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

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Version of record first published: 24 Sep 2006

To cite this article: John Biteau, Frederic Chaput & Jean-Pierre Boilot (1997): Dynamics of a Spirooxazine in Doped Hybrid Xerogels, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 297:1, 49-56

To link to this article: http://dx.doi.org/10.1080/10587259708036102

Mol. Cryst. Liq. Cryst., 1997, Vol. 297, pp. 49–56
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DYNAMICS OF A SPIROOXAZINE IN DOPED HYBRID XEROGELS

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Abstract : The normal photochromism of a spirooxazine in gel thin films obtained by polymerizing the methyltriethoxysilane was analyzed as a function of the degree of cross-linking of the gel matrix. When doped-gel films contain a high fraction of silanol groups, the thermal decay of the coloration is governed by the hydrogen bond interaction between the metastable merocyanine and the silanol groups. By increasing the number of siloxane groups, the gel matrix imposes a gaussian distribution of localized barriers to the steric requirements of the reaction.

INTRODUCTION

The sol-gel process is a synthetic route to trap organic molecules in a solid matrix. The polymerization process was usually initiated by adding water to a solution of alkoxide (such as the tetraethoxysilane $Si(OC_2H_5)_4$ or TEOS) in ethanol. The preparation of doped-xerogels generally consisted in adding a solution of the desired dopant to the initial polymerizing system. Numerous materials and their applications were proposed, such as sensors, optical limiters, information recording materials, dye-laser materials [1,2].

Concerning photochromic materials, two types of photochromic behavior were observed for spiropyran[3] and spirooxazine[4] trapped in sol-gel matrices. The normal photochromism was observed in matrices prepared by polymerizing $RSi(OC_2H_5)_3$ (R= methyl, ethyl, vinyl,...) sol-gel precursors. In contrast, when the precursor was $Si(OC_2H_5)_4$ (TEOS), materials exhibited reverse photochromism. The photochromic behavior was related to the polarity of the cage within which the spiro-molecule was trapped. For the former precursor, the cage surface was composed of apolar R groups which did not stabilize the merocyanine form and led to a normal photochromism. For the latter precursor, the merocyanine zwitterionic form was stabilized by strong hydrogen bonds to the silanols of the cage and the photochromism was reversed.

In this paper, we present a quantitative analysis of kinetics for the normal photochromism of a spirooxazine in gel thin films obtained by polymerizing $CH_3Si(OC_2H_5)_3$ (MTEOS). We mainly show that the dynamics of photochromic molecules is directly related to the advancement of the condensation reaction in the xerogel film .

EXPERIMENTAL SECTION

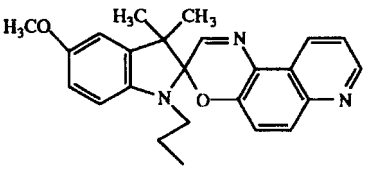
Preparation of photochromic materials

Doped xerogels were prepared by hydrolysis - condensation of an organically modified alkoxide precursor under acid - catalyzed conditions with acetone as common solvent. The matrix was hereafter noted as the molecular precursor : MTEOS.

In the starting mixture, the alkoxide : water (pH=2.5) : acetone molar ratios were respectively 1:3:3. After hydrolysis for several hours at room temperature, a small amount of aminopropyltriethoxysilane (10^{-3} mol/l) was added both to partially neutralize protonic species, thus avoiding subsequent chemical degradation of the dyes, and to catalyze condensation reactions[5]. An acetonic solution of a spirooxazine was then added and the sol was exposed to the ambient air with magnetic stirring until the dye concentration reached 10^{-2} mol/l.

Coatings were prepared by spreading the viscous sol on slide glass substrates, using the spin coating technique (the angular velocity of the spinner was 1000 rpm). For IR spectra, recorded on a Fourier transform spectrometer Bomem MB100, the sol was spread on silicon wafers.

The photochromic molecule employed in this study is a spirooxazine derivative supplied by PPG Industries (Scheme 1) : the 5- methoxy- 3,3 - dimethyl- 1 n - propylspiro [indoline -pyrido benzoxazine] noted SO1.



SO1
Scheme 1

The set-up for kinetics measurements of the photochromism.

Either visible or UV light from 150 W Xe lamp was selected by using filters for the illumination of the samples. Visible light was firstly used for 10 min to completely decolorate the sample (123 W/m^2 on the surface of sample). UV was then used for 30 min to activate the photocoloration in the photochromic sample (10 W/m^2 on the surface of the sample). Finally, the light beam was off to follow the dark decoloration. The absorption spectra for kinetics of photocoloration and dark fading were recorded on a Zeiss spectrophotometer.

RESULTS

In order to explore the effects of the inorganic polymerization on the dynamics of photochromism, thin films made from MTEOS, aminopropyltriethoxysilane and SO1 were dried at the following temperatures : 25°C, 72°C, 100°C and 130°C. By following the time evolution of the condensation at various temperatures we were able to obtain films whose cross-linking had reached a degree of polymerization high enough so that it did not change at room temperature. The kinetics of polymerisation was studied by transmission infrared spectroscopy (FTIR). Cross-linking could be followed by the decrease of the silanol bands (897 cm^{-1}, 1030 cm^{-1}, 3300-3500 cm^{-1}) and the increase of siloxane bands (mainly 1087 cm^{-1}). The intensity of the band at 897 cm^{-1} was recorded to quantitatively estimate the change of the proportion of silanols in a layer. Finally the following samples were chosen for our study : 25°C for 456 hours, 72°C for 111 hours, 100°C for 14 hours and 130°C for 4 hours. FTIR spectra (figure 1) clearly show that the four films present different degrees of cross-linking.

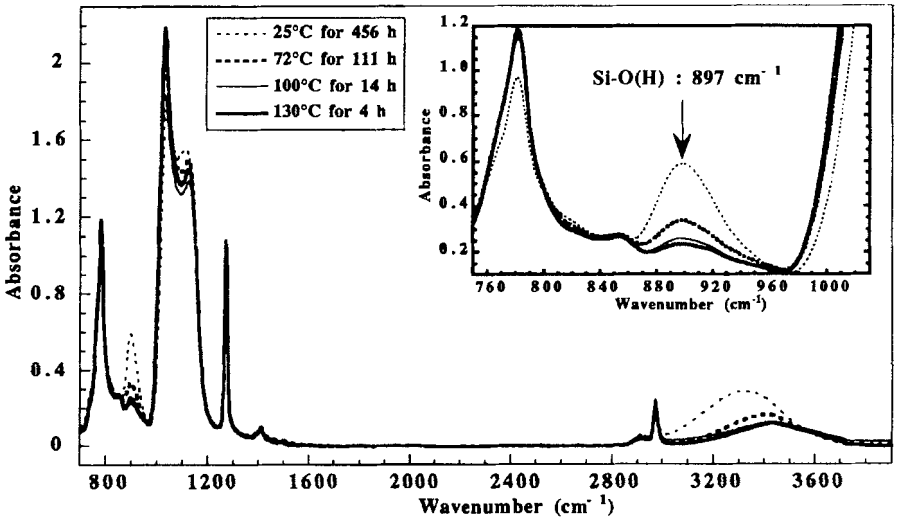


FIGURE 1 : Infrared absorbance spectra of films of various condensation rate. Spectra are normalized by using the Si-CH_3 band at 1270 cm^{-1}.

A cycle of UV photocoloration-thermal bleaching was recorded for the different samples. At the photostationary state of the coloration (just after the UV light was off), the normalized absorption spectra of films dried at 72, 100 and 130°C were totally superimposable, while the spectrum of the 25°C-dried film presented a two nanometer blue shift (fig. 2). Moreover the contribution of the shoulder around 570 nm was greater for

this low condensed film.

The kinetics of ring closure reaction was studied following the fading of the absorption maximum in the visible. Figure 3 presents a coloration - bleaching cycle characteristic of the normal photochromism for spirooxazines trapped in organically modified gel matrices.

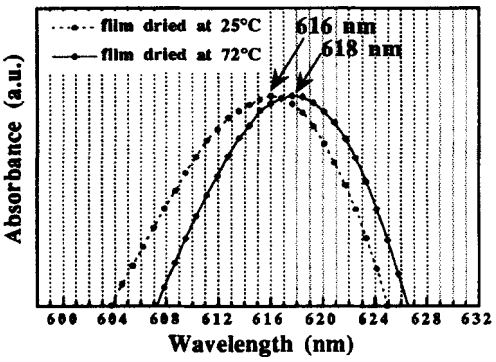


FIGURE 2 Normalized absorption spectra of photocolored thin films.

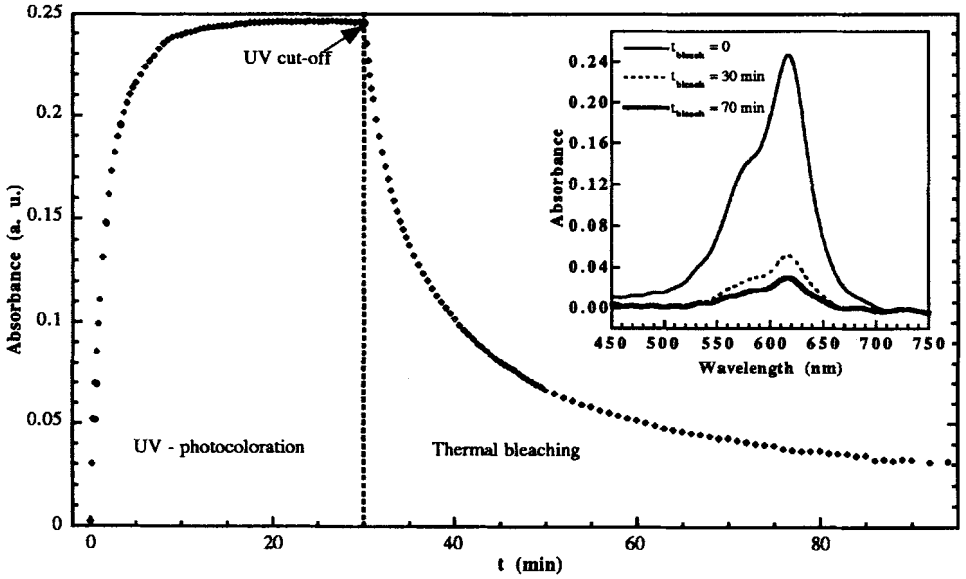


FIGURE 3 Photochromic cycle measured on the film dried at 100°C. Inset: Evolution of the absorption spectrum after the UV light was off.

DISCUSSION

Analysis of the thermal bleaching kinetics : the gaussian distribution model.

The thermal bleaching of photochromic molecules is useful to characterize the molecules-matrix host system. This process is a free evolution, then it represents the pure effects of the interactions between the molecules and the matrix without other stimulus that the temperature. The study of this process in the photochromic cycle also avoids the introduction of quantum yields for which the value of the molecular concentration is

needed. The accurate value of the concentration is not easy to know in films because it requires to determine the density of a 2-4 μm-thick sample.

As it is the case for polymers, the kinetics of thermal unimolecular reactions of spirooxazines from metastable species to stable ones did not proceed in a first-order kinetics. In fact, it was generally accepted that the common observation of non exponential isomerization kinetics in polymers indicates matrix effects by imposing a distribution of localized barriers to the steric requirements of the reaction [6].

Taking into account this distribution of environments around molecules in a polymer matrix, it seems more coherent to analyze the kinetic results with a model based on a distribution rather than with a discrete model like the biexponential one. A gaussian distribution of activation energies has been used by Richert et al.[6] to study spiropyrans in organic polymers. We used the gaussian model developed by Albery et al.[7], which has been applied to porous silica by Samuel and co-workers[8]. The basic assumption of this model is a distribution of energies of activation around some mean value $\overline{E}^*$:

$$E^* = \overline{E}^* - \gamma x RT$$

- x is the parameter describing a normal gaussian distribution $\exp(-x^2)$.
- γ is the spread of the dispersion.

Considering Arrhenius law the dispersion in the first order constants is : $k = k_{av} \cdot e^{\gamma x}$

The thermal free evolution of the absorbance after coloration of a molecule is (A_{th} being the absorbance at the thermal equilibrium) :

$$A(t) = A_0 e^{-k \cdot t} + A_{th}$$

Then for the population of molecules the expression of the absorbance becomes :

$$A(t) = A_0 \frac{\int_{-\infty}^{+\infty} e^{-k(x) \cdot t} \cdot e^{-x^2} dx}{\int_{-\infty}^{+\infty} e^{-x^2} dx} + A_{th}$$

The value of the integral at the denominator is $\pi^{1/2}$. We can write this expression showing explicitly the distribution of rate constants k :

$$A(t) = A_0 \cdot \pi^{-1/2} \int_{-\infty}^{+\infty} e^{-k \cdot t} \cdot \exp\left[-\left(\frac{\ln k - \ln k_{av}}{\gamma} \right)^2 \right] \frac{d(\ln k)}{\gamma} + A_{th}$$

The numerical calculation of this integral is explained in reference 7. The distribution of energies leads to a distribution of ln(k) around some $\ln(k_{av.})$, where k_{av} is the average constant of the reaction and γ the half width of the gaussian in ln(k) at 1/e. γ characterizes the dispersion and gives a quantitative estimation of the extent of the heterogeneity of the matrix.

Figure 4 indicates the excellent agreement between this model and the experimental thermal bleaching of gels in respect with the fit obtained with the biexponential model :

$$A(t) = A_1 e^{-k_1 t} + A_2 e^{-k_2 t} + A_{th}$$

where A_1 and A_2 are contributions to the initial optical density A_0 of each kind of merocyanine.

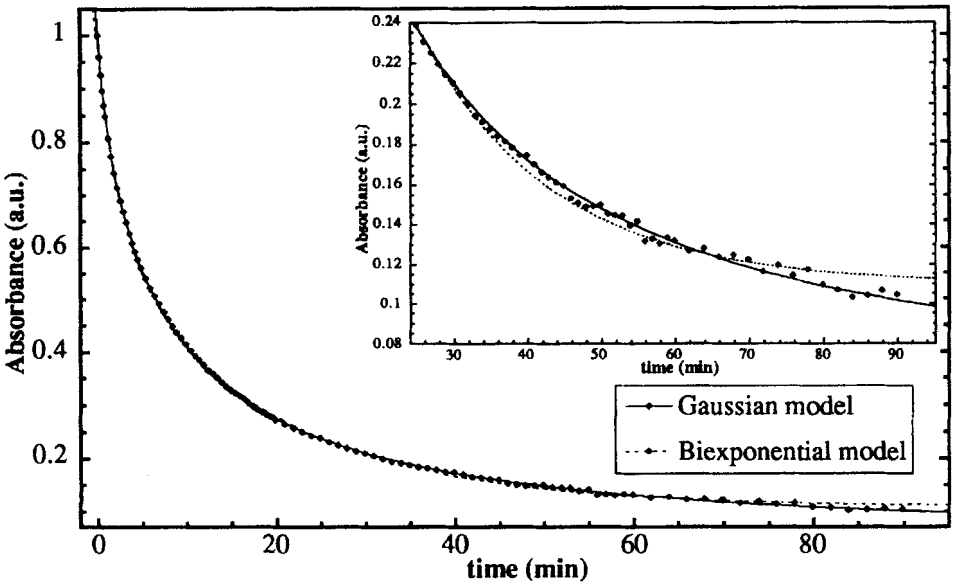


FIGURE 4 Gaussian and biexponential fits for the thermal bleaching at 20°C of the film dried at 100°C for 14h.

The gaussian distribution and the rate constants obtained by the two models are presented in figure 5. As expected the two constant values of the biexponential expression are inside the gaussian curve which covers three orders of magnitude.

The following points are in favor of the gaussian distribution model :

- From a physical point of view the use of this model for an amorphous matrix is more satisfying than a discrete one.
- It better fits the thermal bleaching.
- There is one parameter less for this model than for the biexponential one.

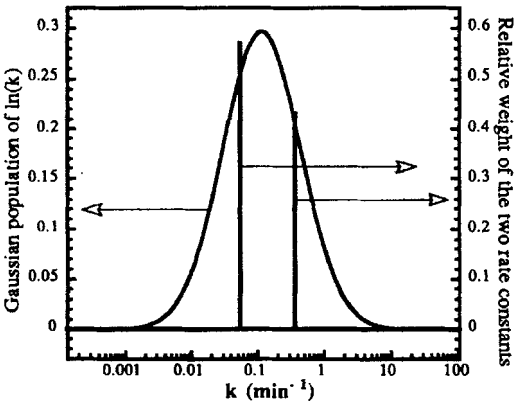


FIGURE 5 Distribution of rate constants deduced from the fit with the gaussian model. The vertical lines represent the constants obtained with the biexponential model.

Consequences of drying on photochromism : a kinetic study.

This model of a gaussian distribution of activation energies was then applied to the thermal bleaching kinetics of the films dried at various temperatures. Gaussian curves are reported in figure 6. The bleaching of the film dried at room temperature is much slower than the bleaching of the others. This is consistent with a more pronounced coloration of this sample at the thermal equilibrium (absorbance of 0.025 instead of about 0.008 for the other samples). As regards the other three, the bleaching of xerogel dried at 100°C is slightly more rapid.

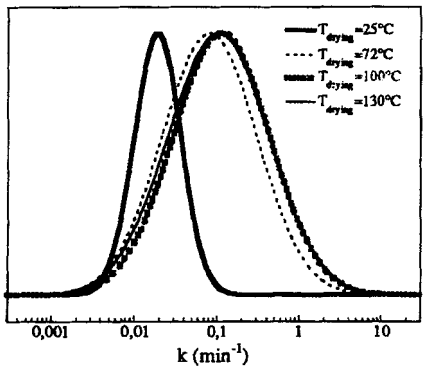


FIGURE 6 Distributions deduced from the films with different condensation rate.

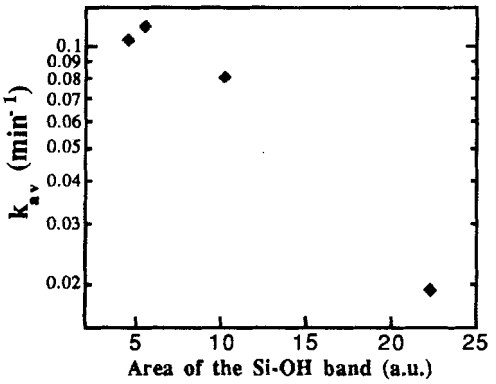


FIGURE 7 k_{av} versus the area of the Si-OH IR band (representing the proportion of Si-OH)

Figure 7 represents the evolution of k_{av} in respect with the quantity of silanols. The dynamics of molecules were slowed down by the presence of the polar protic groups when their concentration was sufficient in the film. When the condensation went on, the proportion of silanols decreased, then the merocyanines were less stabilized and the thermal bleaching was accelerated. An analogy can be made with a previous work where the concentration of silanols had been increased by hydrolysis of a tetraethoxysilane/vinyltriethoxysilane mixture instead of pure vinyltriethoxysilane[4]. In these TEOS/VTEOS mixtures a blue shift of the merocyanine absorption band appeared corresponding to hydrogen bond interactions with silanols. When the proportion of TEOS was high enough, the stabilization of the merocyanine was sufficient to reverse photochromism. The blue shift observed in the low condensed MTEOS film confirms the relative stabilization of the merocyanine by the silanols via hydrogen bond type interactions. But, the acidity of a silanol from hydrolyzed MTEOS is weaker than the one of a silanol from hydrolyzed TEOS. In consequence, in the low condensed MTEOS gel, the hydrogen bond type interactions were not strong enough to generate reverse photochromism.

Concerning the sample dried at 130°C, which exhibits the highest degree of cross-

linking, the bleaching was slower than for the film dried at 100°C. The slight decrease of k_{av} can be explained by a decrease of the average free volume in the matrix resulting from the condensation of silanols. Then the steric hindrance became the dominant contribution in the interactions between the molecules and the matrix, and the thermal ring closure was slowed down.

An interesting result is that, for the film dried at room temperature, the bleaching kinetics was fitted by a narrow gaussian. In fact, when the concentration of silanols is high, the gaussian model did not fit as well as the biexponential one. When there are specific interactions with the matrix like hydrogen bond type interactions the distribution significantly deviates from the gaussian model.

CONCLUSION

To sum up, we have established a clear relation between the dynamics of the photochromic molecules and the degree of cross-linking in spirooxazine doped-gels. After being dried at room temperature, doped-gel films contain a high fraction of non-bridging silanol groups. The experimental thermal decay of the coloration is then governed by the hydrogen bond interaction between the metastable merocyanine and the silanol groups. There is a predominant high activation energy which slows down the ring closure. When the drying temperature rises, thus increasing the number of bridging siloxane groups, the agreement between the Gaussian model and the experimental bleaching becomes remarkable. The gel matrix imposes a gaussian distribution of localized barriers to the steric requirements of the reaction. At the end of the condensation process, the reaction is again slowed down by the shrinkage of the matrix which broadens the distribution of activation energies.

Acknowledgments : This work was supported by Essilor International, Research and Development. We thank F. Piotrowski, G. Baillet, P. Tardieu and J-P. Cano, all of Essilor International, for their helpful collaboration.

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