

Photochromic properties of a silylated spirooxazine in sol-gel coatings

L. Hou ^{a,*}, H. Schmidt ^b

^a Shanghai Institute of Optics and Fine Mechanics, Academia Sinica, P.O. Box 800-21, 201800 Shanghai, China

^b Institut für Neue Materialien, Geb.43, Im Stadtwald, D-66123 Saarbrücken, Germany

Abstract

For the first time a silylated spirooxazine was introduced into organically modified ceramics (Ormocer) coatings by the sol-gel method and its photochromic properties are studied and compared with the free (non-silylated) spirooxazine. The results reveal that the silylation has little influence on the spectroscopic properties and the photochromic intensity of the silylated dye in Ormocer coatings is at the same level as that of the free dye, though the decolouration rate of the dye is reduced by the silylation and the decolouration exhibits a significant deviation from first-order kinetics which the free dye obeys. This is due to the dye-to-matrix connectivity.

Keywords: Silylated spirooxazine; Sol-gel; Photochromic coating

1. Introduction

A photochromic material is characterized by its ability to undergo reversible colour change between two states having different optical absorption spectra. This colour change is induced in at least one direction, usually the colouration direction, by electromagnetic radiation (e.g. UV light). Spirooxazines are well known as typical photochromic compounds which are based on light induced heterolytic cleavage of the C-O bond, resulting in the formation of merocyanine, the coloured form, as is illustrated in Fig. 1 [1].

Since a photochromic compound in its crystalline state is totally inactive, then either for fundamental

research or for application development it must be dissolved in an appropriate solvent or dispersed in a suitable solid matrix to form a photochromic system. The interaction between the photochromic compound and the solvent or solid matrix strongly affects the overall photochromic properties of the system, i.e. photochromic intensity and colouration and decolouration rates. Spirooxazines have been the subject of many researches recently, mainly due to their inherently higher photostability than another kind of spiro-compounds, spiropyrans. Moreover, it was reported that the photostability of spirooxazines can be significantly improved by encapsulating the dyes into sol-gel derived Ormocer (organically modified ceramics) coatings with both the photochromic intensity and the spontaneous thermal decolouration rate being almost the same as in ethanol solutions [2].

The successful utilization of sol-gel process in the preparation of solid matrices for photochromic

* Corresponding author.

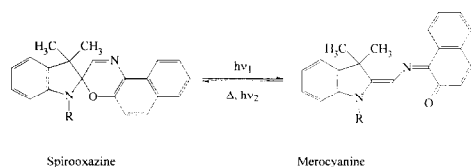


Fig. 1. Photochromic transformation of spirooxazine.

dyes is attributed to its unique advantages. It starts from alkoxide solutions at room temperature and the gel formed by the hydrolysis–condensation reaction of alkoxides can be cured at a temperature much lower than the decomposition point of the introduced dye. The pores within the gel are ideal cages for the dye molecules. It is also possible to modify the degree of freedom of the dye molecules to different extents by grafting them to the matrix network. In this paper, experimental results are reported for the first time on the photochromic properties of a silylated spirooxazine in sol–gel derived Ormocer coatings. The effect of silylation on photochromic intensity and decolouration kinetics is discussed in terms of the dye-to-matrix connectivity, which determines the degree of freedom of the dye molecules.

2. Experimental

Ethyltriethoxysilane (ETES) and 3-glycidoxypropyltrimethoxysilane (GPTMS) were used as starting materials at a molar ratio of 3:7 for the preparation of the Ormocer coatings. The molecular structure of the silylated (silane-substituted) spirooxazine, in which the spirooxazine molecule is covalently coupled to a trimethoxysilane via the $-\text{CH}_2-\text{CH}_2-$ spacer, is illustrated in Fig. 2. For the synthesis of sols for coating, appropriate amounts of ETES, GPTMS and half-stoichiometric quantity of water were first mixed by magnetic stirring for 10

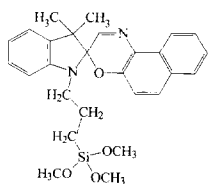


Fig. 2. Molecular structure of the silylated spirooxazine.

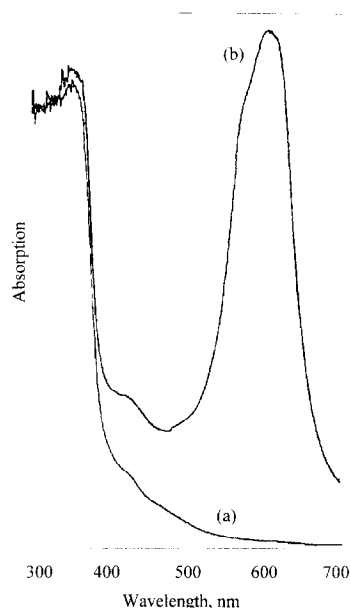


Fig. 3. Absorption spectra of the photochromic coating: (a) before, (b) after UV irradiation.

min, and then subjected to 20 kHz ultrasonic radiation at a power of 20 W for 20 min. Into the sols thus obtained ≈ 8 wt% Triton X-100 was added, followed by the introduction of the silylated dye and additional magnetic stirring for 1 h. Viscous sols were obtained in this way and used for the preparation of coatings of different thickness by spreading on microscopic slides.

3. Results and discussion

The absorption spectra of the photochromic coating before and after UV irradiation are shown in Fig. 3. Since the decolouration rate is too high at room temperature to take the absorption spectrum of the coloured form, the coating was first cooled down to -20°C and then irradiated by the Hg-lamp to gain a saturated colouration, and immediately after removal of the Hg-lamp the absorption spectrum was measured. We see in Fig. 3 an absorption maximum at 614 nm and a shoulder around 570 nm in the upper absorption curve, which is a typical absorption spectrum of the coloured form of spirooxazine. This

suggests that the silylation of spirooxazine has little influence on the spectroscopic properties.

The photochromic properties of the coatings heat treated at 110°C for 2 h were measured using our computer-controlled apparatus in which a Hg-lamp was used as the UV source and He–Ne laser (633 nm) as a probing light beam. From the colour-fading curves taken at various temperatures, the equilibrium absorbance at the photostationary state under UV irradiation, ΔA_0 , and the absorbance at the fading time (t) after cessation of UV light, ΔA_t , were extracted and the relative photochromic intensity, $\Delta A_t/\Delta A_0$, were calculated. First-order plots for the decolouration of the photochromic coating at different temperatures were drawn as the $\log \Delta A_t/\Delta A_0$ versus t curves, from which the half-life time ($t_{0.5}$) and the thermal decolouration rate (k) of the coloured form were deduced.

Our experimental results show that the equilibrium absorbance (ΔA_0) of the photochromic coating containing the silylated spirooxazine when irradiated by the UV light at an on-surface intensity of 10 mW/cm² for 15 s reaches the same level as in the case of the non-silylated dye under the same conditions, implying that the photochromic intensity of the dye is not degraded by the silylation. The decolouration rate of the silylated dye, however, is slower than that of the free one. In ethanol solutions both dyes exhibit a first-order decolouration kinetics with the $t_{0.5}$ at 22.5°C being 1.5 and 1.8 s, respectively, suggesting that silylation of the dye leads to the retardation of the decolouration process. In addition, the decolouration of the silylated dye in the sol–gel coatings is not a first-order reaction as is depicted in Fig. 4.

The first-order plots are not straight lines and, the higher the temperature, the greater the deviation from first-order kinetics. In this case the following approximation method was employed to deduce the apparent $t_{0.5}$ and k from the decolouration curves: the time lengths between $\Delta A_0/2$ and $\Delta A_0/4$, $\Delta A_0/8$ and $\Delta A_0/16$, as well as $\Delta A_0/32$ and $\Delta A_0/64$ were taken as $t_{0.5}(a)$, $t_{0.5}(b)$ and $t_{0.5}(c)$, respectively, and the corresponding $k(a)$, $k(b)$ and $k(c)$ were calculated from these $t_{0.5}$ values based on the assumption that first-order mechanism is obeyed in these relatively short time intervals to a first approximation. It was established that the decolouration

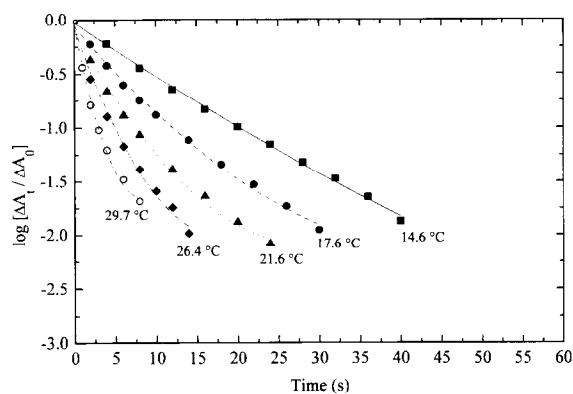


Fig. 4. First-order plots for the decolouration of the coating at different temperatures.

rate of the silylated spirooxazine in the Ormocer coatings is considerably lower than the corresponding ethanol solution and undergoes a gradual decrease with the progress of the decolouration process, as is reflected by the decrease of k , $k(a) > k(b) > k(c)$, and the Arrhenius slope shown in Fig. 5.

This result is strongly indicative of the different levels of freedom by which the silylated spirooxazine molecules exist in the coatings. Owing to the involvement in the hydrolysis–condensation reactions of the trimethoxysilane, the spirooxazine molecules which are tethered to the trimethoxysilane may exist in different environments where the hydrolysis–condensation degree of the three $-\text{OCH}_3$ groups in the silane might vary over a wide range, giving rise to different dye-to-matrix connectivity.

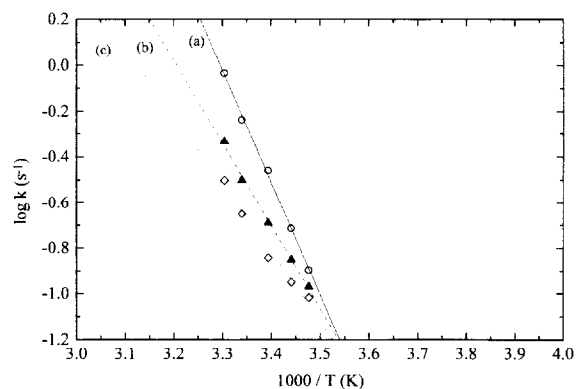


Fig. 5. Arrhenius plots for the decolouration of the photochromic coatings.

The degree of freedom of the dye molecules in the coating decreases with increasing connectivity to the matrix. The higher the connectivity, the slower the decolouration rate. Consequently, a gradually slowing-down decolouration process is demonstrated.

4. Conclusions

To conclude, the silylation of photochromic spirooxazine results in little influence on the pho-

tochromic intensity, but leads to an evident deviation of the decolouration kinetics from first-order mechanism and gives rise to a considerable decrease in the decolouration rate.

References

- [1] G.H. Brown, Photochromism – Techniques of chemistry, Vol. 3 (Wiley-Interscience, New York, 1971).
- [2] L. Hou, M. Mennig and H. Schmidt, SPIE Vol. 2288, Sol-Gel Optics III (1994) 328.