0.036 mol) of TEOS, 5.05 g (0.112 mol) of ethanol, 1.30 g (0.072 mol) of water, and 0.0003 mol of MHAB was stirred, and 0.55 g of concentrated HCl was added to this mixture as a hydrolytic catalyst. The mixture was stirred for 2 h at room temperature, and 7.20 g of ether was added. Before coating, the mixture was kept standing for 1 h at room temperature. Solution B and C were prepared in the same way.

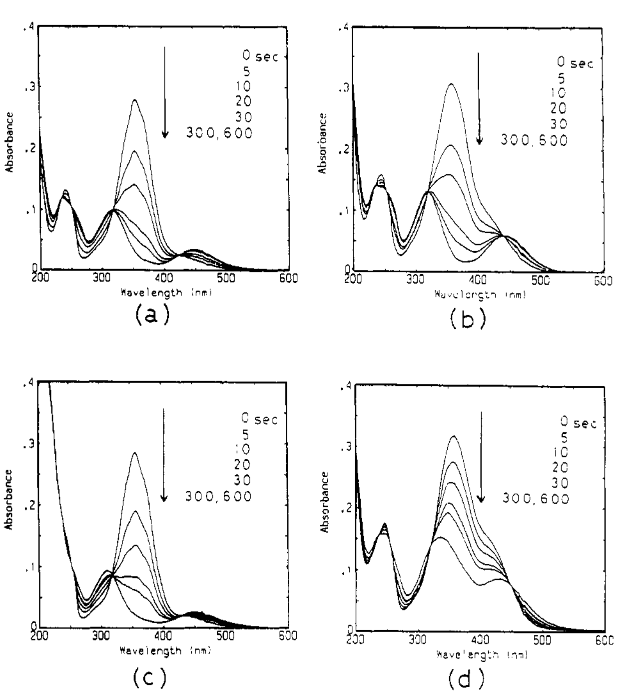

Figure 2. Change in UV spectra of *trans*-MHAB during 365-nm light irradiation at room temperature: (a) in ethanol, (b) in a 1:9 mixture of ethanol and water, (c) in PMMA, and (d) in a sol–gel film (solution A, heating condition: 110 °C, 15 h).

The PMMA film was prepared by solvent-casting onto a quartz substrate from a 10 wt % PMMA solution containing 0.004 mol L^{-1} of MHAB in THF. The film was kept at room temperature for 6 h and then heated under vacuo at 70 °C for 12 h to remove residual solvent.

Measurements of Photoisomerization and Thermal Isomerization. A sample film was irradiated at 365 nm from a Jasco CRM-FA irradiator (2-kW xenon arc lamp with a monochromator) at room temperature for the measurements of the trans-to-cis photoisomerization of MHAB. Absorbance measurements were made with a Hitachi UV-320 spectrometer. To measure the thermal cis-to-trans isomerization, the irradiation was discontinued after reaching the photostationary state, and the sample was moved to the thermostated sample holder placed in the spectrometer to follow the absorbance at the absorption maximum of the trans isomer.

Reference experiments for the trans-to-cis photoisomerization and thermal isomerization of HMAB in a dilute solution were carried out in ethanol or DMSO. The concentration of HMAB in the solutions was adjusted so as to give the same absorbance as in the thin-film sample at the absorption maximum.

Results and Discussion

Absorption Spectra in Sol–Gel Films. Since azobenzene itself was scarcely soluble in the coating solutions for sol–gel films, MHAB bearing hydrophilic substituents was used in order to enhance the solubility. Absorption spectra of HMAB before and after UV irradiation were measured in ethanol, ethanol/water (1:9) mixture solution, PMMA and the sol–gel film (solution A, heating condition: 110 °C, 15 h) and are shown in Figure 2. A shoulder at somewhat longer wavelength than that of π–π^* absorption band is observed in a 10% ethanol aqueous solution and in the sol–gel film of *trans*-MHAB, in contrast to that in ethanol. Wyman et al. ascribed the shoulder in 10% ethanol aqueous solution to the formation of a hydrogen bond between the azo group and water molecule[24] causing

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Table I. Photochemical Conversion of MHAB

matrix	cis fraction in a photostationary state (%)
ethanol	93
10% ethanol aqueous solution	92
PMMA	93
sol–gel film (solution A, heating condition: 110 °C, 15 h)	60
sol–gel film (solution A, heating condition: 60 °C, 2 h)	64
sol–gel film (solution B, heating condition: 60 °C, 2 h)	82
sol–gel film (solution C, heating condition: 60 °C, 2 h)	61

the blue shift of the n–π* transition. In the case of the sol–gel film, the shift of the absorption band may be owing to the hydrogen bond between the azo group and Si–OH at the surface of silica matrix. Some reports have demonstrated hydrogen bonding between organic molecules doped in sol–gel glasses and silanol groups which surround the molecules.[25,26] Another possibility is the effect of a hydrogen bond between the azo group and residual water molecules in silica matrix. The latter interpretation is less reasonable because the shoulder of absorption spectrum was not altered in intensity even after the sample was heated under vacuo at 200 °C for 12 h to remove residual water.

Trans-to-Cis Photoisomerization at Room Temperature. Figure 2 shows that the photoisomerization rate of MHAB on irradiation with 365-nm light depends on the reaction media. Using eq 1, the cis fraction ([cis]/[trans]$_0$) in the photostationary state under various conditions were estimated and are summarized in Table I. Here, [cis] and [trans]$_0$ denote the concentration of the cis isomer in the photostationary state and that of the trans isomer before UV irradiation, respectively, ϵ_{cis} and ϵ_{trans} are the absorption coefficients, whereas A_0 and A are the absorbances at λ_{max} before and after UV irradiation:

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

Table I shows that the final cis fraction in the sol–gel film is much less than in ethanol and PMMA. The cis fraction in the photostationary state in a 10% ethanol aqueous solution, which resulted in spectra similar to those in the sol–gel films, is almost the same as in ethanol, suggesting that the formation of the hydrogen bond between the azo group and silanol groups has no effect on the final cis fraction. In addition, it is not likely that residual solvents (water and ethanol), ethoxysilyl and silanol groups which exist in the sol–gel glass alter photophysical properties of MHAB considerably to quench the photoisomerization, because the trans–cis photoisomerization proceeds in a sol solution as well as in an ethanol solution. Hence, it may be noted that photoisomerization of *trans*-MHAB is suppressed in the sol–gel film owing to the rather small critical free volume available in this matrix (Table I). Such an effect of the free volume was reported for azobenzene in a polycarbonate film at extremely low temperature[15] and for azonaphthalene in cross-linked epoxy resins at room temperature.[16] However, the quenching of the photoisomerization of azobenzene in the polycarbonate is considerably relaxed at ambient temperature to result in a conversion to the cis isomer similar to that in PMMA or polystyrene.[15–20] This suggests that the partial suppression of the trans-to-cis photoisomerization in the sol–gel films is caused by the highly cross-linked network, which is more rigid than the polymer matrices at room temperature.

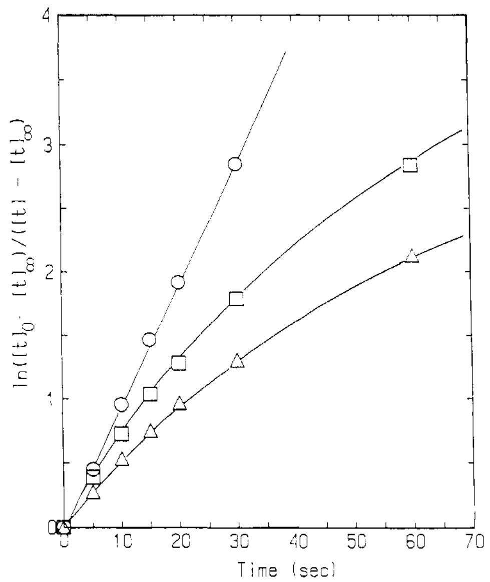

Figure 3. First-order plots for trans → cis photoisomerization of MHAB at room temperature: in ethanol (○), in PMMA (□) and in a sol–gel film (△) (solution A, heating condition: 110 °C, 15 h).

Quinson et al. have measured the radius of pores of the wet silica gel by thermoporometry.[27] The pore radius distribution of a wet gel prepared by the sol–gel process is very narrow and centered at around 25 Å, and the shape factor indicates cyrindrical interconnected pores. The pore size of the xerogel (dry gel) should be smaller than that of the wet gel. Scherer et al. have demonstrated that the pore diameter distribution of the xerogels prepared by acidic hydrolysis is very wide below 40 Å.[28]

The free volume which is required for the trans-to-cis photoisomerization of photoprobes is the volume swept out by the van der Waals area of the displacing group. Victor and Torkelson have calculated these sweep volumes of several photoactive compounds[18] after the method of Bondi[29] and estimated the free volume needed by azobenzene to isomerize as 127 Å^3. The sweep volume of MHAB is larger than that of azobenzene because of the presence of substituents. Some portion of MHAB molecules may exist at least partially in the pores with much smaller size (probably the pore diameter below ca. 10 Å) in sol–gel films, and the photoisomerization can then not take place.

According to Horie et al.,[15] when the *trans*-azobenzene with an initial concentration of [t]$_0$ is irradiated at 365 nm, the change in *trans*-azobenzene concentration, [t], approaching its equilibrium value, [t]$_\infty$, is given by

$$\ln\frac{[\mathrm{t}]_0 - [\mathrm{t}]_\infty}{[\mathrm{t}] - [\mathrm{t}]_\infty} = \frac{[\mathrm{t}]_0}{[\mathrm{t}]_0 - [\mathrm{t}]_\infty}At = \frac{[\mathrm{t}]_0}{[\mathrm{t}]_\infty}(B + K)t \qquad (2)$$

where A, B, and K are the rate constants for the trans-to-cis photoisomerization, the cis-to-trans photoisomer-

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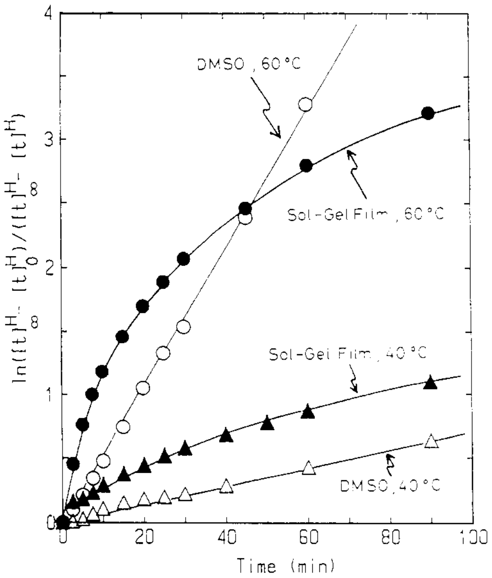

Figure 4. First-order plots for thermal cis → trans isomerization of MHAB: (△) in DMSO at 40 °C, (○) in DMSO at 60 °C, (▲) in a sol–gel film (solution A, heating condition: 110 °C, 15 h) at 40 °C and (●) in a sol–gel film (solution A, heating condition: 110 °C, 15 h) at 60 °C.

ization, and the thermal cis-to-trans isomerization, respectively.

The first-order plots according to eq 2 for the trans-to-cis photoisomerization of MHAB in ethanol, PMMA and the sol–gel film (solution A, heating condition: 110 °C, 15 h) at room temperature are shown in Figure 3. The reaction is first order in solution, whereas in PMMA and in the sol–gel film it deviates from first-order kinetics. The degree of the rate reduction in the sol–gel film was more marked than in PMMA. This also suggests that the sol–gel matrix is more rigid than the polymer matrix.

Thermal Cis-to-Trans Isomerization in Sol–Gel Films. The thermal cis-to-trans isomerization of MHAB in the sol–gel films and in DMSO was followed at 40 and 60 °C. DMSO was employed here as a high boiling point solvent in order to avoid a change in the concentration of the azobenzene during the spectroscopic measurement.

The thermal cis-to-trans isomerization follows first-order kinetics:

$$\ln \frac{[t]^{H}_{\infty} - [t]^{H}_{0}}{[t]^{H}_{\infty} - [t]} = Kt \qquad (3)$$

where [t] is the *trans*-azobenzene concentration, $[t]^{H}_{0}$ and $[t]^{H}_{\infty}$ are the concentration of the trans isomer of the azobenzene in the photostationary state and after the thermal reversion is completed, respectively. First-order plots for the thermal cis-to-trans isomerization of MHAB at 40 and 60 °C in the sol–gel films (solution A, heating condition: 110 °C, 15 h) and in the solution are shown in Figure 4. The reaction proceeds by first-order kinetics in solution whereas in the sol–gel films the reaction is initially faster than in solution and decreases gradually with time. Such a thermal reversion kinetics in the sol–gel films was not eventually affected by additional heating, indicating that there is no remarkable change in the composition at the pore walls and in the pore size distribution. Such a rate enhancement in the beginning of the thermal isomerization was also observed in polymer matrices and attributed to residual strain in the *cis*-azobenzene produced by UV irradiation.[30] In analogy with polymer matrices, in the sol–gel matrix a part of the cis isomer is produced in a strained conformation and can revert more easily to the trans isomer than the relaxed cis species. The low rate of reaction, at 60 °C in the terminal phase of the thermal isomerization in the sol–gel film may be ascribed to the interaction between MHAB molecule and the silica matrix (e.g., the hydrogen bond between MHAB and silanol groups).

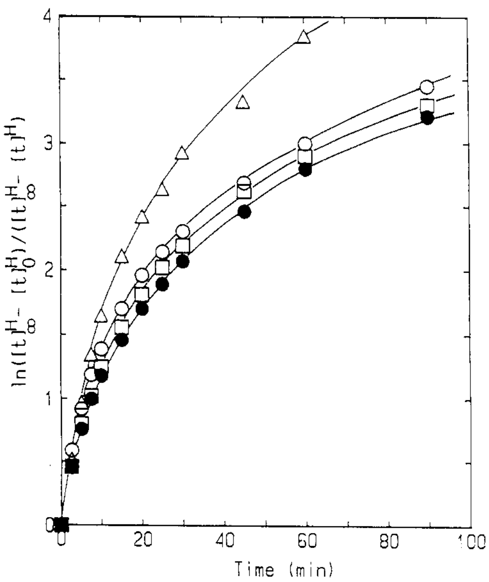

Figure 5. Preparation condition dependence of the first-order plots for thermal cis → trans isomerization of MHAB in sol–gel films at 60 °C. The preparation conditions were as follows: (●) solution A, heating condition: 110 °C, 15 h. (○) solution A, heating condition: 60 °C, 2 h. (△) solution B, heating condition: 60 °C, 2 h. (□) solution C, heating condition: 60 °C, 2 h.

These results, in conjunction with the composition of the photostationary state, suggest that MHAB in the sol–gel glass contains three fractions. In the first the local free volumes are smaller than a critical size necessary for the photoisomerization. In the second fraction the reaction can take place but the produced cis isomer is in a strained conformation. In the third fraction the reaction rate is lower than in solution because of the interaction between MHAB and the silica matrix.

Dependence of the Matrix Rigidity on the Preparative Method. The sol–gel process is composed of two reactions, the hydrolysis of metal alkoxides and polycondensation. These reactions are influenced markedly by the preparative conditions (e.g., preparation composition, catalyst (acid/base), reaction temperature, etc.)[1–5] and determine the matrix rigidity of sol–gel glasses. Brinker and his colleagues[31] have studied the hydrolysis and condensation to give a silica gel made by a two-step process.[32] The first step consists of hydrolysis under acidic condition (pH = 0.3) with the reactants added in a molar ratio of TEOS/alcohol/H_2O/HCl = 1/3/1/0.0007. This causes a rapid hydrolysis, but the reaction cannot go to completion because of the substoichiometric quantity of water, resulting in the formation of lightly cross-linked polymers. The second step (additional water plus acid) resulted in completely hydrolyzed polymers. As given in Table I, the cis fraction at the photostationary state depends on the water content. Although the cis fraction is low when $[H_2O]/[TEOS] \geq 2$, the content of water ($[H_2O]/[TEOS]$

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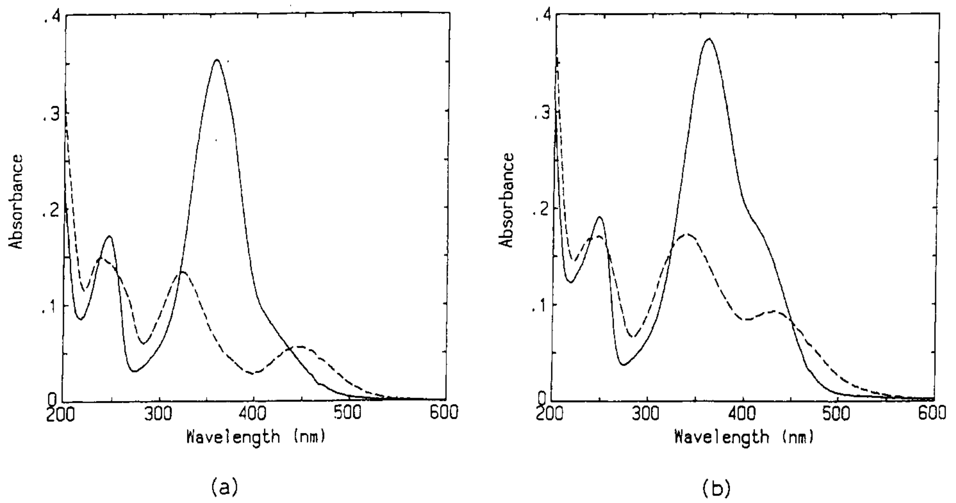

Figure 6. Absorption spectra of MHAB: (a) (—) in a sol–gel film (solution B, heating condition: 60 °C, 2 h) and (- - -) after prolonged irradiation with a UV light; (b) (—) in a sol–gel film (solution C, heating condition: 60 °C, 2 h) and (- - -) after prolonged irradiation with a UV light.

= 1) favors the cis-isomer formation.

The thermal isomerization is also affected by the water content. Figure 5 shows first-order plots for the thermal cis to trans isomerization of MHAB in the sol–gel films at 60 °C under various preparative conditions. Films prepared under different heating conditions (● and ○), exhibited almost the same thermal isomerization reaction rates, suggesting that the matrix rigidity in the sol–gel glasses prepared from solution A is scarcely altered by changing the annealing condition. However, in the sol–gel film prepared from solution B, the first-order (△) is different from the others, i.e., the reaction rate of MHAB in the sol–gel film prepared from the low water content solution is higher.

The gel formed from a solution with such a low water content is weakly cross-linked and linear polymeric in nature since the hydrolysis reaction does not proceed to completion.[32–34] Consequently, the sol–gel film prepared from solution B, may have a more weakly cross-linked structure leading to effective cis–trans isomerization.

Absorption spectra of MHAB in the sol–gel films prepared from solution B and solution C are shown in Figure 6. The solid lines and dotted lines show the spectra of the trans form and the photostationary state, respectively. The shape of the absorption spectra of the trans form in the sol–gel film prepared from solution B is quite similar to that in ethanol (Figure 2a). The shoulder arising from the formation of hydrogen bond between the azo group in MHAB and silanol group in silica matrix is scarcely recognized. Under such a low water concentration condition a large quantity of residual Si–OC_2H_5 groups remains on the surface of silica matrix.[35] The trans-to-cis photoisomerization goes almost to completion since the silica matrix may be weakly cross-linked. However, in the case of the sol–gel film prepared from solution C, the final cis fraction is lower because of the highly cross-linked structure formed after complete hydrolysis (Figure 6b). In Figure 5, the first-order plot of MHAB in the sol–gel film prepared from solution C (□) is similar to that in the sol–gel film prepared from solution B (○). This is probably because the total reaction of the sol–gel process is insensitive to a $[H_2O]/[TEOS] > 2$.

Conclusion

The following conclusions can be drawn about the isomerization behavior of the azobenzene derivative in the sol–gel films:

(1) Hydrogen bonds are formed between the azo group in azobenzene probe and silanol group in sol–gel glass matrix whose films were prepared with a relatively high water concentration ($[H_2O]/[TEOS] \geq 2$).

(2) The azobenzene probes in the sol–gel glass are of three types when the glass is prepared from a solution of $[H_2O]/[TEOS] = 2$. (a) At sites with smaller pores in which the trans-to-cis photoisomerization is quenched, (b) at sites in which the cis isomer is formed in a strained conformation enhancing the thermal reversion, (c) at sites in which the thermal reversion rate is reduced by the hydrogen bond between the guest molecule and silanol groups.

(3) The rigidity of the matrix in sol–gel glass depends on the water content of the solution from which it was prepared. In the case of $[H_2O]/[TEOS] = 1$, the photoisomeriation takes place readily in a sol–gel film possibly because of inefficient network formation.

Registry No. MHAB, 144225-85-4; TEOS, 78-10-4; PMMA, 9011-14-7; H_2O, 7732-18-5; SiO_2, 7631-86-9.

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