This article was downloaded by: [University of California, San Diego]
On: 20 August 2012, At: 22:11
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromism as a Probe of Gellation in Aluminosilicate Gels Doped with Spirooxazine

Xiaodong Sun [a] , Meigong Fan [b] & Edward T. Knobbe [a]

[a] Department of Chemistry and the University Center for Photonics and Laser Research, Oklahoma State University, Stillwater, OK, 74078-0447, USA

[b] Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing, 100101, P.R. China

Version of record first published: 24 Sep 2006

To cite this article: Xiaodong Sun, Meigong Fan & Edward T. Knobbe (1997): Photochromism as a Probe of Gellation in Aluminosilicate Gels Doped with Spirooxazine, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 297:1, 57-64

To link to this article: http://dx.doi.org/10.1080/10587259708036103

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1997, Vol. 297, pp. 57–64
Reprints available directly from the publisher
Photocopying permitted by license only

© 1997 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in India

PHOTOCHROMISM AS A PROBE OF GELLATION IN ALUMINOSILICATE GELS DOPED WITH SPIROOXAZINE

XIAODONG SUN[1], MEIGONG. FAN[2] and EDWARD T. KNOBBE[1]*

[1] *Department of Chemistry and the University Center for Photonics and Laser Research, Oklahoma State University, Stillwater, OK 74078-0447, USA*
[2] *Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, P. R. China*

Abstract Aluminosilicate gels containing photochromic spiro(1,3,3-trimethylindolo-2,3′-naphth[1,2-*b*]-1,4-oxazine) were prepared by the sol–gel route. The spirooxazine compound has been used as a photochromic probe for studying the sol to gel transitions of aluminosilicate host gels. Absorption and luminescence spectroscopy were used to elucidate physicochemical changes to the gel network. The photochromic probe compound was found to be very sensitive to local changes that occur during the gel formation process.

INTRODUCTION

The sol–gel process is a synthetic route that promotes the preparation of amorphous guest-host media comprised of transparent oxide matrices doped with organic species. Syntheses of this type are typically performed at room temperature. Thus organic molecules, which may have poor thermal stability at high temperatures, can be incorporated within the inorganic matrix leading to novel hybrid materials.[1-4] Practical device considerations dictate the encapsulation of monomeric photofunctional compounds into a stable, chemically inert solid state host matrix for use in. Development of photonically-active media requires a good understanding of the structure of doped sol–gel networks and of the conditions that the oxide matrix imposes on the dopant at a molecular level. Such interactions have important effects on the optical properties of entrapped photonically-active species. Spiro(1,3,3-trimethylindolo-2,3′-naphth[1,2-*b*]-1,4-oxazine), a photochromic compound, which will be referred as SP1 hereinafter, has been used to probe changes within the gel network at the molecular

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

level.

SP1 photochemistry has been studied by many researches.[5-7] The structures of the SP1 before and after UV irradiation are shown in Figure 1. Photochromism in SP1 generally involves the reversible breaking of a C–O bond in the oxazine ring (SP1) to form a photomerocyanine structure, PMC1. Recently, the authors found that SP1 has unique properties in acidic alcoholic solutions[8,9]. We have coined the phrase "acidichromic" to indicate the observed phenomenon, wherein the spectral characteristics of a photochromic species (*i.e.* SP1) are reversibly changed by varying the pH.

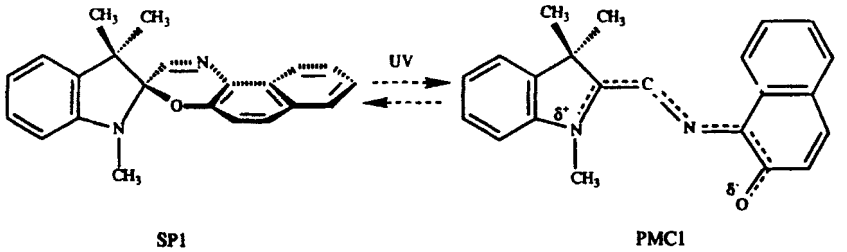

Figure 1. Chemical structure and of SP1 and the corresponding UV-induced photomerocyanine form

This study examines the nature of spectroscopic changes to SP1 doped in transparent gels prepared by the sol–gel process. The host gels which serve as the focus of this work are prepared using di-*sec*-butoxyaluminoxytriethoxysilane (DBATES), a silicon-aluminum double-alkoxide precursor which may be used to prepare porous inorganic aluminosilicate polymers. SP1 proved to be a useful molecular-level probe of physicochemical changes within the aluminosilicate gel. Changes to the spectral character of spirooxazine dopant yielded insights into the evolution of the DBATES-derived gel due to the strong influence exerted by the local chemical environment on the luminescent photochromic guest.

EXPERIMENTAL

1. Materials and Sample Preparation

Spiro(1,3,3-trimethylindolo-2,3′-naphth[1,2-*b*]-1,4-oxazine) was synthesized from 2-methylene-1,3,3-trimethylindoline and 1-nitroso-2-naphthol. A detailed summary of the synthesis of SP1 appears elsewhere[10]. DBATES was obtained from United Chemical Technology and used without further purification. Anhydrous reagent grade isopropanol was purchased from the Fisher Scientific Company. The water was deionized and

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

distilled.

Bulk gel specimens were prepared using a modified sol–gel process which was previously reported by Pouxviel *et al.* and others[11-13]. Briefly, the DBATES precursor was diluted using isopropanol to get a 1:1 volume ratio binary solution (solution 1). A separate solution containing a 1:1 volume ratio of water to isopropanol was prepared. SP1 was dissolved in the latter, forming solution 2. Solution 2 was subsequently added, in a dropwise fashion with constant stirring, to solution 1, producing the initial sol. The final SP1 concentration was 0.1 mM. The resultant sol was hydrolyzed in a covered container at room temperature overnight, poured into polystyrene cuvettes, covered, and allowed to gel. Gellation of specimens prepared in this manner occurred within three days. Gels were aged in the covered cuvettes for two weeks. After aging, the covers were perforated to allow solvent evaporation. Gel specimens were allowed to dry under ambient conditions for three weeks. Optical characteristics of the precursor solutions, aged gels and the dried xerogels were periodically determined. The dopant molecular number densities (N_D) of entrapped SP1 in the dried xerogel specimens were calculated, based upon the final dimensions of the dried bulk monoliths, to be 8.2×10^{16} cm^{-3}.

2. Apparatus and Spectral Measurements

The ultraviolet excitation source was a model 160-W UV Lamp (Fisher Scientific Company) with peak emission at 365 nm and a manufacturer-specified irradiation intensity of 11,600 $\mu W/cm^2$. Absorbance spectra were determined using a Cary 5E spectrophotometer (2.0 nm spectral band pass). Continuous wave front face excitation and emission spectra were measured using a Spex Industries Model F112A spectrofluorimeter; excitation and emission band passes were 5.55 and 2.58 nm, respectively. All luminescence spectra were collected in the dark at room temperature and corrected for instrumental response.

RESULTS AND DISCUSSION

1. SP1 Spectra in the DBATES

Figure 2 shows the fluorescence emission spectra of SP1 doped aluminosilicate sol excited at 350 nm (Curve 1) and 540 nm (Curve 2). The intense emission band centered at 430 nm was observed to remain essentially unchanged over excitation wavelengths ranging from 320 to 370 nm. A much smaller peak which is not apparent on the scale shown can be found at 643 nm in curve 1. The weak 643 nm emission band was also observed when an excitation wavelength of 540 nm was used (Curve 2 of Figure 2; intensity increased 6-fold with respect to Curve 1). These results may be interpreted as

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

follows: An equilibrium state exists between SP1 and PMC1 in the DBATES sol, as indicated in equation 1. The intense emission band at 430 nm is assigned to radiative relaxation from the lowest excited singlet state of SP1. The weak 643 nm is attributed to radiative relaxation from the lowest excited singlet state of PMC1, which is present in low concentration in the sol but is selectively probed by the 540 nm excitation source.

$$\text{SP1} \rightleftharpoons \text{PMC1} \qquad (1)$$

The emission band of PMC1 is not observable in isopropanol solution since there is strong interaction between the solute and solvent species in solution. It is expected that strong solute-solvent interactions provide a very rapid collisional deactivation pathway for electronically excited states. In the sol stage, however, the viscosity has greatly increased with respect to alcoholic solution. Thus, the PMC1 product may be observed in the sol even though it is not readily studied in alcoholic solution.

Photochromic effects were studied in the sol as given shown in Figure 3. The optical absorption spectrum of SP1 dissolved in an aluminosilicate sol is shown in Curve 1 of Figure 3. This spectrum consists is composed of two absorption shoulders peaking at 320 nm and 350 nm in the absence of UV irradiation, and corresponds to the SP1 form of the molecule. After 2 minutes of UV irradiation, a new absorption band centered at 610 nm appeared (Curve 2 of Figure 3). The onset of a 610 nm absorption band is associated with the formation of the ring-opened merocyanine or PMC1 conformation, a result which is consistent with findings reported by Schneider *et al.* using laser photolysis method.[14]

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

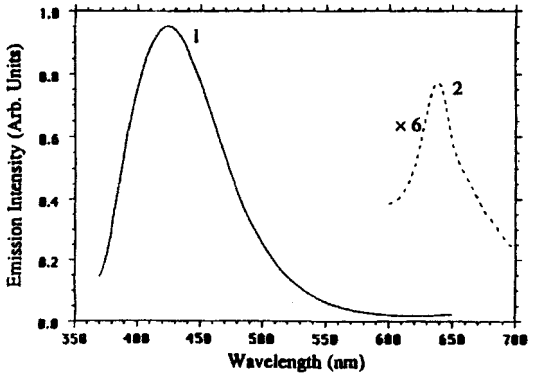

Figure 2. Fluorescence spectra of SP1-sol at different excitation wavelength. (1). λ_{ex} = 350 nm; (2). λ_{ex} = 540 nm.

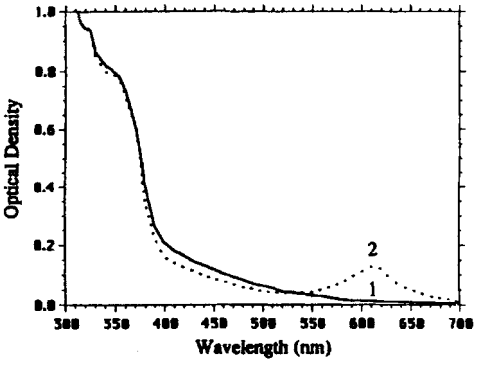

Figure 3. Absorption spectra of SP1-doped DBATES sol (1). before UV irradiation (2). after 2-min. UV irradiation.

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

The PMC1 form exhibited a lifetime of approximately 30 seconds in the aluminosilicate sol, a relaxation rate to the SP1 form which is much slower than that observed in isopropanol, which typically has a lifetime of approximately 0.5 seconds.[15] This result indicates that the local viscosity is much higher in the DBATES sol, showing the molecular rearrangement responsible for the regeneration of SP1 from PMC1.

The most dramatic macroscopically-observed physical changes occur during gellation, when the initial sol is transformed into a rigid solid. At gellation the solvent phase consists of excess isopropanol and water with the additional ethanol and butanol produced by the hydrolysis of the DBATES alkoxy groups. In the unaged gel, SP1 is not constrained by the ramified and open gel structure. Thus, the luminescence spectra of SP1 and PMC1 species in the unaged gel are essentially the same as those observed for these species in a liquid solution.

2. SP1 Spectra in the Aged Gel

During aging, the gel is kept in a closed container and no evaporation of the organic molecules occurred. Thus, a substantial amount of solvent remains in the 2-phase matrix of an aged gel. The fluorescence spectra of an aged SP1-doped specimens are shown in Figure 4. The fluorescence band centered at 440 nm (Curve 1 of Figure 4; λ_{ex} = 370 nm) is essentially the same as that observed in the sol (Curve 1, Figure 2). An intense new fluorescence band, centered at 540 nm, was observed when the excitation wavelength was increased to 435 nm (Curve 2 of Figure 4). This peak is quite similar to one found in isopropanol solutions acidified by the addition of HCl.[8] This band was previously assigned to the acidichromic product of SP1, SP1•HCl complex, in acidic alcoholic solution. The absence of HCl from the preparation, however, necessitates consideration of other possibilities. The authors propose the formation of a new species in the aged gel, SP1•HO-M, which is postulated to result from complexation between SP1 and acidic metal hydroxide sites in the aluminosilicate network according to equation 2:

$$\text{SP1} + \text{HO-M} \rightleftharpoons \text{SP1•HO-M} \qquad (2)$$

where M represents Si or Al , and SP1•HO-M is the acidichromic product.

Similarly, the thermochromic compound PMC1 (equation 1) may also interact with HO-M to yield the acidichromic product of PMC1, PMC1•HO–M, as shown in equation 3:

$$\text{PMC1} + \text{HO-M} \rightleftharpoons \text{PMC1•HO-M} \qquad (3)$$

When the excitation wavelength was increased to 540 nm, in addition to the weak emission band centered at 643 nm (previously attributed to singlet state emission from (PMC1)*, see Curve 2 of Figure 2), a new band centered at 580 nm was also

observed (Curve 3 of Figure 4). The authors suggest that the new band results from the excited state of a PMC1•HO–M complex. Aged aluminosilicate gels consist of network polymers formed by Si–O–Si, Si–O–Al and Al–O–Al linkages. These systems contain large quantities of charged polar species such as Si–OH and Al–OH groups. SP1 and PMC1 may interact electrostatically with these inorganic species, resulting in the formation of the SP1•HO-M and PMC1•HO-M type complexes. The ready formation of open-form merocyanine conforms indicates that the aged gel is still comparatively low in density, permitting the necessary molecular rearrangement of SP1 to proceed.

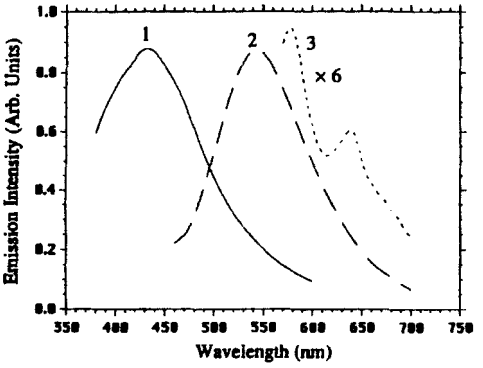

Figure 4
Fluorescence spectra of SP1-aged gel at different excitation wavelength.
(1) λ_{ex} = 370 nm; (2) λ_{ex} = 430 nm
(3) λ_{ex} = 540 nm

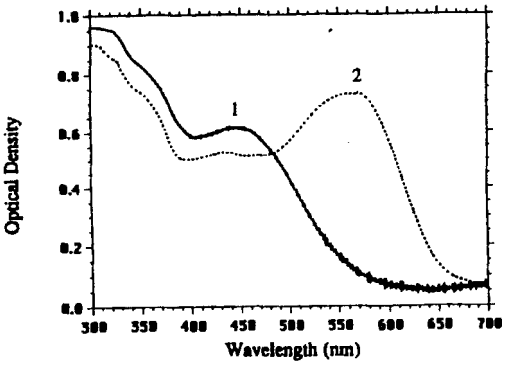

Figure 5.
Absorption spectra of SP1-aged gel
(1). before UV irradiation
(2). after 2-min. UV irradiation.

Photochromic behavior of SP1 is retained in the solvent-rich aged gels, as shown in Figure 5. Curve 1 of Figure 5 shows the absorption spectrum prior to UV irradiation. Two shoulders peaking at 320 nm and 350 nm are observed, corresponding to the SP1 conformation as previously seen in Curve 1 of Figure 3. The intense absorption band centered at 450 nm is assigned to the SP1•HO-M species. After 2 minutes of 365 nm irradiation, an intense peak centered at 560 nm was observed (Curve 2 of Figure 5). The new band is postulated to result from the formation of a photomerocyanine complex derived from SP1•HO-M(*e.g.*, PMC1•HO-M). This result is very similar to the acidichromic effects previously reported for SP1 in alcoholic solutions[8].

The colored merocyanine complex form (PMC1•HO-M) generated by irradiation with ultraviolet light slowly decays, by a thermally activated mechanism, to SP1•HO-M. The thermal decay event obeys first order kinetics with a rate constant of 0.359 min^{-1} at

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

room temperature (correlation coefficient is 0.992). Because of the interactions between the photochromic compound and condensing polymeric host material, the decay process in the aged gel is orders of magnitude slower than that in alcoholic solutions.

3. SP1 Spectra in Dried Xerogel Specimens

The third stage of the process is the drying of the gel. When the solvents are removed, the gel structure collapses and the gel shrinks dramatically. The final volume is approximately one fifth that of the aged wet gel. The oxide network becomes substantially more compact, and the flexibility decreases with the departure of the solvent.

The four species SP1, PMC1, SP1•HO-M and PMC1•HO-M are still present in the xerogel stage as shown in Figure 6. As discussed early, the intense emission band from the lowest excited singlet state of SP_1 is moved to 460 nm. This band exhibited a bathochromic shift of 30 nm compared with the result in the aluminosilicate sol, which is due to the environmental change at this stage. The 643 nm peak is from the photochromic product PMC1. SP1•HO-M is responsible for the fluorescence band centered at 540 nm, whereas PMC1•HO-M is for the peak centered at 580 nm. All of the four species are also observable at the final stage of the xerogel, but no photochromic behavior can be observed.

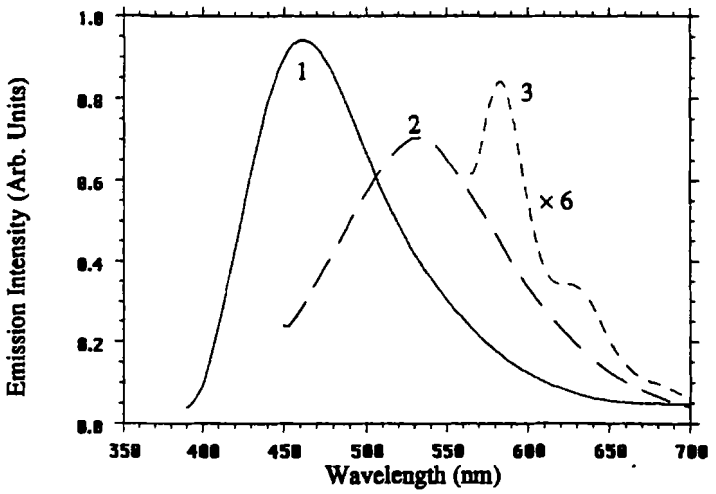

Figure 6.

Fluorescence emission spectra of SP1-Xerogel at different excitation wavelength. (1). λ_{ex} = 370 nm; (2). λ_{ex} = 435 nm; (3). λ_{ex} = 540 nm.

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

Downloaded by [University of California, San Diego] at 22:11 20 August 2012

CONCLUSION

The photochromic compound, SP1, is found to be sensitive to changes in the local environment associated with the various stages of the sol–gel process. The sol, aged gel and xerogel transitions can be monitored by the evolution of absorption, luminescence and photochromic behavior of SP1 doped into the aluminosilicate host gel. Photochromism is retained through the aged gel stage, but is lost in the initial dry xerogel. The appearance of new fluorescence peaks, such as those shown in Figure 5, is consistent with the formation of complexes between the probe chromophore and HO-M surface groups in the gel. This is in good agreement with previously reported results implying the formation of spirooxazine•HCl complexes in alcoholic solution.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support for this research from the National Science Foundation, National Natural Science Foundation of China and the Chinese Academy of Sciences.

REFERENCES

1. D. Levy and D. Avnir, J. Phys. Chem., 92, 4734 (1988).
2. D. Avnir, D. Levy and R. Reisfeld, J. Phys. Chem., 88, 5956 (1984).
3. D. Levy, R. Reisfeld and D. Avnir, Chem. Phys. Lett., 109, 593 (1984).
4. D. Preston, J. C. Pouxviel, T. Novinson, W. Kaska, B. Dunn and J. I. Zink, J. Phys. Chem., 94, 4167 (1990).
5. T. Yoshida and A. Morinaka, J. Photochem. Photobiol. A: Chem., 78, 179 (1994).
6. A. Zelichenok, F. Buchholtz, J. Ratner, E. Fischer and V. Krongauz, J. Photochem. Photobiol. A: Chem., 77, 201 (1994).
7. D. Levy, S. Einhorn and D. Avnir, J. Non-Cryst. Solids, 113, 137 (1989).
8. X. D. Sun, M. G. Fan, X. J. Meng and E. T. Knobbe, J. Photochem. Photobiol. A: Chem., (in press).
9. Y. C. Liang, Y. F. Ming and M. G. Fan, Science in China B: Chem., (submitted).
10. X. Y. Zhang, S. Jin, Y. F. Ming, Y. C. Ling, L. H. Yu, M. G. Fan, J. Luo, Z. H. Zuo and S. D. Yao, J. Photochem. Photobiol. A: Chem., 80, 221 (1992).
11. J. C. Pouxviel, J. P. Boilot, J. P. Lecomte and A. Dauger, J. Phys. Paris, 48, 921 (1987).
12. J. Mckiernan, J. C. Pouxviel, B. Dunn and J. I. Zink, J. Phys. Chem., 93, 2129 (1989).
13. L. M. Yates, III, X.-J. Wang and E. T. Knobbe, J. Sol–Gel Sci. Tech., 2, 745 (1994).
14. S. Schneider, A. Mindl, G. Elfinger and M. Melzig, Ber. Bunsenges. Phys. Chem., 91, 1922 (1987).
15. C. Bohne, M. G. Fan, Z. J. Li, Y. C. Liang, J. Lusztyk and J. C. Scaiano, J. Photochem. Photobiol. A: Chem., 66, 79 (1992).