Thermal decoloration kinetics of spirooxazines in Ormocer coatings prepared via sol–gel processing

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Two free and one silylated (silane-substituted) photochromic spirooxazines are doped into organically modified ceramics (Ormocer) coatings by sol–gel processing and the thermal decoloration kinetics of these coatings are investigated and compared with the corresponding ethanol solutions and PMMA coatings. The decoloration behaviour of the two free dyes (SO-1 and SO-2) in the Ormocer coatings is similar to that in ethanol solutions, obeying a first-order mechanism and possessing almost the same decoloration rates as in ethanol. This suggests that the dye molecules encapsulated within the pores of the solid matrix are as free as those in ethanol solutions. The silylated dye (SO-3) in the Ormocer coatings, however, exhibits a considerably lower decoloration rate than the corresponding free dye (SO-1) and evident deviation from the first-order mechanism. This indicates apparently that the degree of freedom of the dye molecules is reduced by the silylation. These results are discussed on the basis of solvent polarity, porous structure of the Ormocer coating, and the dye-to-matrix connectivity.

1. Introduction
Substances capable of undergoing photoinduced reversible colour changes are referred to as photochromic materials. In addition to the well-known inorganic silver halides, most photochromic materials are organic compounds based on different photochromic transformation mechanisms. Spirooxazines are typical photochromic compounds in which molecular rearrangement (ring opening–closure) occurs upon UV irradiation. They have been the subject of intensive investigation since they were first reported in 1961 [1]. Increasing interest in this kind of photochromic material is mainly due to their inherently higher photofatigue resistance with respect to photoexcitation as compared with spiropyrans [2], even though they have a similar molecular structure and behave by the same photochromic transformation mechanism as shown in Fig. 1. This has made spirooxazines the most attractive photochromic materials for practical applications [3–5].

For practical applications, a high photochromic response of the dye dispersed in suitable matrices is always advisable, and the rates of the photochromic transformation, especially the thermal decoloration rate, determine the feasibility of specific applications. If both the colouring and fading process are sufficiently fast, the photochromic system can be used as high-speed optical switches. On the other hand, if the coloured form is also very stable, e.g. as stable as the colourless form, the decoloration rate will be so slow that spontaneous thermal decoloration at room temperature is impossible, and then the photochromic system can be used for optical storage. Therefore, the decoloration kinetics of a photochromic material is of great importance in determining its practical applications.

In view of the fact that the coloured merocyanines have in general a very strong tendency to aggregate in liquid solvents because of their high polarization and large dipole moment, solid matrices are expected to restrict the aggregation by virtue of their higher rigidity and, as a result, higher concentrations of the dye could be achieved to benefit both the photochromic intensity and the photofatigue resistance. This will render it possible to produce thin coatings with sufficiently high photochromic intensity and satisfactory photofatigue resistance as well as an acceptable thermal decoloration rate, which is usually retarded by a solid matrix. So far the most extensively and intensively studied solid matrices for photochromic dyes are polymers due to their low temperature and low cost preparation procedures. There has already been a great deal of research and development activity in this field [6]. The heterogeneity of a polymer structure has been shown to greatly influence the kinetics of the photochromic transformation in organic dyes such as spiropyrans and spirooxazines, leading to a deviation of the decoloration reaction from first-order kinetics and reduction of the decoloration rate [7,8].

Organically modified ceramics (Ormocer) synthesized by a sol–gel process provide an attractive solid matrix for photochromic dyes [9]. The purpose

of this work is to establish the effect of the Ormocer matrix on the thermal decoloration behaviour of three spirooxazines, two free and one silylated, and to see whether the retardation of the decoloration process by the solid matrix is tolerable to certain applications. The experimental results show that for the two free spirooxazines first-order decoloration kinetics are demonstrated in the Ormocer coatings, with the half-life time and decoloration rate of the merocyanine being almost the same as in ethanol solutions, while in the case of the silylated spirooxazine deviation from the first-order kinetics was evident and the decoloration rate is slower than that of the same dye in ethanol. These results are explained in terms of the interaction between the dyes and the porous Ormocer matrix.

2. Experimental details
2.1. Preparation of photochromic coatings
Ethyltriethoxysilane (ETES) and 3-glycidoxypropyl-trimethoxysilane (GPTMS) were used as starting materials for the sol–gel preparation of photochromic Ormocer coatings in the 30 ETES–70 GPTMS system. Appropriate amounts of the two organically modified silanes were first mixed in a plastic container (30 mm dia. × 70 mm) for 10 min using a magnetic stirrer and a half-stoichiometric quantity of water in the form of 0.1 N HNO_3 solution was then added, followed by an additional 10 min stirring and a 20 min sonication by 20 kHz ultrasonic radiation at the power of 20 W and duty cycle of 70%. The ultrasonic radiation was generated by a SONIFIER Model 450 device (Branson Ultrasonic CT) and supplied to the liquid mixture through a standard horn tip. The plastic container was immersed in an ice–water bath during the sonication. In order to promote monomeric dispersion of the dyes and enhance adhesion of coatings to the microscope slides a non-ionic surfactant, Triton X-100, was introduced at 8 wt% into the sol prior to the addition of the dye–ethanol solution. Three spirooxazine (SO) dyes were used in this work; their molecular structures are shown in Fig. 2. After stirring for 1 h, the sol
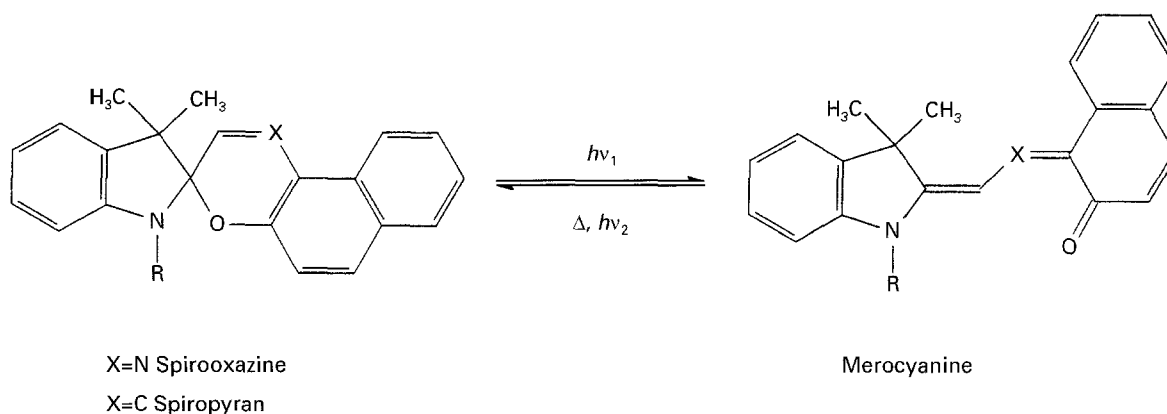

Figure 1 Photochromic transformation of spirooxazine and spiropyran.
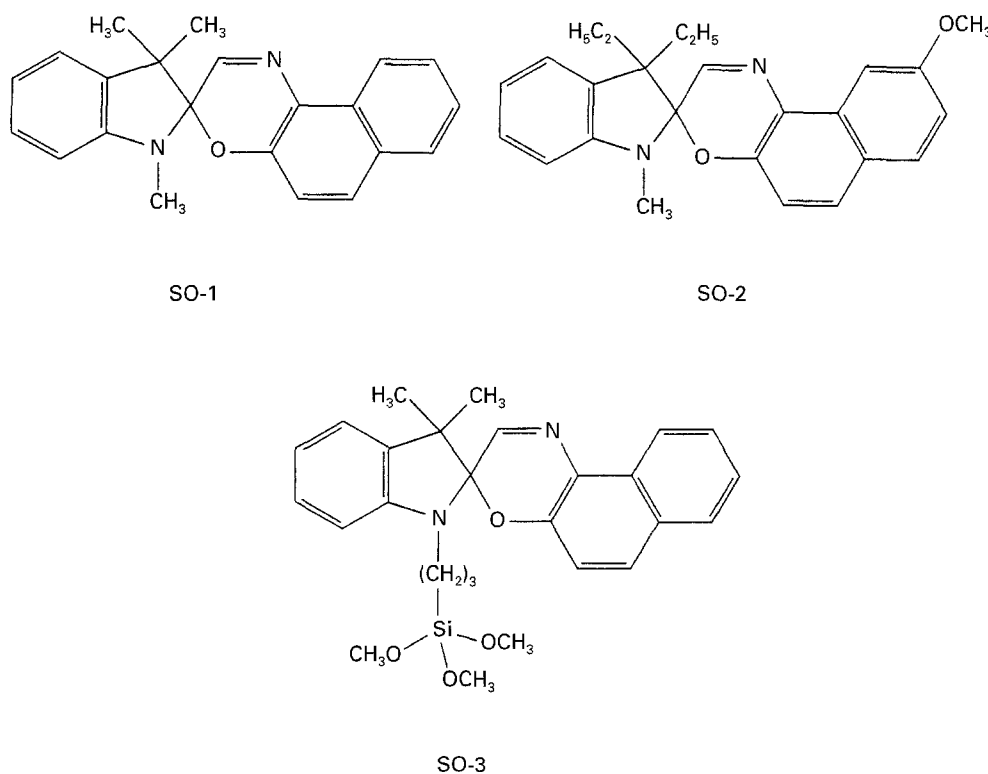
X=N Spirooxazine
X=C Spiropyran

Merocyanine

SO-1

SO-2

SO-3

Figure 2 Spirooxazines used in this study.

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was exposed to ambient air whilst continuing gentle stirring until the dye concentration in the sol reached 10^{-3} moll^{-1}. Coatings were prepared by spreading appropriate volumes of the viscous sols on defined areas of the microscope-slide glass substrates. After being held overnight in ambient air, the coatings were heated to 65 °C and maintained at temperature for 15 h, and then at 110 °C for 2 h, followed by unforced furnace-cooling down to room temperature.

For the purpose of comparison, PMMA coatings doped with SO-1 were also prepared on microscope glass slides by spreading PMMA–EA (ethylacetate) solution containing 15 g PMMA in 100 ml EA and with the same concentration of SO-1 as in the sols. These coatings were subjected to the same drying and heat treatment as the Ormocer coatings.

2.2. Kinetics measurement

Fig. 3 shows schematically the computer-controlled apparatus used for the kinetics measurement. A Hg lamp is employed as the UV source and a UV-pass filter (Schott UG5) is used to reduce the influence of heat from the Hg lamp on the temperature-dependent colouring and fading process. The variation of absorbance with time during the colouring–fading process is probed by a He–Ne laser (633 nm) and processed by a personal computer.

A typical colouring–fading process is illustrated in Fig. 4. The equilibrium absorbance of a sample at a photostationary state under UV irradiation at an on-surface intensity of 10 mW cm^{-2} for 15 s, ΔA_0, is equal to $A_0 - A_1$. Similarly, absorbance of a sample at a fading time t after shut-off of the UV light, ΔA_t,
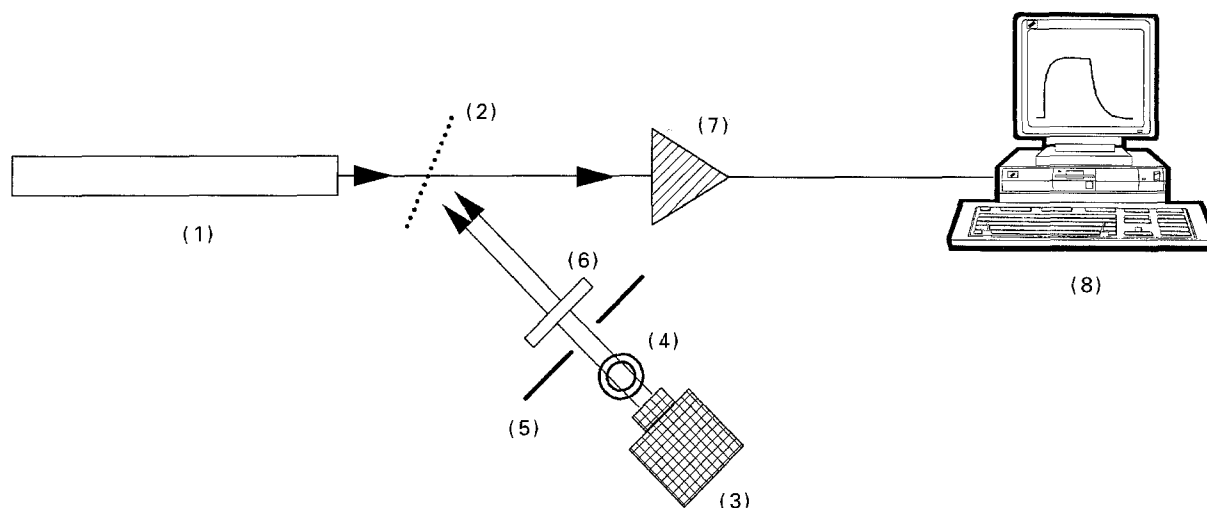

Figure 3 Layout of the apparatus used for kinetics measurement: (1) laser, (2) sample, (3) Hg lamp, (4) focusing system, (5) shutter, (6) UG5 filter, (7) detector, (8) PC.
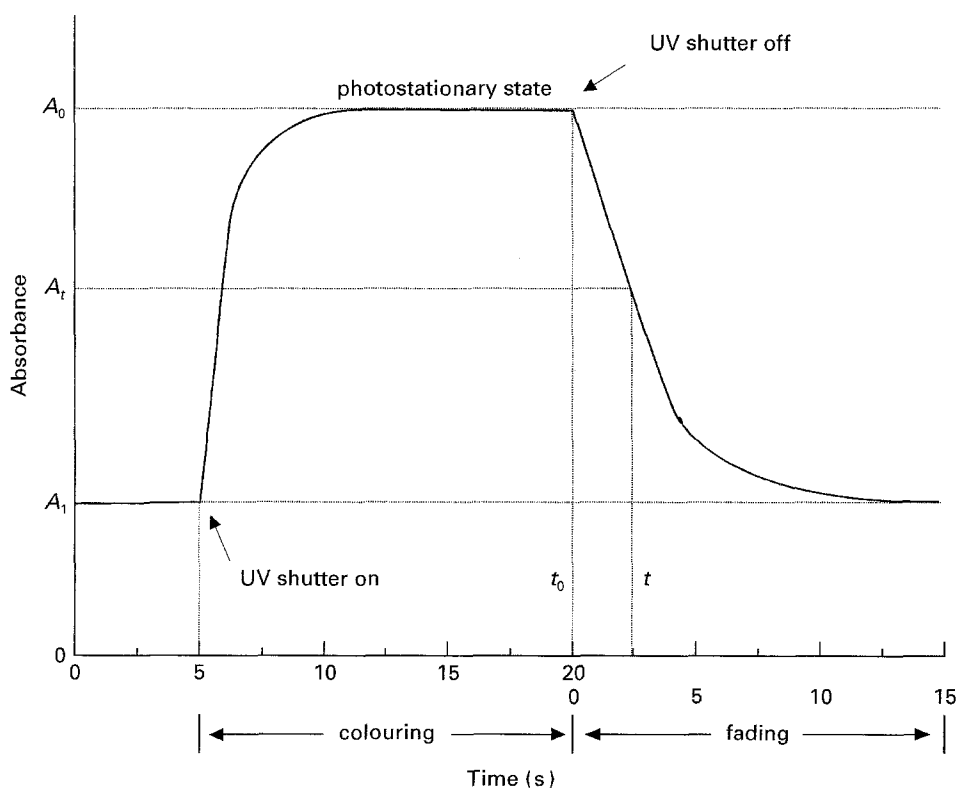

Figure 4 Schematic illustration of the colouring–fading process.

equals $A_t - A_1$. If the decoloration is a first-order reaction, the log $\Delta A_t/\Delta A_0$ versus t plot will be a straight line. From the slope (S) of the straight line, the half-life time ($t_{0.5}$) of the coloured form, i.e. the fading time required to halve the photochromic absorbance, and the decoloration rate (k) can be calculated according to the following equations:

$$t_{0.5} = -0.3010/S \qquad (1)$$

$$k = -2.303\,S \qquad (2)$$

3. Results and discussion
3.1. Free spirooxazines: SO-1 and SO-2
SO-1 and SO-2 are called free spirooxazines here as they are non-silylated. The colouring–fading curves for them in ethanol and the Ormocer coatings were measured at various temperatures and it was found that all the first-order plots deduced from these curves are straight lines. The Arrhenius plots for the decoloration processes are shown in Figs 5 and 6, respectively.

It is evident that the Arrhenius plots for either of the two free spirooxazines in ethanol and the Ormocer coatings are similar; no statistically significant differences can be found between them. This means that the dyes in the Ormocer coatings are as free as in ethanol solutions, implying that the environment around the photochromically active dye molecules in the Ormocer coatings is similar to that found in ethanol solutions.

This can be explained in terms of the porous structure of sol–gel derived Ormocer coatings. The pores created within the organic–inorganic matrix during drying and subsequent curing (110 °C) provide ideal cages for the dye molecules provided their dimensions are large enough for the ring opening–closure transformation of the dye molecules to take place. In this case the dye molecules are photochromically active, and on the pore walls there are certainly some unpolycondensated silanol groups which contribute towards creating a similar environment to that in ethanol, as is schematically illustrated in Fig. 7. On the other hand, some dye molecules are inevitably tightly bound in the matrix outside the pores and thereby become photochromically inactive. Nevertheless, as long as a certain portion of the dye is located inside the pores with sufficient space for the photochromic transformation, these dye molecules must be as free as in ethanol.

The decoloration behaviour of the free spirooxazines in PMMA coatings is greatly different from that in the Ormocer coatings. Fig. 8 presents a comparison between the first-order plots for the decoloration of SO-1 in PMMA coating, PMMA–EA solution and ethanol. It can be clearly seen that the decoloration is largely retarded by the PMMA matrix and is by no means a first-order reaction. This is because the high rigidity of the polymer matrix greatly restricts the degrees of freedom of the dye molecules and the heterogeneity of the polymer structure results in different local environments surrounding the dye molecules so that the colour decay is no longer a monoexponential process.

Convincing evidence supporting the dye-in-pore model illustrated in Fig. 7 are the different effects of heat treatments on the half-life time of SO-1 in PMMA and Ormocer coatings. Heat treatment up to
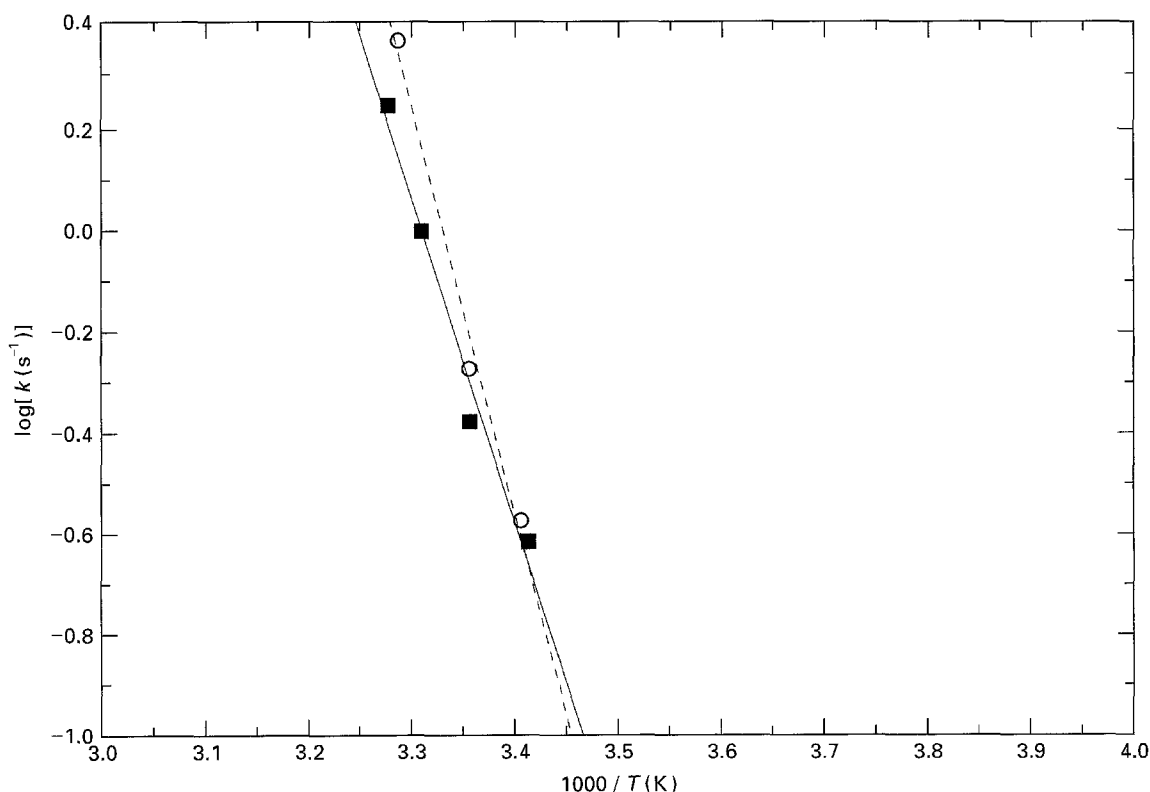

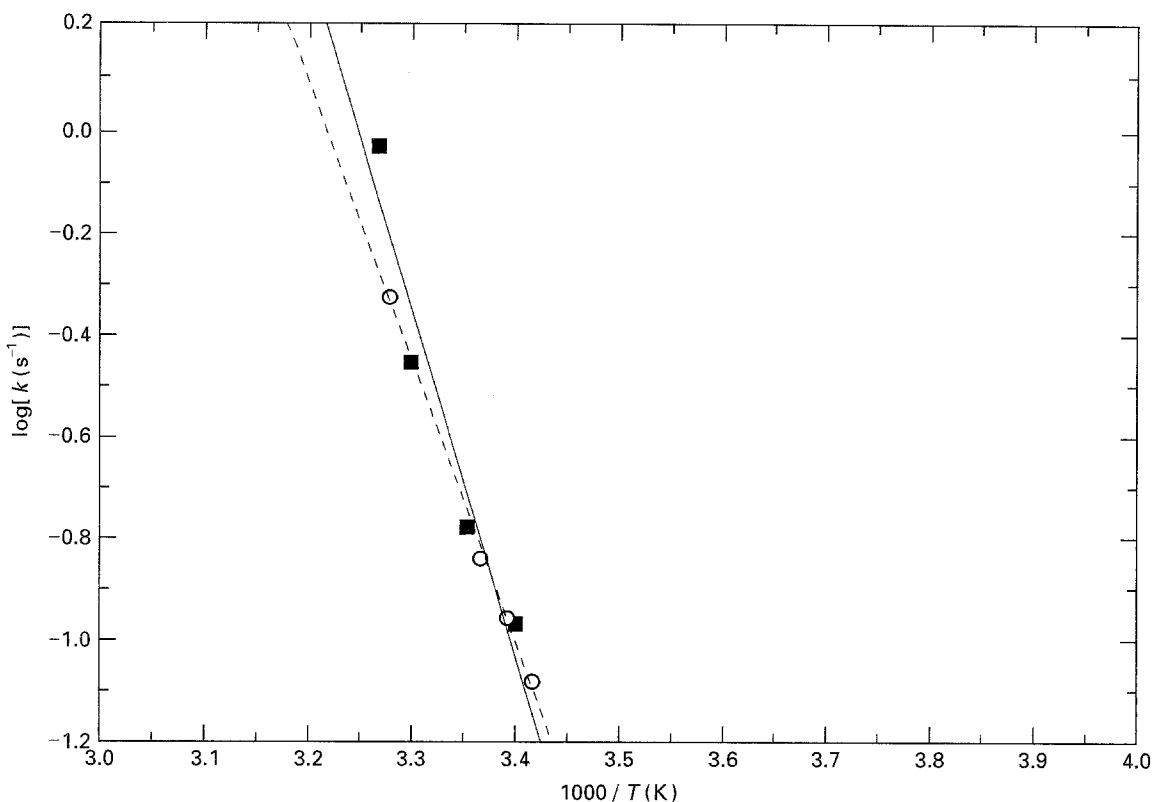*Figure 5* Arrhenius plots for the decoloration of SO-1 in (■) ethanol and (○) Ormocer coating.

Figure 6 Arrhenius plots for the decoloration of SO-2 in (■) ethanol and (○) Ormocer coating.
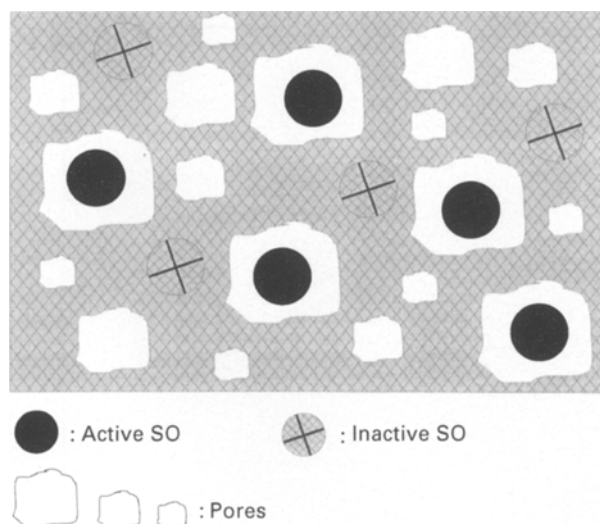

Figure 7 Schematic illustration of the active and inactive spirooxazine molecules.

120 °C gave rise to a gradual increase in the $t_{0.5}$ of the PMMA coatings, but caused no change in the $t_{0.5}$ of the Ormocer coatings [10].

The decoloration of SO-1 in the PMMA–EA solution, however, is much faster than in ethanol and follows first-order kinetics. The reason for this is that the predominant factor affecting the decoloration kinetics is the polarity of the solvent (EA) but not the structure of the solute (PMMA) in this case. It is generally recognized that the higher the polarity of the solvent, the higher the thermal stability of the coloured form [11], which implies a higher photochromic intensity and a lower thermal decoloration rate. The polarity of EA is much lower than that of ethanol, therefore the decoloration rate of SO-1 in EA is higher than in ethanol.

3.2. Silylated spirooxazine: SO-3

In SO-3, the spirooxazine is covalently bonded to trimethoxysilane through the $-CH_2-CH_2-CH_2-$ spacer. Our experimental results revealed that under the same experimental conditions the ΔA_0 of SO-3 reaches a similar level to that of the corresponding free spirooxazine, SO-1, both in ethanol and in the Ormocer coatings. This implies that the photochromic response of the dye is not degraded by the silylation. The decoloration rate of SO-3, however, is slower than that of SO-1 whether in ethanol or in the Ormocer coatings, though the silylated dye in ethanol also exhibits first-order decoloration kinetics as depicted in Fig. 9. This is to say, silylation of the dye results in the retardation of the decoloration process.

Fig. 10 shows that the decoloration of SO-3 in the Ormocer coating is not a first-order reaction since the first-order plots are not straight lines. In this case an approximation method was used in deducing apparent $t_{0.5}$ and k from the decoloration curves in Fig. 10. The time lengths between $\Delta A_0/2$ and $\Delta A_0/4$, $\Delta A_0/8$ and $\Delta A_0/16$, $\Delta A_0/32$ and $\Delta A_0/64$ are taken as $t_{0.5}$(a), $t_{0.5}$(b) and $t_{0.5}$(c), respectively, and the corresponding k(a), k(b) and k(c) are calculated from these $t_{0.5}$ values, assuming that the first-order mechanism is obeyed to a first approximation in the relatively short time intervals. It is established that the decoloration rate of the
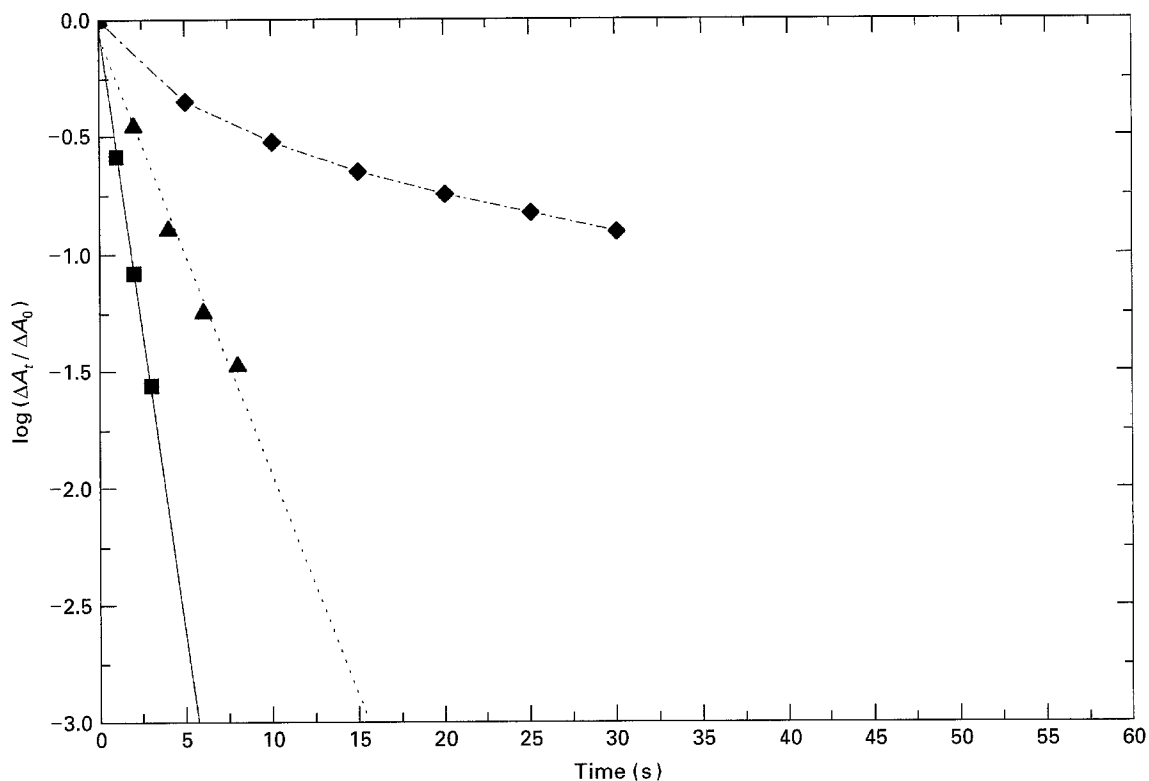
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Figure 8 First-order plots for the decoloration of SO-1 in (■) PMMA–EA solution (26.1 °C), (▲) ethanol (26.2 °C), and (◆) PMMA coating (26.3 °C).
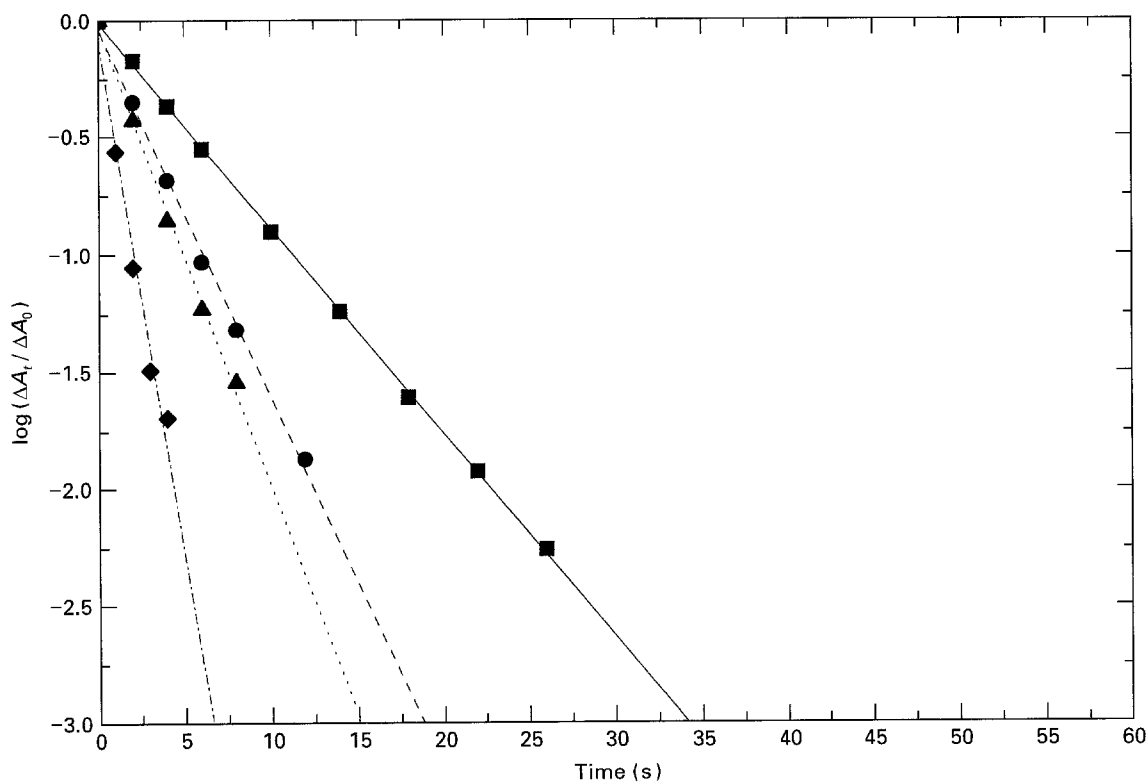

Figure 9 First-order plots for the decoloration of SO-3 in ethanol. Key:◆ 29.7 °C; ▲ 25.0 °C; ● 22.8 °C; ■ 19.5 °C.

silylated spirooxazine in the Ormocer coatings is considerably lower than in the corresponding ethanol solution and what is more, it undergoes a gradual decrease with the progress of the decoloration process, as is reflected by the decrease of k, k(c) $<$ k(b) $<$ k(a),

and decrease of the Arrhenius slope demonstrated by Fig. 11.

This result is strongly indicative of the different levels of degrees of freedom for the silylated dye molecules in the matrix. Owing to the involvement in the
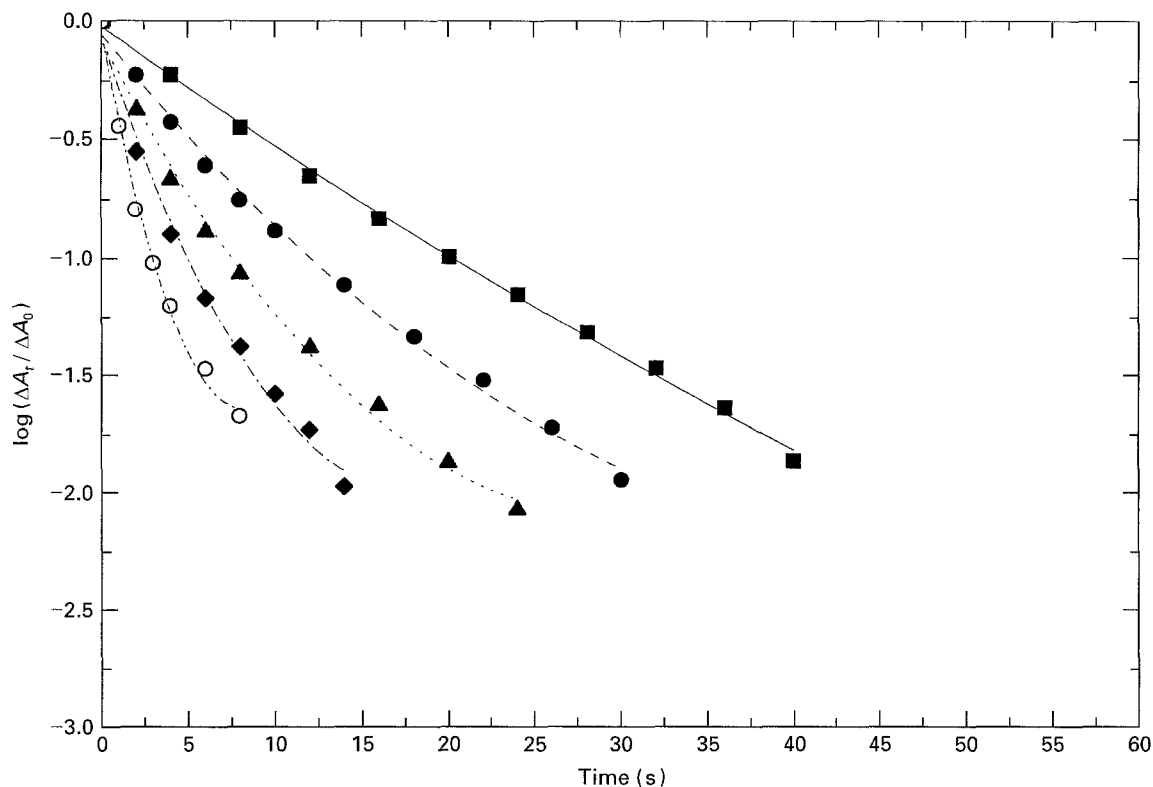
Figure 10 First-order plots for the decoloration of SO-3 in Ormocer coating. Key: ○ 29.7 °C; ◆ 26.4 °C; ▲ 21.6 °C; ● 17.6 °C; ■ 14.6 °C.
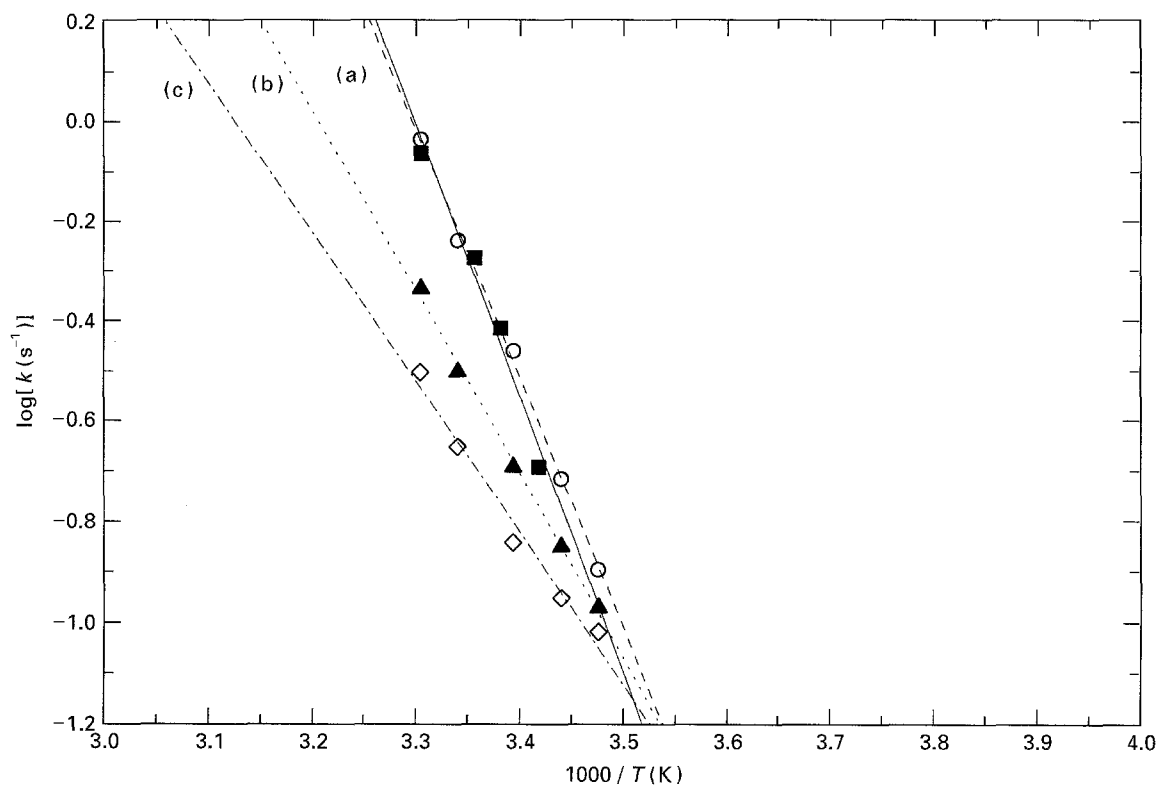
Figure 11 Arrhenius plots for the decoloration of SO-3 in (■) ethanol and Ormocer coating (Key: (○) a; (▲) b; (◇) c; see text for explanation).

hydrolysis–condensation reaction of the trimethoxy silane, the spirooxazine molecules, which are covalently bonded to the trimethoxysilane, may exist in different environments because the degree of hydrolysis of the three $-OCH_3$ groups and the degree of polycondensation of the resulting silanol groups might vary over a wide range, leading to different dye-to-matrix connectivity as is schematically represented by Fig. 12. It is obvious that the degree of freedom of the dye molecules in the Ormocer coatings decreases with increasing connectivity to the matrix. The higher the connectivity, the lower the decoloration rate. Accordingly, a gradually slowing-down decoloration process is demonstrated.
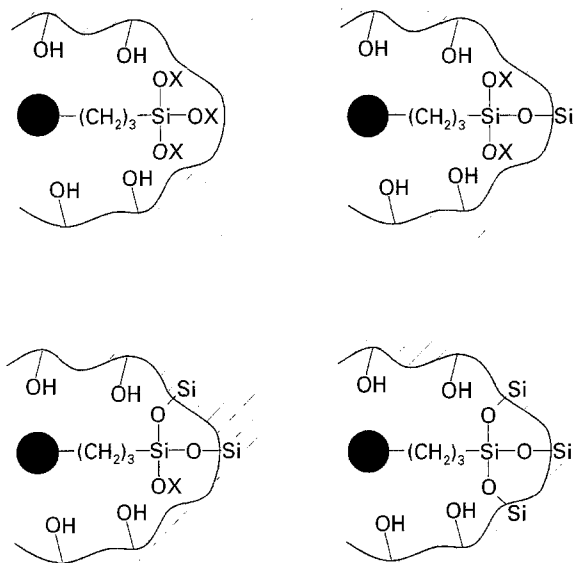
Figure 12 Schematic representation of the different connectivity of SO-3 to the matrix. ● = spirooxazine and X = H, CH$_3$.

4. Conclusions

The thermal decoloration kinetics of free spiro-oxazines, SO-1 and SO-2, in the Ormocer coating are similar to those in ethanol solution: first-order mechanism, similar decoloration rate and Arrhenius slope. The encapsulation of the dye molecules within the pores of the Ormocer matrix is responsible for the similarity. In contrast, the thermal decoloration of SO-1 in PMMA coatings does not obey a first-order mechanism and exhibits a very low decoloration rate. In contrast, the decoloration of SO-1 in PMMA–EA solutions follows a first-order mechanism and the decoloration rate is much higher than in ethanol.

The thermal decoloration of the silylated spirooxazine, SO-3, in the Ormocer coatings does not follow a first-order mechanism. The decoloration rate undergoes a gradual decrease during the decoloration process from a similar level to that of the same dye in ethanol to roughly half that value. This is attributed to the different dye-to-matrix connectivity caused by the different degrees of hydrolysis–condensation of the trimethoxysilane to which the dye is bonded via the –CH$_2$–CH$_2$–CH$_2$– spacer.

References

1. R. E. FOX, Research reports and test items pertaining to eye protection of air crew personnel. Final Report on Contract AF 41 (675)-215, AD440226, April 1961.
2. N. Y. C. CHU, in Proceedings of the 10th IUPAC Symposium on Photochemistry, Interlaken, 1984
3. N. Y. C. CHU, SPIE Inst. Ser. IS4 (1990) 102.
4. J. C. CRANO, C. N. WELCH and B. VAN GEMERT, R. Soc. Chem. Spec. Publ. 125 (1993) 179.
5. A. ARCOZZI, L. CRISCI and F. RENZI, Pigments 181 (1991) 296.
6. C. B. MCARDLE, Applied Photochromic Polymer Systems (Chapman and Hall, New York, 1992).
7. M. KRYSZEWSKI, B. NADOLSKI and A. M. NORTH, J.C.S. Faraday II 76 (1980) 351.
8. A. ZELICHENOK, F. BUCHHOLTZ and S. YITZCHAIK, Macromolecules 25 (1992) 3179.
9. L. HOU, M. MENNIG and H. SCHMIDT, Proc. SPIE 2255 (1944) 26.
10. L. HOU, M. MENNIG and H. SCHMIDT, Chim. Chron. New Ser. 23 (1994) 175.
11. A. FLANNERY, J. Amer. Chem. Soc. 90 (1968) 5660.