Preparation and Photochromic Properties of Dye-Doped Aluminosilicate and ORMOCER Gels and Coatings

Code: F3

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Abstract. Aluminosilicate and ORMOCER gels and coatings containing photochromic dyes, 1, 3-dihydro-1, 3, 3-trimethylspiro-[2H-indole-2, 3′-[3H]-naphth-[2, 1–b][1, 4]-oxazine] (SO) and 1′, 8a′-dihydro-2′, 3′-dimethoxycarbonyl-spiro [fluorene-9, 1′-indolizine] (DHI), were prepared by the sol-gel method and the photochromic activity was monitored in the course of the sol-wetgel-xerogel transformation. The photochromic activity of the aluminosilicate gels decreases rapidly and even vanishes in the wetgel-xerogel stage while that of ORMOCER gels and coatings levels off in the early wetgel-xerogel stage at a reasonably high photochromic intensity with the colour-fading speed similar to that in ethanol and the photostability being considerably improved. The experimental results are discussed in terms of the matrix effect on photochromism of organic dyes.

Keywords: ORMOCER, organic dye, photochromism

1. Introduction

One of the most attractive advantages of the sol-gel method is the near-room temperature wet-chemical synthesis of gels. These gels offer encouraging possibilities for the incorporation of a wide variety of organic dyes. Although much less research work has been done on the photochromic dyes doped in sol-gel derived solid matrices as compared with those devoted to laser [1] and non-linear [2] dyes, the existing results published by several authors on spiropyranes (SP) [3–5] and 2, 3-diphenylindenone oxide (DPIO) [6] incorporated in gels of different composition, i.e. pure SiO_2, Al_2O_3–SiO_2 and ORMOCER show that the rigidity of the matrices has profound influence on the photochromic properties of the dyes. In a previous paper [7], we reported on the photochromic properties of spirooxazine (SO) dyes in ORMOCER gels and coatings with respect to the concentration dependence, temperature dependence and effect of heat treatment. It was found that ORMOCER derived from organically modified silanes is a promising matrix for SO dyes.

In the present work, two photochromic dyes, SO and DHI were incorporated in aluminosilicate gels derived from di-iso-butoxy-aluminoxy-triethoxysilane (ASE)

and in ORMOCERs using mixed organically modified silanes, $R'Si(OR)_3$, as starting compounds. The evolution of the photochromic activity was monitored during the sol-wetgel-xerogel transformation. The thermal decay rate (k) and photostability of SO in ORMOCER and ethanol were measured and compared. Our experimental results show promising prospects for photochromic dye-ORMOCER hybrid materials.

2. Experimental

The aluminosilicate samples were prepared via normal sol-gel route from ASE using isopropanol (i–PrOH) as solvent and with different volume ratios of H_2O: i–PrOH: ASE as shown in Table 1. At first, the H_2O–i–PrOH mixture was added dropwise to the ASE–i–PrOH mixture under vigorous stirring for 1h. Then the dye-in-ethanol solution was added slowly also under vigorous stirring. After an additional 1h-stirring the resultant sols were poured into polystyrene cells (10 × 10 × 45 mm) with stoppers and left to gel and age.

Ethyltriethoxysilane (ETES), Methyltrimethoxysilane (MTMS) and 3-Glycidoxypropyl-trimethoxysilane (GPTMS) were used as starting materials for the prepa-

Table 1. Composition, gelling time and relative hardness of aluminosilicate gels.

System	H_2O:i-PrOH:ASE (volume ratio)	H_2O:ASE (molar ratio)	C_{ASE} (mol/l)	Gelling time (h)	Hardness [8] (relative)
A1	1:4:1.6	12.5	0.67	20	< 31
A2	1:4:2.0	10.0	0.79	17	31
A3	1:2:4.0	5.0	1.58	24	170
A4	1:0:4.0	5.0	2.22	12	400

Table 2. Variation of ΔA_0 and $t_{0.5}$ (s) of SO and DHI (1×10^{-4} mol/l) in aluminosilicate gels.

Dye	System	Sol $t_{0.5}$	Sol ΔA_0	Fresh gel $t_{0.5}$	Fresh gel ΔA_0	14 days later $t_{0.5}$	14 days later ΔA_0	60 days later $t_{0.5}$	60 days later ΔA_0
SO	A_1	2.0	1.024	2.2	0.857	2.4	0.336	–	0
	A_2	–	–	–	–	2.8	0.138	–	0
	A_3	–	–	–	–	30.0	0.398	–	0
	A_4	–	–	–	–	36.0	0.156	–	0
DHI	A_1	108.0	1.538	156.0	1.210	192.0	1.073	588.0	0.351
	A_2	–	–	–	–	210.0	0.815	828.0	0.261
	A_3	–	–	–	–	372.0	0.115	1020.0	0.104
	A_4	–	–	–	–	228.0	0.056	280.0	0.021

ration of ORMOCERs. Ultrasonic stirring was employed in the early stage of hydrolysis-condensation reactions without any solvent. For the preparation of a sol equivalent to 0.1 mol SiO_2, appropriate amounts of ETES (or MTMS), GPTMS and water in the form of 0.1 N HNO_3 solution were first mixed in a plastic container ($\emptyset 30 \times 70$ mm) by magnetic stirring for ten minutes and then subjected to 20 kHz ultrasonic radiation supplied by a SONIFIER Model 450 ultrasonic device (Branson Ultrasonics CT) at a power of 200 W for 20 minutes. The sols thus prepared were cooled down to room temperature and about 8 wt% Triton X-100 was added, followed by the introduction of appropriate amounts of dye-in-ethanol solution and subsequent exposure to the open air under magnetic stirring. When a final volume of 20 ml was reached the sols became viscous and the containers were then capped.

Samples used for monitoring the evolution of photochromic intensity (ΔA_0) and half-life time ($t_{0.5}$) were prepared by pouring the viscous sols into polystyrene cells of 4 mm optical path and keeping them open to the atmosphere throughout the sol-wetgel-xerogel transformation process. Coatings of various thickness were also prepared from the viscous sols by spraying on slide glass substrates. They were used for kinetics and photostability studies.

An OMEGA 10/20 UV-VIS-NIR spectrophotometer was used to measure the absorption spectra. The apparatus used for the measurement of photochromism was described in our previous work [7]. Two He-Ne-lasers are used as probing beams, one (633 nm) is for SO, the other (545 nm) is for DHI. A Schoot UV pass filter UG5 is used to reduce the influence of heat from the Hg-lamp as the UV source. A CONATEX 9010 thermometer was used to measure the temperature of the samples in kinetics investigations.

3. Results and Discussion

3.1. Dyes in Aluminosilicate Gels

Table 1 gives the composition, gelling time and relative hardness [8] of the four aluminosilicate systems. ΔA_0 and $t_{0.5}$ of SO and DHI in these systems at different time after preparation are collected in Table 2. It turns out from these tables that (1) ΔA_0 decreases and $t_{0.5}$ increases with increasing ageing time for both SO and DHI in all four systems. The decrease of ΔA_0 of SO is much faster than DHI while the increase of $t_{0.5}$ of DHI is much greater than SO. The photochromic intensity of SO in all four gels disappeared within 60 days. (2) With the increase in the concentration of ASE, the decrease of ΔA_0 of DHI is more considerable than SO whereas the increase of $t_{0.5}$ of SO is more pronounced than DHI. It is well known that both SO and DHI undergo ring-opening reactions under UV ir-
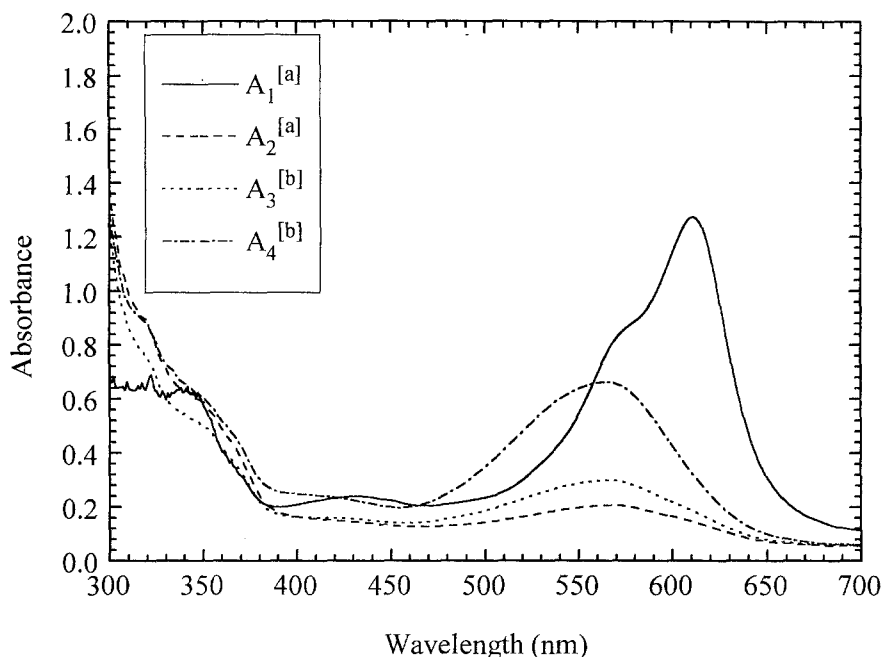
Fig. 1. Absorption spectra of SO (1×10^{-4} mol/l) in 14 day-old aluminosilicate gels (10 mm thick) after UV-irradiation (measured at ca. $-20°C^{[a]}$ or at R.T.$^{[b]}$).

radiation. These structural changes would encounter greater and greater steric hindrance during the ageing process of the gels due to the increase in the degree of condensation of the inorganic Al–O–Si network. As a result, fewer and fewer dye molecules are allowed to undergo photochromic transformation while the transformation speed is lowered, leading to decreased ΔA_0 and increased $t_{0.5}$. The harder the matrix, the greater the $t_{0.5}$ and the smaller the ΔA_0. In addition, the disappearance of the photochromic activity of SO after a 60-day ageing may also be associated with certain chemical reactions between Al in the matrices and O in the coloured form of SO molecules.

The variation of the absorption spectra of the coloured form of SO with the gel composition is shown in Fig. 1. Curve A_1 is typical of photoactivated SO and consists of two overlapping bands, an absorption maximum at 610 nm and a shoulder around 575 nm. These bands were ascribed to two merocyanine isomers which are in thermal equilibrium with each other [9]. In the other three curves, however, only the absorption maximum at 575 nm remains, the photochromic transformation associated with the 610 nm band has been completely blocked. This result can also be explained by the increase in relative hardness resulting from the increase in the concentration of ASE. The photochromic transformations associated with the 610

nm band requires a more flexible environment than that associated with the 575 nm band.

3.2. SO-ORMOCER Gels and Coatings

The utilization of GPTMS and MTMS (or ETES) as starting materials at appropriate molar ratios led to moderate gelling time (100 ~ 200 h) and volume shrinkage (around 50%), making it possible for us to monitor the evolution of the photochromic response of the dyes during the sol-wetgel-xerogel transformation process. Fig. 2 depicts the variation of ΔA_0 and $t_{0.5}$ of SO in a ETES-GPTMS ORMOCER as a function of time. It can be seen that: (1) ΔA_0 decreases rapidly in the initial stage, then continues decreasing but more slowly, and levels off in about one month after preparation. (2) $t_{0.5}$ increases in the early stage (< 100 h), then decreases and levels off much earlier than ΔA_0. These observations can be explained as follows: In the sol-wetgel stage the viscosity of the sol increases gradually due to the increase in the extent of condensation. As a result, on one hand, a greater and greater portion of dye molecules is more and more tightly confined and even completely blocked from undergoing colour change, so that the possibility of photochromic transformation decreases gradually in a statistical sense. On
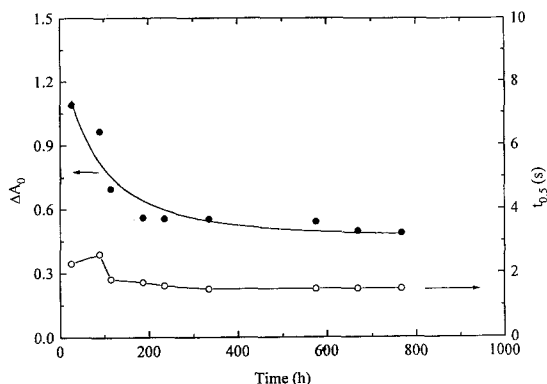
Fig. 2. Photochromic intensity (ΔA_0) and half-life time ($t_{0.5}$) of SO (2.5×10^{-3} mol/l) vs time during the sol-wetgel-xerogel transformation in an ETES-GPTMS ORMOCER gel (4.0 mm thick).
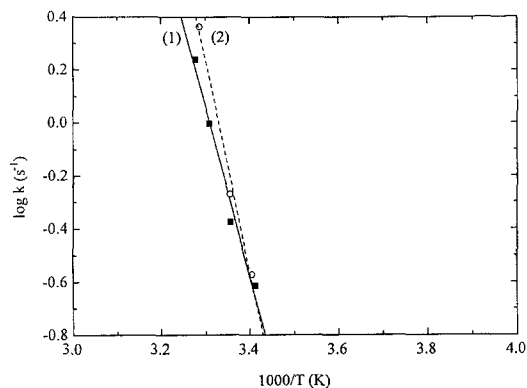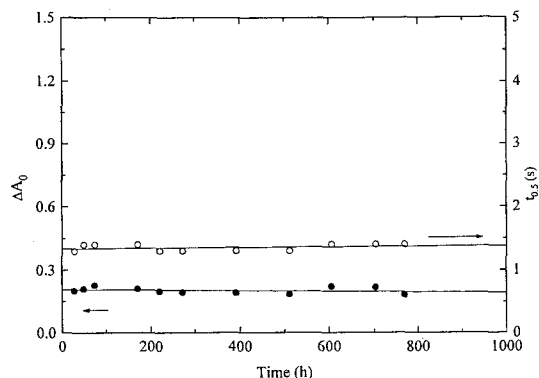

Fig. 3. Arrhenius plots of the colour-fading reactions of SO in (1) ethanol (1×10^{-4} mol/l, 10 mm-cell), (2) ETES-GPTMS ORMOCER gel (1×10^{-3} mol/l, 1.3 mm thick).

Fig. 4. Photochromic intensity (ΔA_0) and half-life time ($t_{0.5}$) of SO (2.5×10^{-3} mol/l) vs time during the sol-wetgel-xerogel transformation in a MTMS-GPTMS ORMOCER coating (0.2 mm thick).

the other hand, the fading speed of the coloured form of the dye decreases due to the increasing hindrance stemming from the viscosity increase. At the gelling point, a certain portion of dye molecules have been "killed"

and lose their photochromic activity. Only those caged in the pores in the gel remain photochromically active and these molecules are as free as in ethanol. Therefore, in the xerogel both ΔA_0 and $t_{0.5}$ reach a steady value. It is worth highlighting that both ΔA_0 and $t_{0.5}$ show no further decrease up to the present (4 months since preparation). From the Arrhenius plots of the colour-fading reactions shown in Fig. 3 it is clear that the thermal decay rate (k) of the coloured form of SO in ethanol and in ORMOCER gels has similar values indicating that the dye molecules in the ORMOCER gels are indeed as free as those in ethanol. This situation can occur only when the dye molecules are caged in the pores whose sizes are large enough to allow the photochromic transformation to take place as quickly as in ethanol.

The variation of ΔA_0 and $t_{0.5}$ of SO in a MTMS-GPTMS ORMOCER coating (0.2 mm thick) is shown in Fig. 4. It can be seen from this figure that the early sol-wetgel stage is so short that one can hardly distinguish it from the wetgel-xerogel stage. Linear fitting of the experimental data of ΔA_0 and $t_{0.5}$ leads to straightlines parallel to the abscissa. This is because evaporation of alcohol from a coating is much faster than from a thick gel. Comparing Fig. 2 and Fig. 4 it can also be found that the photochromic intensity (ΔA_0) of the 0.2 mm-thick coating is approximately half that of the 4 mm-thick gel sheet, although both the dye concentration and the UV intensity are the same. It was noticed during the UV-irradiation experiments that photochromic reaction occurs only within a depth of less than 2 mm from the surface of a thick gel sheet. This is the reason for the above observation.
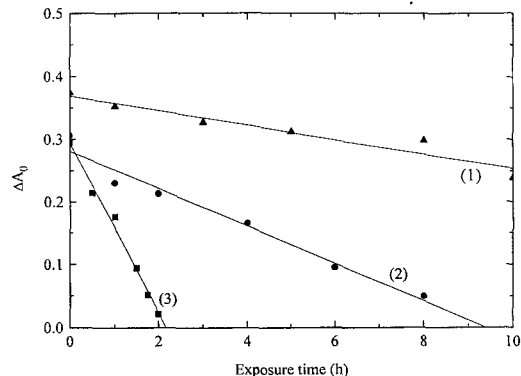

Fig. 5. Photochromic intensity (ΔA_0) of SO vs UV-exposure time in (1) ETES-GPTMS ORMOCER gel (1×10^{-3} mol/l, 1.4 mm thick), (2) ETES-GPTMS ORMOCER gel (1×10^{-3} mol/l, 0.9 mm thick) and (3) ethanol (2×10^{-4} mol/l, 4 mm-cell).

The photostability of SO in ethanol and ORMOCER coatings was tested using a Hg-lamp as UV source at an intensity of 30 mW/cm². The decrease of ΔA_0 with UV-exposure time is shown in Fig. 5. It is obvious that considerable improvement is achieved by trapping the dye in ORMOCER coatings. The thicker the coating, the greater the improvement. This is because the surface layer of a thicker coating screens the sublayer from UV-exposure.

4. Conclusions

For the SO and DHI dyes incorporated in aluminosilicate gels, the photochromic intensity decreases and half-life time increases with increasing ageing time and concentration of ASE. Especially in the case of SO, the photochromic intensity vanishes within 60 days and the shape of the absorption spectra of the coloured form changes with the concentration of ASE, too. The situation is much better with SO-ORMOCER gels and coatings. Although the photochromic intensity decreases in the sol-wetgel stage it level off during the wetgel-xerogel process and remains almost unchanged for over 4 months. The colour-fading speed is similar to that in ethanol while the photostability is considerably improved. This suggests promising prospects for the photochromic dye-ORMOCER hybrid materials.

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