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Photochromism of spiropyran and diarylethene-doped silica gels prepared by the sol–gel process

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Spiropyran and diarylethene were doped in silica gels which were prepared from $Si(OCH_3)_4$ and $Si(OC_2H_5)_4$, respectively, and their photochromic properties were compared. In the gels, both organics are incorporated with open modifications and show the photochromism between red and colourless modifications. The closed form of spiropyran, which is converted from the open one by irradiation with light, is thermally backed into the open form after the light is blocked. The activation energy of thermochemical reaction is 0.86 eV. Diarylethene shows no thermochemical reaction below 140 °C, but shows a photochemically reversible change on alternate irradiation by light of 436.5 and 578 nm.

1. Introduction

The sol–gel method is a low-temperature route widely used to obtain inorganic glasses and ceramics. One of the most promising directions of this process is to incorporate organic molecules into inorganic materials. The incorporated organic molecules can be used to probe the structure changes at a molecular level occurring in the sol–gel process; for example, polymerization, ageing and drying of the gel. This method also opens up the possibility for new applications of organic–inorganic hybrid materials, such as optical memories, dye lasers or photochromism, etc. Since Avnir *et al.* [1] first reported the preparation of silica gels doped with organic dyes, several studies have been carried out using organic molecules which induce the new optical properties in the materials [2–11]. Among the many organic compounds, spiropyran is one of a fascinating group of molecules showing photochromism. Photochromism in spiropyran and its derivatives is generally supposed to involve the reversible change between the open and closed structure of the pyran ring. We recently reported photochromism in spiropyran-doped silica and aluminosilicate gels, which were prepared by hydrolysis of silicon and aluminium alkoxides under acid conditions [12]. Spiropyran incorporated with the open modification in a gel exhibits an optical absorption band with peaks at 405 nm and in the ultraviolet ranges. Upon irradiation by visible light, the open form of spiropyran transforms into the colourless closed form. In addition to the photochemical reaction, a structure change of spiropyran is also activated thermally. This thermal fatigue reaction might limit the use of these materials to practical applications. Irie and Mohri recently synthesized diarylethene derivatives which were more stable than spiropyrans at 80 °C [13]. Work to develop very thermally stable compounds is important in order to utilize an inorganic matrix with high stability.

In this work we studied the photochromism of spiropyran- and diarylethene-doped silica gels. Coloured modifications of these organics are red; their absorption spectra have peaks at 515 and 535 nm, respectively. Compounds activated at long wavelength are desirable for use as laser lights. The photochromic properties, including thermal stability, are compared for both organics in the gel.

2. Experimental procedure

2.1. Sample preparation

The spiropyran and diarylethene chosen as photochromic compounds are 1,3,3-trimethylindolino-6′-nitrobenzopyrylospiran and *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene, respectively (Tokyo Kasei Kogyo). The gel matrices were prepared from $Si(OCH_3)_4$, (TMOS) and $Si(OC_2H_5)_4$, (TEOS). The TMOS was first hydrolysed with a solution of H_2O and CH_3OH each with the molar ratio of 1 mol/mol TMOS. No catalyst was used for the hydrolysis of TMOS. After this solution was stirred for 1 h, spiropyran dissolved in CH_3OH was added, of which concentration was 1×10^{-4} mol/mol metal alkoxide, and then stirred for 1 h at room temperature. In the case of incorporation of diarylethene, TEOS was used instead of TMOS. TEOS was hydrolysed with a solution of H_2O, C_2H_5OH, and HCl of which molar ratios 1, 1, and 0.0027 mol, respectively. The resultant homogeneous solutions were poured into polystyrene cuvettes and left covered for 1 week to form a stiff gel. After gelling, the gel was further dried for 2 weeks without cover. The gel was in the form of a disc about 0.5 mm thick, and was kept in the dark before measuring the absorption spectra.

2.2 Photochromic measurements

The gel, placed in a Jasco U-best 50 optical spectrophotometer, was irradiated with near ultraviolet and visible lights using an Ushio 500 W super-high-pressure mercury lamp through optical band-pass filters.

3. Results and discussion

3.1. Structure changes of organics and their photochromism

Photochromic compounds change the structures between open and closed ring modifications upon irradiation with lights. Three modifications of spiropyran are known in organic solvents, as shown in Fig. 1. In alchohol solvents, spiropyran is converted into a red-coloured form (B) from a colourless one (A) with closed-ring structure by irradiation of light. Another kind of yellow-coloured form (C) is stabilized when acid is added into a solution of forms (A) and (B). Forms (B) and (C) are converted back into the colourless form (A) by irradiation with light. These modifications are applicable to the interaction with gels. Spiropyran is a polar molecule, the modifications of which are strongly influenced by the polarities of the matrices. In a previous study, spiropyran was doped in gels prepared by the hydrolysis of TEOS under acid conditions [12]. In these conditions, form (C) is stabilized and the photochromic act is the structure change between forms (A) and (C) by irradiation with ultraviolet and visible lights. However, TMOS was used instead of TEOS in this study. The fast hydrolysis rate of TMOS makes hydrolysis possible without using an acid catalyst. Spiropyran is incorporated with form (B), in which the O^- radical is stabilized by strong hydrogen bonds to the silanols of the silica gels. Fig. 2 shows the colour spectra of spiropyran-doped gel before and after irradiation with 436.5 nm light. The spectrum before irradiation is composed of three absorption bands peaking at 515, 360, and < 300 nm, and the gel is coloured red. Upon exposure to light at 436.5 nm, the spectrum is dominated by a single band, decreasing at 515 nm, though there is little change in the other bands. The change in the absorption coefficient, $\Delta\alpha$, at 515 nm on irradiation was examined using various band-pass filters of 365–578 nm, and the results are also shown in the inset of Fig. 2. Spiropyran is sensitive to lights of a wide visible range peaking around 500 nm.

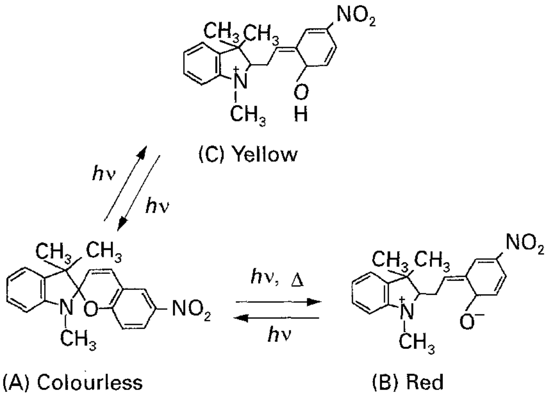

Figure 1 Photochromic modifications of spiropyran used in this study.

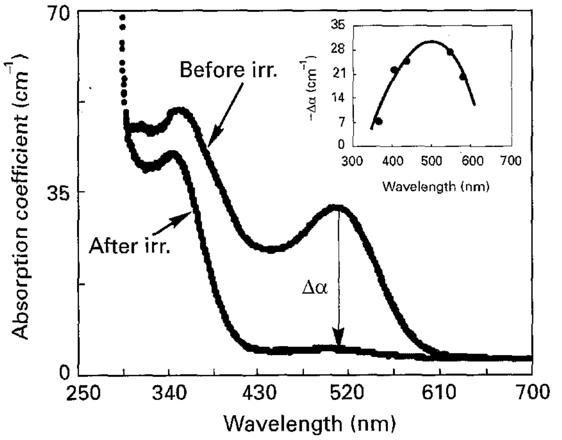

Figure 2 Absorption spectra of spiropyran-doped silica gel before and after irradiation with a mercury lamp through a band-pass filter of 436.5 nm. The inset shows the change of absorption coefficient at 515 nm after irradiation with 405–545 nm of the mercury lamp, the intensity of which was not corrected.

The molecular structures of diarylethene are given in Fig. 3. Photochromism in diarylethene is based on the reversible change between open (A) and closed (B) modifications. The gel doped with diarylethene is transparent and colourless and does not become coloured as long as storage is in the dark. These results indicate that diarylethene is stabilized with the form (A) in the gel structure. The reason for this must be related to the chemical bonds containing no O^- or OH groups in diarylethene. Fig. 4 shows the absorption spectra of gel before and after irradiation by

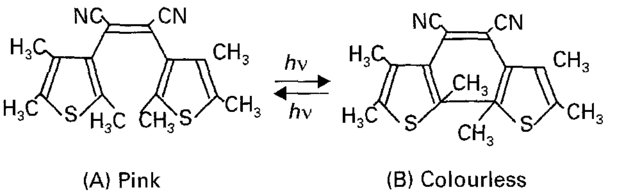

Figure 3 Photochromic modifications of diarylethene used in this study.

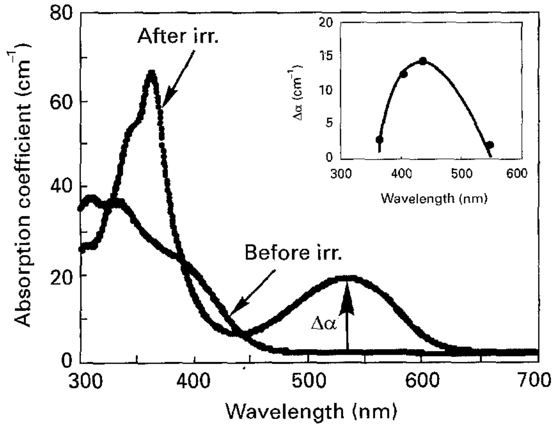

Figure 4 Absorption spectra of diarylethene-doped silica gel before and after irradiation with a mercury lamp through a band-pass filter of 436.5 nm. The inset shows the change of absorption coefficient at 535 nm after irradiation with 405–545 nm of a mercury lamp, the intensity of which was not corrected.

436.5 nm light. The spectrum of the gel doped with form (A) of diarylethene shows absorption in the ultraviolet range starting at ~450 nm. Upon exposure to light the colour is turned to pink, and the spectrum is dominated by bands increasing at 370 and 535 nm. The photochromic gap ($\Delta\alpha$) at 535 nm is most pronounced by irradiation of 405 to 436.5 nm, which are near to the absorption edge wavelength (see inset of Fig. 4).

3.2. Stability of photochromism

A common observation for many photochromic compounds is that turning off the light allows isomerization back to other form gradually at room temperature. This photochromic fatigue is a serious problem for practical applications. Fig. 5 shows an example of absorption spectra around 515 nm for spiropyran during storage in the dark at room temperature (15 °C) after light of 436.5 nm is blocked. It is apparent that absorbance gradually increases as the time increases. The rate of colour recovery becomes faster as the temperature increases and the colour development is completed in 10 min at 70 °C.

In the reaction shown in Fig. 1, the rate of conversion from (A) to (B) can be written as

$$dI/dt = \kappa\,(I_0 - I) \tag{1}$$

where I_0 and I denote the concentration of form (A) and the concentration of converted (A) (equal to the concentration of induced form (B)) after time, t, respectively, and κ is a rate constant. In this study, the concentration of form (B) was estimated from the absorptivity, $\alpha(t)$. I and $\alpha(t)$ are connected by

$$\alpha(t) = \varepsilon_B \cdot I \tag{2}$$

where ε_B denotes the molar extinction coefficient of form (B). I_0 is given by

$$I_0 = \alpha(\infty)/\varepsilon_B \tag{3}$$

Here $\alpha(\infty)$ is the value of α for which there is no change with increasing time.

Putting Equations 2 and 3 into Equation 1, we obtain

$$d[\alpha(t)]/dt = -\kappa[\alpha(\infty) - \alpha(t)] \tag{4}$$

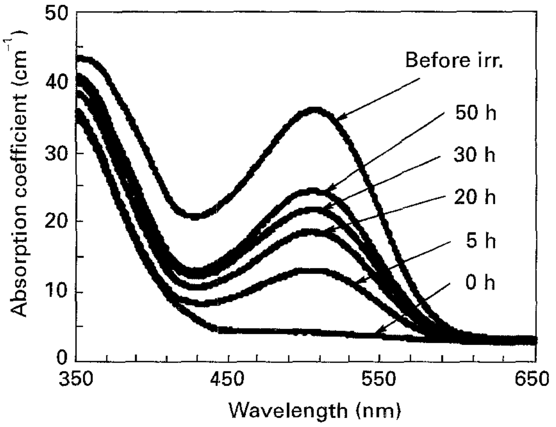

Figure 5 Absorption spectra of spiropyran-doped silica gel during storage in the dark at 15 °C after turning off the 436.5 nm light. The top spectrum is that before irradiation with light.

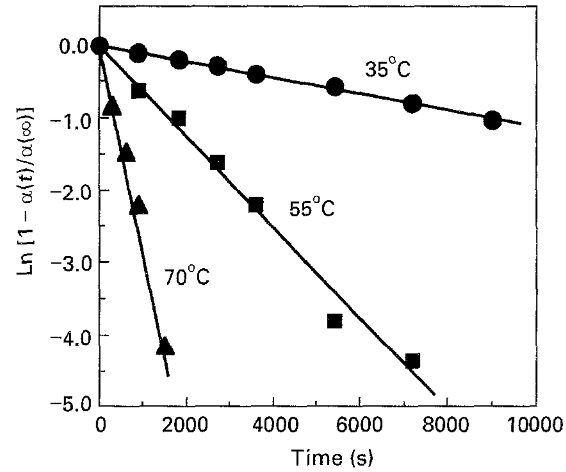

Figure 6 First-order kinetic plots for the intensity of the induced optical absorption band at 515 nm.

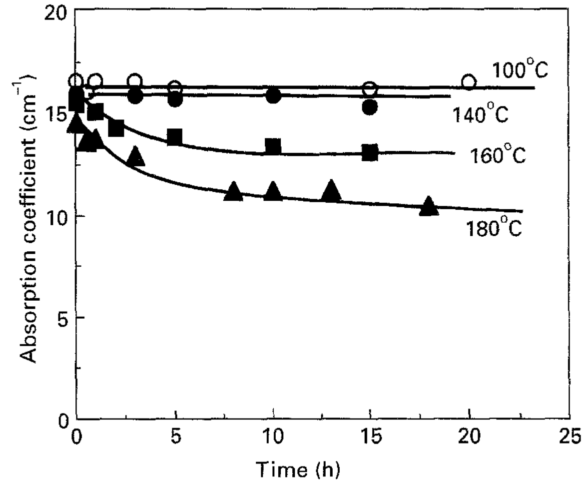

Figure 7 Storage-time dependence of the absorption coefficient at 535 nm of diarylethene after turning off the 436.5 nm light.

Integration of Equation 4 yields the integrated rate law

$$\ln\{1 - \alpha(t)/\alpha(\infty)\} = -\kappa t \tag{5}$$

Fig. 6 shows a semilogarithmic plot of ln $[1 - \alpha(t)/\alpha(\infty)]$ versus time, t, at 35, 55 and 70 °C. The data are well fitted by a linear function, indicating that the scheme in Fig. 1 is consistent with the experimental results. Rate constants of this reaction are calculated as 1.05×10^{-4}, 6.30×10^{-4} and $28.8 \times 10^{-4}\,s^{-1}$ at 35, 55 and 70 °C, respectively. The activation energy determined from an Arrhenius plot for the rate constant is 0.86 eV.

Colour fading of diarylethene was also examined at different temperatures. Fig. 7 exemplifies the photochromic-gap ($\Delta\alpha$ at 535 nm) dependence on the storage time in the dark at various temperatures. Below 140 °C no changes were observed in the absorptivities, even after storage for 50 h. It is a little surprising to observe no colour change at temperature higher than the melting point (121 °C). Concerning the thermal stability, diarylethene has fatigue properties superior to those of spiropyran. This would bring out the advantages of inorganic materials which are stable at high temperature. Nakamura and Irie measured the thermal stability of diarylethene derivatives which remained stable for more than 12 h at 80 °C in toluene solvent [14]. They calculated the state correlation diagram to the open and closed forms of these compounds and showed that the ground-state energy difference between the two forms determines the thermal stability of the closed form.

In the gel network structure, both spiropyran and diarylethene are formed with open structures, which are transformed into the closed forms by irradiation with visible light. Thermochemical backing of the closed form into the open one after blocking of light is dependent on the energy barrier from the closed to the open form. Colour fading of diarylethene was not observed within the experimental period. This indicates that the energy barrier for diarylethene is much higher compared with that of spiropyran (0.86 eV). On the other hand, heating above 160 °C causes a gradual colour fading (Fig. 7). This colour-faded gel was not restored, even by irradiation with light. The reason for this is due to some evaporation of diarylethene through the small pores of the gel at high temperature.

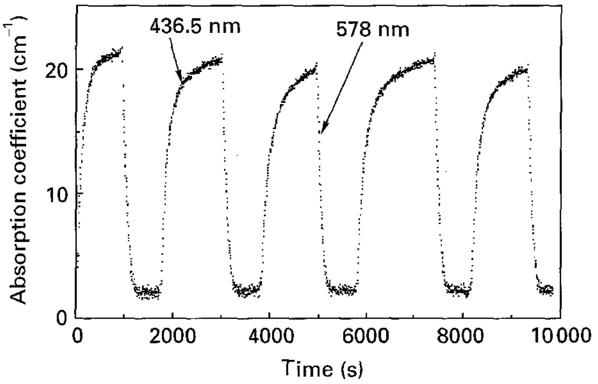

Figure 8 Time-dependence of the absorption coefficient at 535 nm of diarylethene with repeated irradiation with 436.5 and 578 nm light.

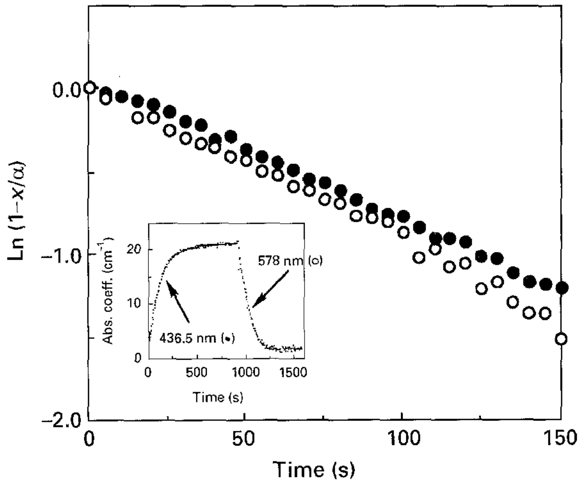

Figure 9 First-order kinetic plots for the absorption coefficient at 535 nm of diarylethene with repeated irradiation with 436.5 and 578 nm light.

3.3. Photochromism of diarylethene

When the red coloured form (B) of diarylethene was irradiated by a mercury lamp through a band-pass filter of 578 nm, it reverted to the colourless open form (A) within a few minutes. Fig. 8 shows the change in absorption coefficient at 535 nm upon alternate irradiation with 436.5 and 578 nm light. The photochromic reactions are reversible and the growth and decay of absorption coefficients hold completely. The photochromic growth and decay rates obey first-order kinetics, as shown in Fig. 9. The reaction rates of growth and decay are almost equal to $8.1 \times 10^{-3}\,s^{-1}$ at room temperature.

4. Conclusion

Photochromism of spiropyran- and diarylethene-doped silica gels, which were prepared by the hydrolysis of $Si(OCH_3)_4$ and $Si(OC_2H_5)_4$, respectively, was measured. Both organics are incorporated into gels with open modifications, and their coloured forms show absorption bands with peaks at 515 and 535 nm. The closed form of spiropyran, which is converted from the open one upon irradiation, is thermally backed into the open form after blocking of the light. The activation energy of the thermochemical reaction is 0.86 eV. On the other hand, the closed form of diarylethene shows no thermochemical reaction below 140 °C but transforms into the open one within a few minutes upon irradiation with 578 nm light. The rate constants of the photochemical reaction are $8.1 \times 10^{-3}\,s^{-1}$.

References

1. D. AVNIR, D. LEVY and R. REISFELD, *J. Phys. Chem.* **88** (1984) 5956.
2. A. MAKISHIMA and T. TANI, *J. Am. Ceram. Soc.* **69** (1986) 4.
3. V. R. KAUFMAN and D. AVNIR, *Langmuir* **2** (1986) 717.
4. D. LEVY and D. AVNIR, *J. Phys. Chem.* **92** (1988) 4734.
5. Y. KOBAYASHI, Y. IMAI and Y. KUROKAWA, *J. Mater. Sci. Lett.* **7** (1988) 1148.
6. K. MATSUI, T. MATSUZUKA and H. FUJITA, *J. Phys. Chem.* **93** (1989) 4991.
7. J. C. POUXVIEL, B. DUNN and J. I. ZINK, *ibid.* **93** (1989) 2134.
8. D. PRESTON, J. C. POUXVIEL, T. NOVINSON, W. C. KASKA, B. DUNN and J. I. ZINK, *ibid.* **94** (1990) 4167.
9. D. LEVY, S. EINHORN and D. AVNIR, *J. Non-Cryst. Solids.* **113** (1989) 137.
10. R. ZUSMAN, C. C. ROTTMAN, M. OTTOLENGHI and D. AVNIR, *ibid.* **122** (1990) 107.
11. D. LEVY, C. J. SERNA and J. M. OTON, *Mater. Lett.* **10** (1991) 470.
12. M. NOGAMI and T. SUGIURA, *J. Mater. Sci.* **12** (1993) 1544.
13. M. IRIE and M. MOHRI, *J. Org. Chem.* **53** (1988) 803.
14. S. NAKAMURA and M. IRIE, *ibid.* **53** (1988) 6136.

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