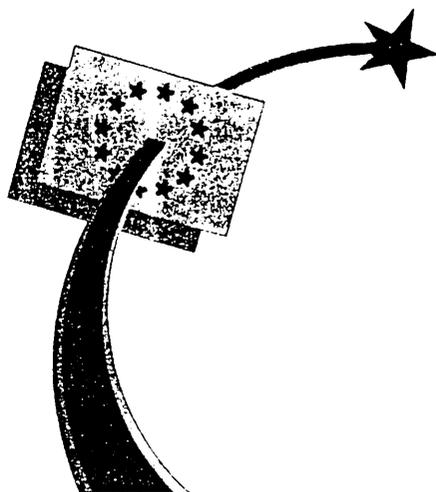


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## PHOTOCHROMIC PROPERTIES OF SPIROOXAZINE DYES IN ORMOCER GELS AND COATINGS

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## ABSTRACT

The wet- and "cold"-chemical characteristic of sol-gel process makes the sol-gel derived materials offer exciting potentials as hosts for photochromic dyes. In the present work, using mixed organically modified silicon alkoxides as starting compounds a novel ORMOCER material has been prepared via the sol-gel process as a host for spirooxazines. The photochromic properties of the dyes in the ORMOCER gel and coating are compared with those in ethanol. The experimental results show that both the photochromic performance and the thermal stability of the dyes are apparently improved in the ORMOCER matrix., while the temperature dependence of the photochromic intensity at higher temperatures needs further improvement.

## INTRODUCTION

The low-temperature solution-chemistry characteristics of the sol-gel process make the sol-gel derived gels offer exciting potentials as hosts for a wide variety of dye molecules. Since the chemical synthesis of gels takes place in organic solutions at much lower temperatures than conventional methods, organic dyes can be incorporated easily into an oxide gel matrix. In addition, the composition, structure and thereby the properties of gels can be tailored to meet different requirements by the chemical design of molecular precursors and the elaborate control of the hydrolysis-condensation reactions. For example, both inorganic oxide gels<sup>[1]</sup> and organic-inorganic hybrid gels (ORMOCER)<sup>[2]</sup> can be prepared by using different molecular precursors as starting compounds.

Research work on laser<sup>[3]</sup> and non-linear<sup>[4]</sup> dyes incorporated in sol-gel derived matrices has been conducted extensively in the past few years, while much less work has been devoted to photochromic dyes. There are only a few publications dealing with this topic. D. Levy et al.<sup>[5]</sup> studied the photochromic properties of spiropyranes in three kinds of pure or modified silica matrices prepared by the sol-gel process, only one system, however, showed normal photochromism. J. I. Zink and B. Dunn<sup>[6]</sup> doped spiropyranes into a Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-system using the alkoxide ASE (di-*s*-butoxy-aluminoxy-triethoxy-silane) as the starting material. They also doped 2,3-diphenylindenone oxide (DPIO)<sup>[7]</sup> into three kinds of gels, i.e. SiO<sub>2</sub>, ASE and ORMOSIL and found that both the photochromic intensity and the lifetime decrease gradually during the ageing and drying process of most gels.

A great many organic dyes have been reported to show photochromic effects<sup>[8]</sup>. Among them is a class of compounds called spiroindolinonaphthoxazine (abbreviated as spirooxazine) which exhibits good photochromic effect and photochemical stability. Unfortunately, little work has been published to date on the incorporation of them into sol-gel derived materials.

In the present work, a novel sol-gel derived ORMOCER material has been developed as a host for spirooxazines. The photochromic behaviours of two spirooxazine dyes in ethanol

solutions, gels and coatings are compared. The use of the ORMOCER matrix leads to an apparent improvement both in the photochromic performance and in the thermal stability of the dyes.

## EXPERIMENTAL

### 1. Sol-gel preparation

A two-step process, i.e. acid-catalysed hydrolysis and base-catalysed polymerisation was used for the preparation of ORMOCER gels and coatings. Mixed organically modified silicon alkoxides were used as starting compounds for the sol-gel preparation. They include tetraethoxysilane (TEOS), methyl-trimethoxysilane (MTMS), 3-glycidoxypropyl-trimethoxysilane (GPTMS), 3-aminopropyl-triethoxysilane (APTES) and dimethyl-diethoxysilane (DMDDES). The typical molar ratio of alkoxides:water:ethanol:acidic catalyst was 1:2:4:0.001. Hydrolysis and polymerisation took place at room temperature under vigorous or moderate stirring at the different stages of the sol-gel reactions. Ethanol solutions of two spirooxazine dyes were introduced into the sols together with certain basic additives.

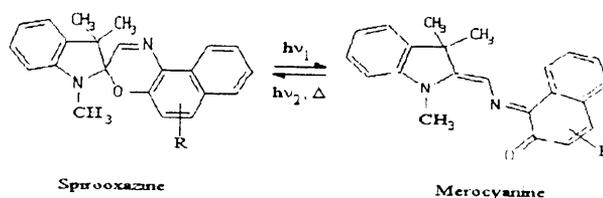


Fig. 1: Schematic representation of the photochromism of spirooxazine

Fig. 1 shows the photochromic transformation of spirooxazine, with R representing either H (SO1, Aldrich) or phenyl group (SO2, Aldrich). Their absorption peak wavelengths are 613 nm and 596 nm, respectively. The sols thus obtained were used for the preparation of coatings by dipping or spraying and of shaped gels by casting. After gelation the gels and coatings were allowed to stay in open air for at least ten days at room temperature and then heated in an electric oven for more than 6h at 70°C.

### 2. Measurement of photochromic properties

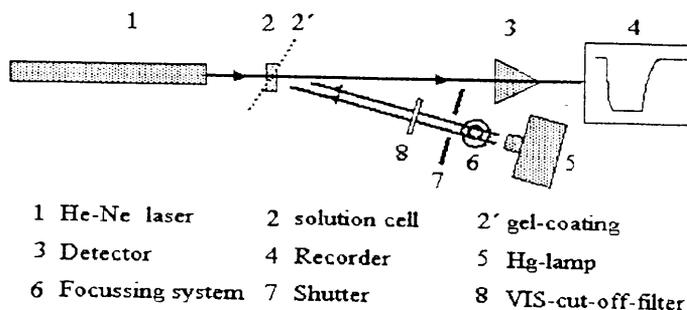


Fig. 2: Schematic layout of the apparatus used for photochromism measurement

An apparatus has been established for the real-time measurement of photochromism. The schematic layout of this apparatus is shown in Fig. 2. A 100W Hg-lamp is used as the UV irradiation source and located at an angle of 30 degree to the He-Ne laser (633 nm) beam which acts as the probing light. The distance between the Hg-lamp and the sample-holder is 25 cm and

the irradiation intensity on the sample surface can be adjusted by a focussing system to mimic the intensity of sun light (ca. 3 mW/cm<sup>2</sup>). Glass cells of 10 mm optical path are used for the measurement of dye-in-ethanol samples. A VIS-cut-off filter is used to minimize the influence of heat from the Hg-lamp.

In order to estimate the thermal stability of the dye-in-ORMOCER system, coatings on glass substrates were heated to different temperatures between 70°C and 180°C for 6h (at 95°C for 12h) and then allowed to cool in the ambient spontaneously down to room temperature (25°C). The photochromism measurements were carried out 1h after the room temperature had been reached.

The temperature dependence of photochromism was examined by taking the colouring-fading curves at different temperatures. Coatings on plastic substrates were first heated up to 50°C or cooled down to -5°C and at various temperatures during spontaneous cooling or heating of the samples in the ambient the colouring-fading curves were taken. A CONATEX 9010 thermometer was used to monitor the temperature on the sample surface. The temperature for each measurement was taken at the moment of the cessation of the UV irradiation.

## RESULTS AND DISCUSSION

### 1. Concentration dependence

The photochromic properties of the two dyes in ethanol and the ORMOCER gels (1.0 mm thick) at different concentrations were measured by monitoring the colouring-fading process. The saturated photochromic absorption is plotted as a function of dye concentration in Fig. 3.

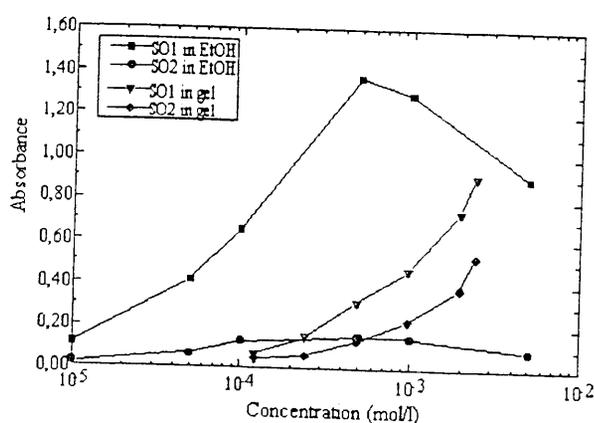


Fig. 3: Photochromic absorption of SO1 and SO2 in ethanol (10-mm plastic cells) and in ORMOCER gels (1.0 mm) as a function of concentration

It can be seen from this figure that (1) in ethanol both dyes show maxima in the absorbance vs. concentration curves and the maximum saturated absorption exists around  $5 \times 10^{-4}$  mol/l. The aggregation of the dye molecules at higher concentrations is responsible for this concentration quenching phenomenon, (2) in the ORMOCER gels the photochromic absorption of both dyes increases monotonically with concentration ranging between  $1 \times 10^{-4}$  and  $3 \times 10^{-3}$  mol/l, implying that the aggregation of the dye molecules in the ORMOCER gels is greatly reduced, (3) improvement in the photochromic performance of SO2 due to incorporation into the ORMOCER matrix is much greater than SO1. Ethanol solutions of SO2 at concentrations higher than  $1 \times 10^{-4}$  mol/l show very heavy blue bottom colour whose screening effect may be responsible for the low photochromic absorption. The difference between the absorption peak wavelengths of SO2 and

the He-Ne laser is nearly twice that of SO1. This is another reason for the lower measured values of photochromic absorbance of SO2 than SO1.

## 2. Effect of heat treatment

The variation of the photochromic absorption with heat treatment temperature was deduced from the colouring-fading curves of SO1 in ORMOCER coating (250  $\mu\text{m}$  thick) heat treated to various temperatures and is given in Fig.4.

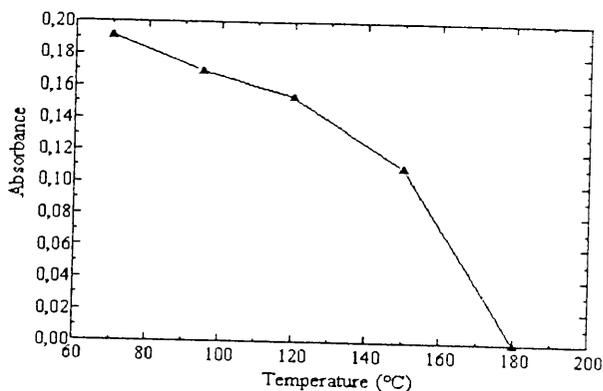


Fig.4: Variation of photochromic absorption of SO1 ( $2 \times 10^{-3}$  mol/l) in ORMOCER coating (250  $\mu\text{m}$ ) with heat treatment temperature

This figure indicates that no serious degradation of both the integrity and the photochromic performance of the coating occurs up to 120°C. Further heat treatment to 150°C led to cracking of the coating and more considerable decrease of the photochromic absorption. Final heat treatment at 180°C made the coating peel off and exhibit no photochromic effect. The vanishing of photochromic effect of the coating heat treated at 180°C is due to the complete thermal decomposition of the dye. Based on these results, however, it can be concluded that the thermal stability of the dye-in-ORMOCER systems is better than dye-in-polymer systems.

## 3. Temperature dependence

The colouring-fading curves of SO1 in ORMOCER gel (0.5 mm thick) at different temperatures are given in Fig.5.

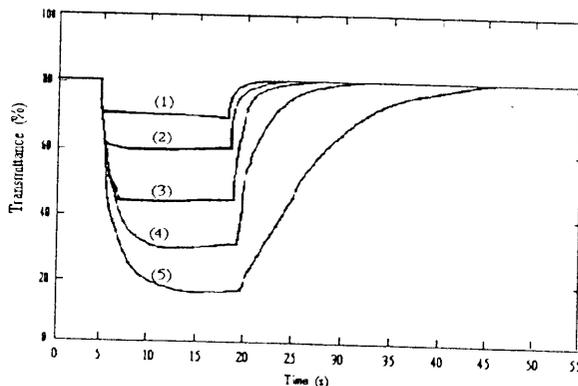


Fig.5: Colouring-fading curves of SO1 ( $2 \times 10^{-3}$  mol/l) in ORMOCER gel (0.5 mm) at various temperatures: (1) 35.9°C; (2) 28.7°C; (3) 24.6°C; (4) 19.6°C; (5) 11.4°C

It is obvious that the saturated photochromic absorption decreases and the fading speed increases with increasing temperature. Figs. 6 and 7 show the temperature dependence of time duration for complete bleaching and photochromic intensity, respectively. It can be seen more clearly from these figures that both the photochromic absorption and the fading speed change with temperature more considerably below room temperature than above room temperature.

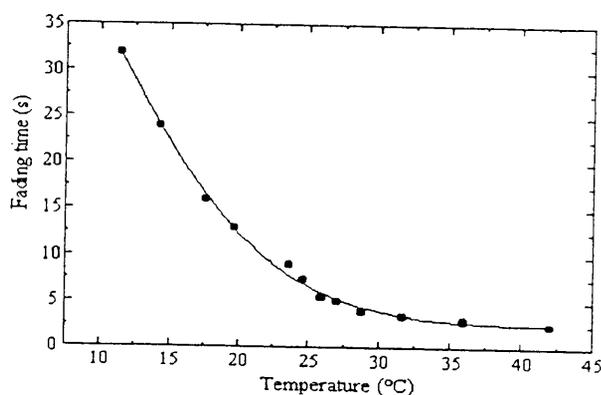


Fig. 6: Temperature dependence of fading time of SO1 ( $2 \times 10^{-3}$  mol/l) in ORMOCER gel (0.5 mm)

From the standpoint of practical applications, the fading speed is much better than acceptable. It can be estimated from Fig. 6 by extrapolation that even at around  $0^\circ\text{C}$  the fading time will fall inside the limit of one to several minutes. This is much shorter than in some polymer matrices. On the other hand, however, the temperature dependence of the photochromic intensity seems unfavourable to the practical use above room temperature. Nevertheless, the coatings can be used for certain purposes at lower temperatures, say, below  $30^\circ\text{C}$ .

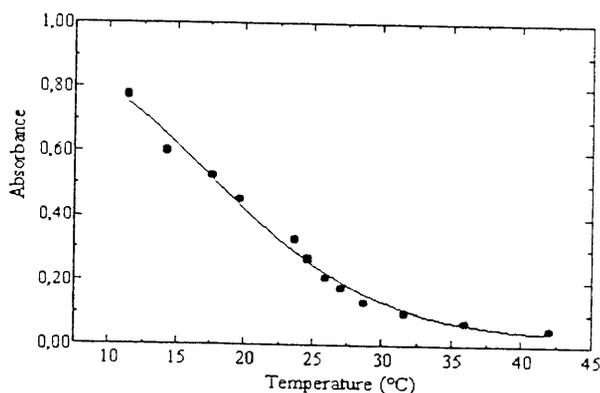


Fig. 7: Temperature dependence of photochromic intensity of SO1 ( $2 \times 10^{-3}$  mol/l) in ORMOCER gel (0.5 mm)

#### 4. On the matrix for photochromic dyes

Besides certain common requirements for matrices hosting organic dyes, e.g. transparent in the UV-VIS region, preventing dye molecules from aggregation, no reaction with dye molecules, high thermal and photochemical stability, high resistance to oxygen, there is one particular requirement for the matrices hosting photochromic dyes, i.e. they should be flexible enough to allow the structural change of the dye molecules. Sol-gel process makes it possible to create more flexible matrix materials, i.e. organically modified ceramics (ORMOCER), for photochromic dyes. Using mixed organically modified silicon alkoxides as starting compounds and the two-step procedure,

ORMOCER coatings and gels in desired dimensions have been successfully tailored. All our samples doped with spirooxazine dyes show strong photochromic effect even after heat treatment at 100°C for more than one week and no detectable deterioration of the photochromic performance has been evidenced up to the present although 7 months has passed since preparation. In addition, it is expected that the concentration of dyes in the ORMOCER matrices can be further increased so as to decrease the coating thickness required for certain practical applications, where thinner coatings are always preferred in order to obtain better mechanical performance.

## CONCLUSIONS

(1) A novel ORMOCER material has been successfully prepared via the sol-gel process starting from mixed organically modified silicon alkoxides. It has been proved to be a good matrix material for photochromic spirooxazine dyes.

(2) The photochromic performance of spirooxazine dyes doped in the ORMOCER material is much better than in ethanol solution. The aggregation of the dye molecules is greatly reduced. The incorporation concentration of the dyes can be further increased.

(3) The thermal stability of the dye-in-ORMOCER system is better than dye-in-polymer system.

(4) The temperature dependence of the photochromic intensity of the dye-in-ORMOCER system at higher temperatures needs to be improved.

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