Photochemical and Thermal Isomerization of Azobenzene Derivatives in Sol–Gel Bulk Materials

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Marked differences in properties of sol–gel silica between bulk materials and thin films was revealed by using azobenzenes as reactive probe molecules. Three types of sol–gel bulk materials and sol–gel films doped with azobenzene chromophores were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of 4-methoxy-4′-(2-hydroxyethoxy)azobenzene (MHAB), 4-methoxy-4′-[*N*-(3-(triethoxysilyl)propyl)carbamoylmethoxy]-azobenzene (MTAB), and 4,4′-bis[*N*-(3-(triethoxysilyl)propyl)carbamoylmethoxy]azobenzene (DTAB), respectively. Azobenzenes were initially protonated by hydrochloric acid as a hydrolytic catalyst, and the deprotonation took place during the drying process to form sol–gel glasses in a bulk system much more slowly than in a film-forming process. The trans–cis photoisomerization of the azobenzenes in the sol–gel bulk materials were traced spectroscopically to compare with those in sol–gel silica films prepared from the same solutions and in poly(methyl methacrylate) (PMMA). The results implied that the pores in the sol–gel bulks are larger than those in the sol–gel films. The cis-to-trans thermal isomerization of MHAB in a sol–gel bulk obeyed first-order kinetics in a rate similar to that of the solution chemistry, whereas the isomerization in a glass film deviated from the first kinetics, indicating that the rate retardation due to steric factors plays no essential role in the bulk matrix. The steric constraint due to the matrix decreased in the following order: sol–gel films > PMMA > sol–gel bulks.

Introduction

The so-called sol–gel process provides various inorganic oxide glasses without melting.[1–4] In this process, metal alkoxides hydrolyze at relatively low temperature to form porous gel glasses, which are then transformed into dense glasses by sintering. There are two methods to yield metal oxide glasses doped with organic molecules. The first consists of putting a thin layer of a sol–gel solution on a substrate to form a thin film, followed by drying for a relatively short period, whereas bulk glasses are formed by the second method in which a sol–gel solution is slowly evaporated at ambient temperature to give a monolithic glass preventing crack formation.

Aside from their use, the porous glass (xerogel) obtained by this process is of particular interest because of its ability to encapsulate organic and organometallic molecules in inorganic matrices.[5–8] Brinker et al. have studied the differences in the structure and properties between sol–gel bulk material and sol–gel thin film utilizing gas adsorption on surface acoustic wave substrate and showed that the structure of films is considerably more compact than that of the bulk xerogels prepared from identical precursors.[9–11] Several studies were concerned with the photophysical properties of organic dye molecules in bulk glass and thin film.[12–14] However, there have been few systematic investigations to reveal the difference in chemical behavior of the doped organic molecules ascribed to the microstructural differences between the bulks and the films.

We studied previously the photoinduced trans–cis isomerization and thermal cis–trans isomerization of azobenzene derivatives in sol–gel silica films,[15,16] taking account of the fact that this type of photochromic compound is sensitive to the microenvironment and

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extensively employed as a photoreactive probe to estimate the free volume and rigidity of solid polymers.[17–23] The results are summarized as follows: (1) The cis fraction of a photostationary state in a sol–gel film was much smaller than in poly(methyl methacrylate) (PMMA), an organic glass, suggesting that the free volume in sol–gel silica films is smaller than in PMMA films.[15] (2) In a sol–gel film, attachment of the chromophore to silica through a single covalent bonding had slight effect on photochemical as well as thermal isomerizations, whereas the photoisomerization was markedly suppressed when an azobenzene is fixed to the silica matrix at both ends of the chromophore.[16] The major concern of this paper is to disclose outstanding differences in microenvironmental structures between a silica bulk and a silica film by means of evaluating the reactivity of doped azobenzenes as probe molecules.

Experimental Section

Materials. Tetraethyl orthosilicate (TEOS), purchased from Tokyo Kasei Kogyo Co., was used without further purification. Ethanol, diethyl ether, dimethyl sulfoxide (DMSO), and water were of spectroscopic grade. 4-Methoxy-4′-(2-hydroxyethoxy)azobenzene (MHAB), 4-methoxy-4′-(*N*-(3-(triethoxysilyl)propyl)carboxymethoxy)azobenzene (MTAB), 4,4′-bis-(*N*-(3-(triethoxysilyl)propyl)carbamoylmethoxy)azobenzene (DTAB), poly (methyl methacrylate) (PMMA) films, and sol–gel films doped with these azobenzene probes were prepared according to a previous paper.[16] The thickness of the sol–gel film was calculated to be ca. 200 nm with use of absorbances of the azobenzenes under the following assumptions; all TEOS is converted into silica, the density of the film is 2.0, and the absorption coefficient of azobenzenes are not affected by embedding. Monodisperse silica particles (a BET surface area: 48 m^2, particle diameter: 150 nm) were obtained from Tokuyama Soda Co. Ltd.

Sample Preparation. *Sol–Gel Process.* The composition to prepare sol–gel bulks by the hydrolysis of TEOS catalyzed by hydrochloric acid in ethanol was the same as a film-coating solution described in our previous report (TEOS:H_2O:ethanol = 1:2:3 in molar ratio).[15,16] MHAB, MTAB, and DTAB were dissolved in ethanol at 7.0×10^{-5} mol/L, respectively. The mixtures were stirred for 2 h at room temperature. Subsequently, a 10 mL portion of each mixture was poured into a flat Petri dish (inner diameter 42 mm; height 23 mm), the surface of which was treated with octadecyltriethoxysilane in advance. The Petri dishes were covered with an aluminum foil and left to gel at room temperature for 3 days. After gelation the aluminum foil was perforated with a few holes (diameter 1 mm) and then with additional holes on subsequent days. After 30 days, the bulk gels were heated at 60 °C for 24 h and at 110 °C for 30 h to give monolithic crack-free bulk samples containing the azobenzene derivatives (diameter 27 mm, thickness 1.2 mm).

Physisorption of MHAB on the Surface of Silica Particles. The physisorption of MHAB on the surface of silica particles was carried out as follows: To a dispersion of the silica particles (0.50 g) in chloroform (25 mL) was added 218 mg of MHAB, and the mixture was stirred for 1 h at room temperature. After being centrifuged, the supernatant was discarded. The residual colloidal silica was repeatedly washed with cyclohexane and dried at 60 °C under vacuo for 10 h. The amount of physisorbed MHAB was determined by means of electronic absorption measurement using the absorption coefficient of MHAB = 21 000 M^{-1} cm^{-1} at 354 nm. An average density was estimated to be one MHAB molecule in 600 Å^2 on the silica surface.

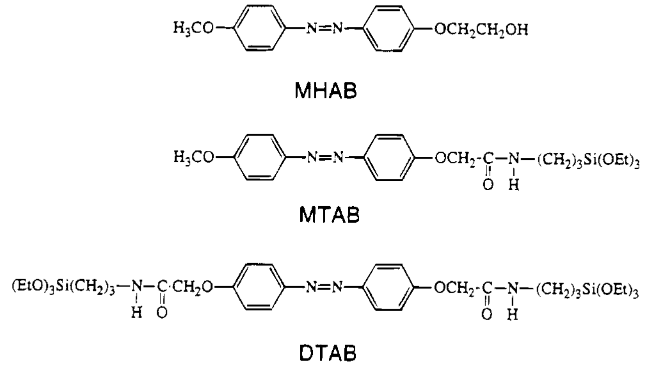

Figure 1. Chemical structure of azobenzene derivatives.

Chemisorption of MTAB on the Surface of Silica Particles. Chemisorbed MTAB silica particles were prepared by the reaction of MTAB with surface silanols of silica particles according to the method of Horner et al.[24] with a silight modification. To a dispersion of the silica particles (0.50 g) in dry benzene (15 mL) was added 539 mg of MTAB, and the mixture was refluxed for 48 h. After centrifugation, the supernatant was discarded. Residual silica particles were washed repeatedly with benzene and methanol and dried at 60 °C in vacuo for 10 h. An average density of the azobenzene was one MTAB molecule in 500 Å^2 on the silica surface.

Measurements. For the trans–cis photoisomerization, a sample was irradiated at 365 nm by using a Jasco CRM-FA irradiator equipped with a 2-kW xenon arc lamp and a monochromator at room temperature. Absorbance measurement was made on a Hitachi UV-320 spectrometer. Azo-modified silica particles were dispersed in cyclohexane because of the good refractive index matching. The thermal cis–trans isomerization was carried out at 60 °C and followed spectroscopically at the same temperature.

Results

Absorption Spectral Changes during Drying Process. Three types of azobenzene having the same chromophoric system were incorporated in silica glass to survey the effect of covalent attachment on the photoactive probe behavior to obtain microstructural information of bulk silica matrices (Figure 1). Ethanolic solutions of TEOS and the corresponding azobenzene were acidified by hydrochloric acid to result in the hydrolysis and subsequent gelation, followed by gradual evaporation of solvents to yield gelled silica in the conventional way. The solutions turned red on acidification due to the protonation of the azobenzene which is a very weak base (p$K = -2.95$ for *trans*-azobenzene).[25] Figure 2 shows the change in absorption spectra of MHAB as a typical example in a bulk system during the drying process. The bulk sample possesses absorption maximum (λ_{max}) at 499 nm assignable to the protonated form even after heat treatment at 60 °C for 24 h. Upon additional heating at 110 °C for 30 h, the color of the sample became light yellow, and λ_{max} was shifted to 353 nm, indicating the completion of the deprotonation.

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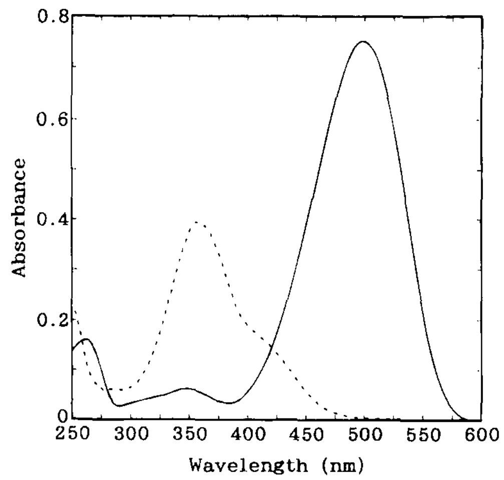

Figure 2. Change in absorption spectra of MHAB during drying stage of a sol–gel bulk: heating at 60 °C for 24 h (—) and then additional heating at 110 °C for 30 h (- - -).

For comparison, silica glass films doped with the azobenzenes were prepared by use of the same solutions according to the so-called dip-coating technique.[15,26] A quite different color change behavior was observed for sol–gel films. Although a thin silica film coated on a quartz plate by means of the dip coating method was red, the color turned light yellow within 10 min when the plate was heated at 60 °C. Actually, the absorption spectrum of the thin film was superimposed upon that of a free azobenzene after heating at 60 °C for 2 h.[15]

Trans–Cis Photoisomerization in Bulk Glasses. After confirming the formation of free base azobenzenes by heat treatment, monolithic bulk plates were exposed to UV light at 365 nm. Figure 3a shows the spectral change of MHAB in a bulk glass. MTAB gave a similar result, implying that a single covalent attachment of the azo chromophore plays no role in the photoisomerizability. In contrast to our previous observation that the photoconversion into the cis isomer is restricted in a sol–gel film, the transformation of the trans isomer in the bulk glass took place quite efficiently without any disturbance. This suggests that the azo chromophores are not incorporated in the silica network but rather localized on walls of porous structures to ensure free volumes for the molecular structural changes. To confirm this assumption, MTAB and MHAB were treated with colloidal silica particles to cover the silica surface with the azobenzene chromophore physically as well as chemically and to review the photoisomerizability. Monodisperse colloidal silica of a diameter of 150 μm was employed because of the large surface area to adsorb a sufficient amount of the chromophore and the availability of a transparent dispersion in cyclohexane owing to good refractive index matching which enabled us to carry out spectroscopic analysis.

Parts b and c of Figure 3 show the absorption spectra of dispersions of colloidal silica particles physisorbed with MHAB and chemisorbed with MTAB respectively before and after UV irradiation. The n–π* transition of the azobenzene chromophores adsorbed on silica particles is blue-shifted so that the absorption band appears as a shoulder at around 420 nm. The blue shift is ascribed to hydrogen bonding between the azo group and silanols and/or water molecules on the silica surfaces.[27] The absorption spectral shapes of the colloidal silica bear a close resemblance to that of the bulk (Figure 3a). Therefore, the azobenzenes on silica particles are intimately adsorbed on the surface since the blue shift is observed even in the nonpolar cyclohexane.

Furthermore, the n–π* absorption of the forbidden transition is enhanced in these cases when compared with solution spectra. As discussed in our previous paper,[16] the increase in the n–π* absorption coefficient can be reasonably explained in terms of the distortion of the azobenzene moiety which leads to the mixing of forbidden n orbitals with allowed π-orbitals. In other words, the ratio of the n–π* absorbance (A_n) to the π–π* absorbance (A_π) can be assumed to be a measure of the extent of molecular distortion of azobenzene chromophoric systems. Although A_n values involve a certain inaccuracy because of the overlap with A_π, the absorbances at 420 nm were employed for A_n values for semiquantitative discussion. The absorbance ratios (A_n/A_π) for the bulk, physisorbed particles and chemisorbed particles were 0.42, 0.31, and 0.26, respectively. These values imply that the molecular distortion due to the surface adsorption appears most markedly in the bulk glass, whereas the chemisorbed chromophore seems to be distortion-free since the A_n/A_π value equals to that in a solution of 1:9 mixture of ethanol and water.

As shown in parts b and c of Figure 3, the trans–cis photoisomerization of azobenzene chromophores on the silica particles went almost to completion without being affected by the strong adsorption on the surface. This means that the photoisomerization of the azobenzene immobilized in silica matrices takes place readily as long as the azo chromophores are bound on the wall of porous silica sol–gel bulk matrices.

Thermal Isomerization. To obtain further information on the mobility of the azobenzene moieties in the bulk glasses, we studied the kinetics of the thermal cis-to-trans isomerization. The thermal cis–trans isomerization is expressed by first-order kinetics according to the following relation:

$$\ln\frac{A^{H}_{\infty} - A^{H}_{0}}{A^{H}_{\infty} - A^{H}_{t}} = Kt \qquad (1)$$

where K is the rate constant for the thermal isomerization. A^{H}_{0}, A^{H}_{t}, and A^{H}_{∞} are observed absorbances in the peak of the π–π* band of the respective trans isomers at subscript times. These absorbances are substantially proportional to concentrations of the trans isomer in view of the low extinctions of the corresponding cis forms at the monitoring wavelength.

In a DMSO solution, the reaction proceeds by first-order kinetics and the slopes (K) of three azobenzene derivatives were the same.[16] First-order plots for the thermal isomerization of three azobenzenes in PMMA films and in the sol–gel bulks and films at 60 °C are shown in Figure 4. In PMMA films, the shapes of the plots are similar with regard to all three probes. The reaction deviates from a straight line gradually with time, and the degree of the rate reduction is in the following order; MHAB < MTAB < DTAB (Figure 4a).

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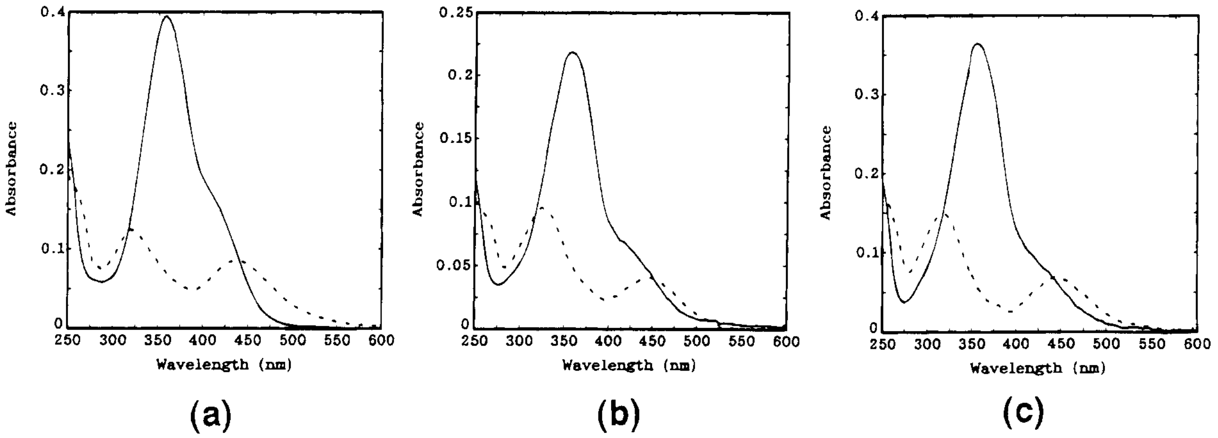

Figure 3. Absorption spectra of azobenzenes: (a) MHAB in a sol–gel bulk; (b) MHAB physisorbing on the surface of silica particles in cyclohexane (concentration: 0.83 g/L); (c) MTAB chemisorbing on the surface of silica particles in cyclohexane (concentration 1.0 g/L). Solid lines and broken lines indicate before and after prolonged irradiation with a UV light, respectively.

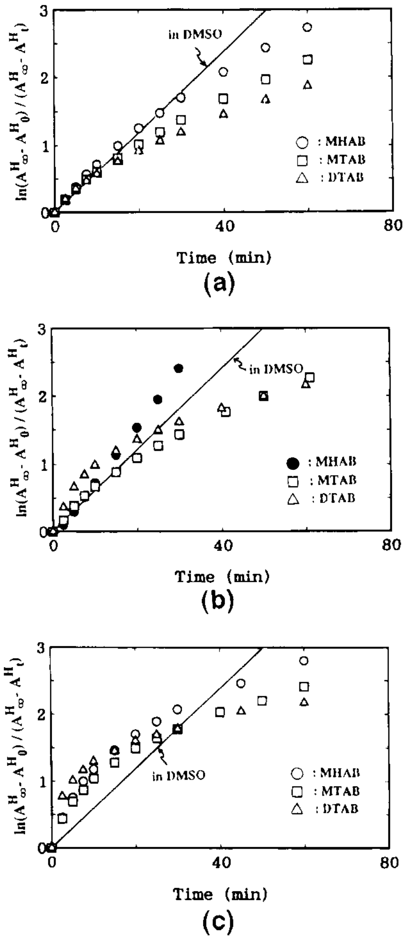

Figure 4. First-order plots for the thermal cis-to-trans isomerization of azobenzene derivatives at 60 °C: (a) in PMMA; (b) in sol–gel bulks; (c) in sol–gel films. The straight solid lines are plots in DMSO. Experimental errors are within the symbols.

The results suggest that the thermal cis–trans isomerization can be retarded by the steric restriction of PMMA matrix. This reduction order can be explained in terms of the size of the sweep volume required for the thermal cis–trans isomerization (MHAB < MTAB < DTAB). On the other hand, a different behavior of the rate between the derivatives was observed in sol–gel bulks (Figure 4b). The reaction of MHAB follows first-order kinetics just as in solution, which implies that the isomerization is not affected by a matrix of sol–gel bulk. While the rate of MTAB slows down with time, the isomerization of DTAB proceeds faster than in solution in the beginning and decreases after that.

Discussion

The n–π^* transition absorption band afforded a 2-fold information concerning microenvironmental polarity and location of the chromophore. As stated above as well as previously,[16] a considerable blue shift of the absorption band indicates hydrogen bond formation of the azo group. Furthermore, the enhancement of the blue-shifted absorbance in the bulk matrix may reflect the strong adsorption of the azo chromophore on walls of highly porous silica.

Some reports dealt with the photochromic behavior of a fulgide and spiropyranes in sol–gel bulk.[28–32] However, these photochromic compounds seem to be inappropriate to estimate the rigidity of the matrix since the molecular movement associated with these 6π electrocyclic reactions is very small and the photochromism of the spiropyrans is too markedly affected by the polarity of matrices. In this respect, for more detailed discussion based on the photochemical behavior of azobenzene as a photoprobe, the cis fractions in the photostationary state (f_{cis}) on the surface of silica and in the sol–gel bulks were estimated by using eq 2 and

$$f_{\mathrm{cis}} = \frac{1 - A/A_0}{1 - \epsilon_{\mathrm{cis}}/\epsilon_{\mathrm{trans}}} \tag{2}$$

summarized in Table 1. The f_{cis} values in sol–gel films and in PMMA obtained in our previous paper[16] are also listed in Table 1. A_0 and A stand for the absorbance at $\lambda_{\max}$ before and after UV irradiation whereas ϵ_{cis} and $\epsilon_{\mathrm{trans}}$ denote the molar absorption coefficients of the cis and the trans isomers at $\lambda_{\max}$, respectively.

As Table 1 shows, the trans–cis photoisomerization goes almost to completion even though azobenzene

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Table 1. Photochemical Conversion of Azo Compounds

	f_{cis} (%)			
species	PMMA	surface of silica particle[a]	sol−gel film	sol−gel bulk[a]
MHAB	93	87	60	91
MTAB	94	90	60	86
DTAB	95		42	66

[a] The experimental errors are within ±2%.

probes are adsorbed on the surface of silica. This suggests that the final cis fraction is affected predominantly by micropore size of the silica matrix. The cis fractions in a photostationary state of three azobenzenes in the sol−gel bulks are much larger than those of the corresponding azobenzenes in the sol−gel films. This implies that there are differences in the structure and properties between sol−gel thin films and sol−gel bulk materials; micropore size or free volume of the bulk material is markedly larger than that of the sol−gel film. There was no marked difference in the photoisomerizability between MHAB and MTAB in the sol−gel bulks. However, the cis formation was considerably reduced for DTAB, just as in the case of a sol−gel thin film. The suppression of the photoisomerizability is obviously ascribable to the fixation of both ends of the azobenzene chromophore to silica matrix through Si−O bondings. Such an effect was not observed in PMMA films in which DTAB is entrapped only physically.

Thermal isomerization analysis disclosed a striking feature of the bulk that the reaction of MHAB in a sol−gel bulk obeys first-order kinetics which is very close to that in the solution phase (Figure 4b). This result also, in conjunction with the photoisomer composition of the photostationary state, suggests that the pore of the sol−gel bulk is so large as to cause essentially no suppressive effect on the isomerization of the azobenzene molecules inside the silica cage. This is in decided contrast with the facts that the thermal isomerization deviates from the first-order kinetics not only in silica films but also in polymeric matrices including a PMMA solid unless the reactions are carried out above their glass transition temperatures. Unexpectedly, the rate was rather slightly higher than that in the solution. This may reflect the alteration of the molar extinction coefficient of the azo chromophore entrapped in the matrix to lead to a slight overestimation of the rate.

In sol−gel films, the nonlinear first-order plots of the cis−trans thermal isomerizations of MTAB were almost the same as those of MHAB (Figure 4c). On the other hand, in the sol−gel bulk materials, the rate for the thermal isomerization of MTAB differs from that of MHAB, and the rate deviated from the first-order kinetics and slowed down gradually with time. These results support the idea that the steric restriction due to smaller pores governs the reactivity in sol−gel films preferentially. Consequently, the reverse isomerization behavior of azobenzene moiety fixed in sol−gel films through a single covalent bond does not differ markedly from that of the chromophore fixed in sol−gel films at the both sides. Contrary to this, the isomerization behavior in the bulk materials is influenced by the fixation mode of the chromophore more evidently since the pores of the matrix are larger than those in sol−gel films so that the free molecular motion is considerably suppressed by attachment of the chromophore on a silica wall. The thermal isomerization of DTAB in the sol−gel bulk is initially faster than in a solution because the photogenerated cis isomer has a strained conformation[19] and decreases gradually with time. A similar phenomenon was observed for these azobenzenes in sol−gel films.

Several reports demonstrated the reason for the microstructural difference between bulk materials and thin films.[9−11] In the film-forming process, the rapid evaporation of solvents forces the chemical precursors into a close proximity with each other and accelerates the condensation reaction significantly. This causes the capillary pressure huge due to the small pores to cause further densification of the matrix.[33−35] The slow vaporization of the bulk systems, on the contrary, allows the structure to stiffen in the early drying stage so that the pores are larger and the capillary pressure smaller.[9−11] This is consistent with our experimental results. As mentioned above, spectroscopic changes clearly show that the evaporation process is much faster during film formation than during bulk formation. As a result, the structure of film becomes more dense than those of the corresponding bulk xerogel prepared from the identical precursor.

Conclusion

The behavior of azobenzenes as probe molecules in sol−gel silica matrix have revealed that bulk materials differ from silica films markedly in the following points.

(1) Azobenzene hydrochlorides, which are formed by protonation with hydrochloric acid from the hydrolysis of TEOS, are subjected to the deprotonation during the baking for drying of sol−gel silica. The deprotonation takes palce in bulk materials much slower than in sol−gel films.

(2) Comparison of absorption spectra of azobenzenes in bulk materials with those adsorbed on colloidal silica particles reveals that the probe molecules are adsorbed more strongly on the silica wall of bulk material so that the molecular frame is distorted although the free volume for the photoisomerization is sufficiently ensured.

(3) The first-order kinetics of the thermal isomerization of the photoinduced cis isomer reveals that the steric restrictions to suppress the molecular motion increases in the following order: sol−gel bulk < PMMA < sol−gel film. In particular it should be noteworthy that the cis-to-trans thermal isomerization of MHAB obeys first-order kinetics even though the probe compound is entrapped in solid bulk material, reflecting much larger free volumes in the sol−gel bulk silica matrix so that the isomerizations of the azo chromophore take place as readily as in solution. These may lead to a novel conclusion that reactions, at least unimolecular reactions, of organic molecules entrapped physically in bulk materials do not undergo suppressive effect caused by silica matrices.

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