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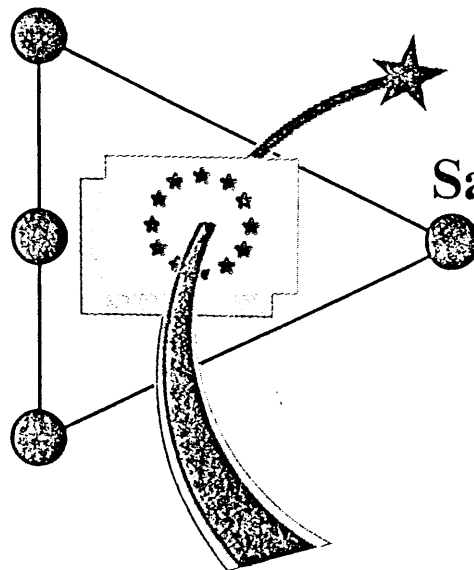
Extended Abstracts

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A novel sol-gel derived ORMOCER material as host for photochromic dyes.

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In recent years, the importance of organic dyes used for various optical purposes has been increasing significantly. Among the others, fundamental and applied researches on photochromic dyes have been receiving more and more interest. One of the most important aspects is the matrix which hosts the dyes. Dyes in liquid matrices (e.g. water, alcohol, chloroform etc.) usually suffer from undesirable aggregation which is responsible for concentration quenching of the photochromic effect. Thus solid state matrices have been pursued and exploited. Up to the present, however, most of the research work on solid matrices for photochromic dyes have been focussed on organic polymer systems[1]. Although dye aggregation is reduced to a certain extent another major limitation arises to the long-term use of polymer matrices, i.e. low thermal and photochemical stability. In order to overcome this limitation it is advisable to use inorganic oxide matrices, which are not only thermally and photochemically but also dimensionally more stable.

The low-temperature characteristics of the sol-gel process make the sol-gel derived gels offer exciting potentials as hosts for a wide variety of dye molecules including photochromic dyes. D. Levy et al.[2] studied the photochromic properties of spiropyranes in three kinds of modified silica matrices prepared by the sol-gel process. Only one system showed normal photochromism. J. I. Zink and B. Dunn[3] doped spiropyranes in a Al_2O_3 - SiO_2 -system using the bialkoxide ASE as the starting material. They also doped 2,3-diphenylindene oxide (DPIO)[4] into three kinds of gels, i.e. SiO_2 , ASE and ORMOSIL and found that both the photochromic intensity and the lifetime decrease gradually during the ageing and drying process.

In the present work, a novel sol-gel derived ORMOCER material has been developed as a host for spirooxazines, one (SO1) is commercially available (Aldrich Chemical Inc.) and another (SO2) is a home-synthesized one with the spirooxazine molecules bonded to Si in the silane molecules through $-\text{CH}_2-\text{CH}_2-\text{CH}_2$ -spacers. Organically modified alkoxides, e.g. MTMS, ETES, GPTMS and DMDES or their mixtures were used as starting compounds. A two-step procedure, i.e. acid-catalysed hydrolysis and base-catalysed polymerisation, was used for the sol preparation. Coatings or monolithic gels have been successfully obtained with this method by spraying and casting respectively.

The colouring and fading processes of the dyes were monitored using a home-made apparatus. A 100W Hg-lamp is used as the light source for UV-irradiation and a He-Ne laser ($\lambda=633\text{nm}$) is used as the monitoring light beam. The irradiation intensity on the

sample surface is adjusted by a focussing system to mimic the intensity of sunlight (ca. 3 mW/cm²).

The following experimental results have been obtained:

Using the established preparation procedure, sols with different viscosity can be tailored by the introduction of different kinds and contents of additives, in response to different viscosity requirements for the preparation of coatings of certain thickness and preparation of shaped gels at desired dimensions.

Coatings and gels containing SO1 are colourless at room temperature, but those containing SO2 have brown bottom colours. Although the fading speeds of the spirooxazines are about 2 times lowered by doping in the coatings and gels, they are still too fast to measure the absorption peak wavelength of their coloured states using the existing spectrophotometer. Therefore the gels were cooled down to -20°C, then irradiated by UV light to get saturated colouring and the absorption spectra were measured. In this way, the absorption peak wavelengths have been determined to be 613 and 614 nm respectively. This indicates that the He-Ne-laser is a fairly suitable probing light.

Heat treatment was exerted to the coatings on glass slides up to 120°C. No significant degradation of the photochromism was detected. In addition, SO2 is more stable than SO1 against heating.

The photochromic absorption level of coatings with a thickness of ca. 500 μm and the dye concentration of 1 × 10⁻³ mol/l is similar to that of the dye solution in ethanol at a concentration of 5 × 10⁻⁴ mol/l (the maximum photochromism concentration) with a 10 mm optical path. This implies that the aggregation problem is greatly improved (by about 10 times) in these ORMOCER matrices.

The mechanical properties of the matrix material remains to be further improved in order to meet the requirements for practical use.

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References

- [1] H. Dürr and H. Bouas-Laurent, <<Photochromism - molecules and systems>>, Elsevier, 1990, Amsterdam
- [2] D. Levy and D. Avnir, *J. Non-Cryst. Solids*, 113 (1989) 137
- [3] J. I. Zink and B. Dunn, *J. Mater. Chem.* 1(6) (1991) 903
- [4] S. A. Yamanka, J. I. Zink, B. Dunn, *Preparation of sol-gel optics II*, San Diego, 1992