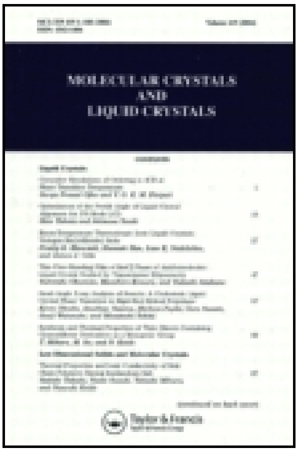

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PHOTOCHROMISM OF DITHIENYLETHENE DERIVATIVES TRAPPED IN SOL-GEL MATRICES

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Abstract : Solid-state materials containing photochromic dithienylethene derivatives were prepared by the sol-gel process in the form of thin films of a few µm-thick. The effect of substituents (pyridyl or methoxyphenyl) of the optically active molecules on photochromic properties was investigated. Thicknesses and refractive indices either at 633 nm or 785 nm were determined in the colored and in the discolored state by using the Attenuated Total Reflexion method. Sol-gel films containing methoxyphenyl substituted molecules show a large refractive index change, $\Delta n \approx 3.10^{-3}$ at 785 nm. This variation is important considering the low doping level (0.7 wt%).

INTRODUCTION

Sol-gel technique provides a low temperature attractive approach to the preparation of hybrid organic-inorganic matrices.[1] The sol-gel chemistry involves the sequential hydrolysis and condensation of alkoxides (usually silicon alkoxides) initiated by acidic or basic aqueous solution in presence of a mutual cosolvent :

$$\equiv\text{Si-OR} + H_2O \rightarrow \equiv\text{Si-OH} + \text{ROH} \qquad \text{Hydrolysis}$$

$$\equiv\text{Si-OH} + \text{H}\underset{\smile}{\text{O}}\text{-Si}\equiv \rightarrow \equiv\text{Si-O-Si}\equiv + H_2O \qquad \text{Condensation}$$

Inorganic gels are formed, which can be dried to produce xerogels. The mild synthesis conditions offered by the sol-gel route allow for the incorporation of optically active organic molecules into the glassy matrix to form doped xerogels with specific optical properties.[2] Variety of shapes, including thin films and monoliths can be prepared. They exhibit good optical quality (transmission in visible range) and mechanical strength (easy machining) required for optical applications.

Photochromic xerogels, i.e., xerogels which contain photochromic molecules in purely inorganic or hybrid organic-inorganic network, are materials of significant scientific and technological interests.[3-6]

In the present paper, we report the incorporation and the study of photochromic molecules (dithienylethenes) in sol-gel matrices. Dithienylethene derivatives exhibit high durability for recycle use and irreversibility of cycle by heat energy.[7] The synthesis and solution photochromism of these molecules have been described earlier.[8] Here we report first the kinetics of photochromism of dithienylethenes in gel thin films obtained by polymerizing an organically modified silicon alkoxide, methyltriethoxysilane ($CH_3Si(OEt)_3$=MTEOS). In the second part photoinduced refractive index changes measured by the Attenuated Total Reflection (ATR) method are presented.

EXPERIMENTAL SECTION

Photochromic molecules and sample preparation

1,2-Bis-[5'-(4''-methoxyphenyl)-2'-methylthien-3'-yl]perfluorocyclopentene (DTE5) and 1,2-Bis(2'-methyl-5'-(pyrid-4''-yl)thien-3'-yl)perfluorocyclopentene (DTE2) the formula of which are shown in figure 1, were used as photochromic compounds. Detailed procedure of their synthesis is given in reference 8.

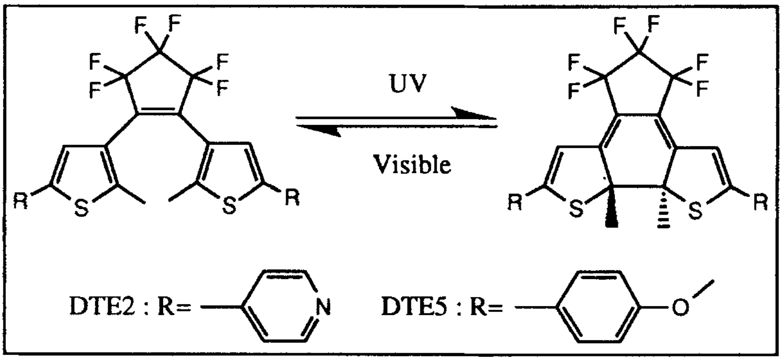

FIGURE 1 : Chemical structure of dithienylethene derivatives.

In order to obtain solid state photochromic material, dithienylethene derivatives were trapped in sol-gel matrices. Doped silica-based sols were prepared from MTEOS according to a previously published procedure.[9] In a typical sol preparation, first an acetonic solution of silicon alkoxide was prepared. Another solution containing the same solvent, hydrochloric acid and distilled water was added to the silicon alkoxide solution under continuous stirring. The initial molar ratios alkoxysilane : water (pH=2.5) : acetone were respectively 1 : 3 : 3. After several hours hydrolysis at room temperature, a small amount of amine modified silane (3-triethoxysilylpropylamine) was added in order to neutralize the acidity of the medium and therefore to increase the condensation reaction rate. Solution of photochromic molecules dissolved in acetone was then added to yield a concentration of 10^{-2} mol.l^{-1}. Afterwards, the as-prepared doped sols were passed through a 0.45 μm filter before deposition. Thin films (0.5 to 5 μm of thickness) were spin-coated on various substrates. Some of them were previously gold coated by thermal evaporation for ATR experiments. The viscous sols were poured onto the glass supports. The angular velocity range of the spinner was 1000-4000 rpm. The sample plates were dried between 70 and 150°C for several hours.

Setup for kinetics measurements of photochromism

The experimental setup for kinetic measurements has been described elsewhere.[6] Either visible or UV light from a 150W Xe lamp was selected by using filters. In our experiments UV light (300-400 nm) selected by UG11 Schott filter, was first used to activate the photocoloration in the photochromic samples (13 W/m^2 on the surface of the sample). A part of visible light (650-800 nm, 1.2 W/m^2) not stopped by the filter can limit the coloration of the samples. After 40 min treatment, the UV light beam was turned off to follow the discoloration of the sample under visible light irradiation (500-600 nm, 70-80 W/m^2 on the surface of the sample). Before starting these experiments all the samples were first completly bleached using visible light. The kinetics of photocoloration and photodiscoloration were recorded on a Zeiss visible spectrophotometer. The measurements were made at 20°C. The absorption spectra were recorded on a Shimadzu UV-vis 160A spectrophotometer.

Attenuated Total Reflection method for refractive index measurements

The ATR method is a well-known technique for the determination of indices and thicknesses of transparent thin films.[10] It is based on the resonant coupling between an evanescent wave, excited in a very thin metallic film, and guided modes supported by the layer under investigation. Due to that resonant condition, this method allows very precise determination of refractive index (accuracy of 10^{-4}) and thickness, but is also very sensitive to inhomogeneities and absorption.

The experiments were performed in Kretschmann's configuration (figure 2).[11] Xerogel films were deposited onto a thin semitransparent gold layer (≈45 nm), vacuum-evaporated onto microscope glass slides. Glass substrates were put in optical contact with the base of a prism by using an index-matching oil. A collimated beam emitted from a He-Ne laser or a laser diode (wavelengths of 633 and 785 nm respectively) propagates through the prism and is reflected by the multilayered structure towards a photodiode detector. The prism and the photodiode are placed on two coaxial rotation stages to record reflectivity as a function of the external incidence angle φ (figure 2), either in Transverse Electric (TE) or Transverse Magnetic (TM) polarization. The reflectivity $R(\varphi)$, recorded as function of the external incidence angle φ, exhibits a set of peaks (minima of reflectance), each of them corresponding to the coupling of the incident wave with one of the guided modes supported by the sol-gel film. These angles correspond to the Fabry-Perot resonances of the film. The precise determination of the angular positions of the TE and TM resonances allows to determine thickness and indices of the guiding film. Generally three TE or TM modes are required to fully characterize the film. Moreover, the width of the resonances and the value of the minimum are very sensitive to the losses induced by the inhomogeneities and absorption of the film.

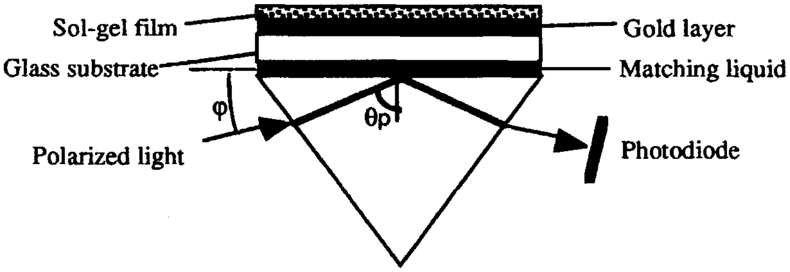

FIGURE 2 : The Kretschmann arrangement used in the ATR measurements. The multilayered structure is deposited onto the surface of the prism and the reflectivity is recorded versus the external incidence angle φ.

RESULTS

Photochromic properties

The absorption spectra of dithienylethene derivatives in sol-gel derived host media before and after UV irradiation (365 nm) are shown in figure 3. Spectra of the photochromic dyes in xerogel films and in $CHCl_3$ solution (as well as in other organic solvents[8]) are quite similar (table I). The observed red shift of λ_{max} from $CHCl_3$ to MTEOS xerogels is explained by a change in the surrounding polarity.

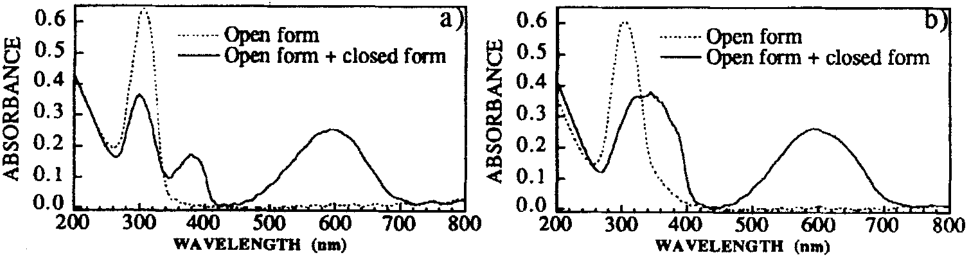

FIGURE 3 : Absorption spectra change of a) DTE2 and b) DTE5 doped xerogels before and after irradiation with 365 nm light.

Whereas the conversions to the closed state are nearly total in solution (≈98%), they are around 50% in the xerogel matrix. The shielding effect due to the absorption of the matrix and of the closed form between 300 and 400 nm (the movement of the molecules in solution allows to obtain high conversion rates), as also the rigidity of the matrix (silica-based backbone can impede the rotational motion of groups involved in the ring closure) can explain this phenomenon.

TABLE I : Spectral data (λ_{max} in nm) for DTE2 and DTE5 molecules in solution and in sol-gel matrix.

Compound	$CHCl_3$	sol-gel matrix
DTE2 open	300	305
DTE2 closed	588	595
DTE5 open	293	303
DTE5 closed	588	591

Typical coloration-discoloration cycles characteristic of the photochromism for dithienylethene molecules trapped in organically modified sol-gel matrices are shown in figure 4. The kinetics of the ring opening reaction was studied following the decrease of the maximum absorption band. In the case of DTE5 dithienylethene the color decay is best fitted by a monoexponential expression. This in agreement with a purely photochemical process. Experimental data corresponding to the color decay of a DTE2 doped sample cannot be fitted by using a monoexponential model. As a first approximation, it can be described by a sum of several exponential equations, with different rate constants. This behavior can be connected with the presence of the pyridyl groups on DTE2 molecules. In spite of the addition of amine in the initial acidic sol, the molecules can be partially protonated (molecules with zero, one or two protonated pyridyl groups). In addition hydrogen bonds between pyridyl and silanol groups can be formed. Thus several photochromic DTE2 species could be present in this material.

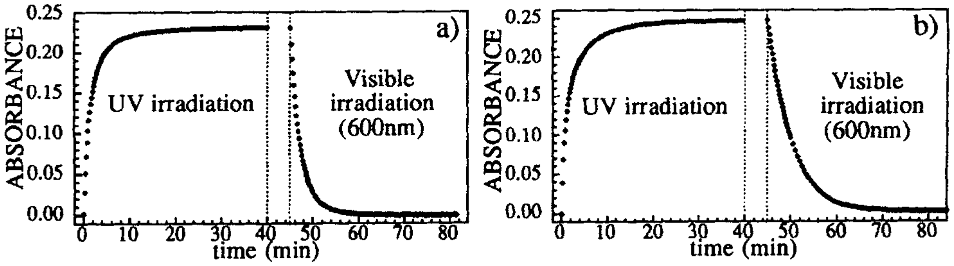

FIGURE 4 : Coloration-discoloration cycles characteristic of the photochromism for a) DTE2 and b) DTE5 molecules trapped in organically modified sol-gel matrices.

Photoinduced refractive index changes

From the experimental recorded TE and TM reflectivity curves, thickness and complex refractive index of the photochromic sol-gel films were calculated by using a least square fitting procedure with the Fresnel reflection formula. Very small divergence (<3') of the laser beam ensures a precise determination of incidence angle measurements. Figure 5a shows the experimental reflectivity measurements recorded at the wavelength of 785 nm for a DTE5 doped sol-gel film. The minima of the reflectivity are related to five resonance TM modes (m=1 to 5). The experimental data for TE polarisation, not represented here, are similar to the TM ones, with different angular positions of the minima. The refractive index and thickness calculated in that case are the same than those determined from TM recording. Consequently these films can be considered as homogeneous and isotropic. The precise measurements of the minima angular positions allow to plot the curves: thickness versus refractive index, as shown in figure 5b. The intersection point provides the values of the thickness h and the refractive index n of the films. In our case, we found $n=1.4245 \pm 0.0005$ and $h=3.03 \pm 0.03$ μm. The theoretical reflectivity curve calculated by using these values and displayed in figure 5a, is in very good agreement with the experimental data. The same procedure applied at the 633 nm wavelength, leads to an index close to $n=1.4295 \pm 0.0005$.

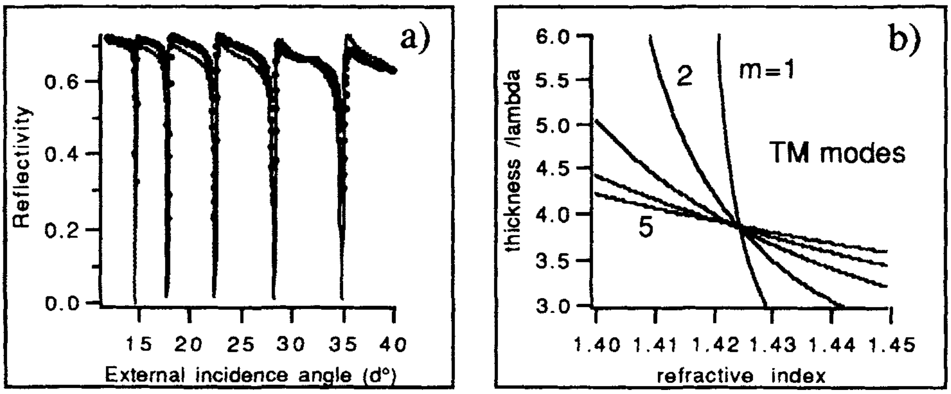

FIGURE 5: a) TM reflectivity versus external incidence angle (experimental points and fitted curve). b) Set of the curves giving the relative thickness versus the refractive index for a TM polarized light calculated from the resonance condition of the film. The intersection point provides the values of the index and thickness of the film.

Similar ATR experiments were performed on a DTE5 doped film after different irradiation treatments (UV or visible irradiation). The incident light beam was used either at 633 nm or at 785 nm. Only the TM polarization results are presented. The experimental measurements, performed at 633 nm are displayed on figure 6. The intensity of the incident collimated beam was strongly attenuated with a neutral density in order to avoid the possible conversion of the molecules to the open form. The closed form has a stronger absorption at 633 nm than the open one (see absorption spectra) and consequently the ATR reflectivity dips are damped and the minima levels are higher, as compared with the results of the figure 5a.

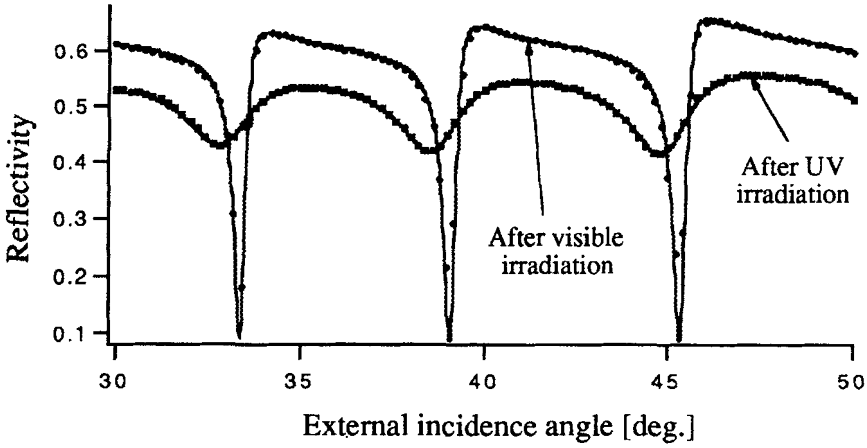

FIGURE 6 : Experimental and theoretical reflectivity curves (λ=633 nm) for a DTE5 doped xerogel film after successive irradiations with UV (365 nm) and visible (633 nm) light. The dots are the experimental data and the solid lines are the theoretical curves obtained from the fitting procedure.

The sample was then strongly illuminated with visible light (633 nm) to convert molecules to their open isomers. As expected, the ring opening leads to a bleached and highly transparent (at 633nm) film. Consequently the ATR reflectivity curve exhibits now sharp dips as shown in figure 6. The width of the peaks differs considerably from those observed in the previous case. Moreover, the peaks are shifted to larger angles. This shift is mainly due to the change of the real part of the refractive index. The values of the refractive index and thickness of the film after UV and visible irradiation were calculated at 633 nm and at 785 nm. The results are given in Table II. In addition the absorption changes are estimated through the imaginary part of the refractive index. Thickness deduced from ATR experiments was close to 3.03 ± 0.03 μm.

At 785 nm, the photo-induced refractive index change (Δn) from the colored to the discolored state is equal to 3.10^{-3}. This large change considering the low doping level, could be optimized and the derived materials could be used for photooptical switching device fabrication.[12]

TABLE II : Refractive index of a DTE5 doped film submitted to UV or visible light (uncolored : raw sample after visible irradiation, colored : sample after UV irradiation, discolored : sample after visible irradiation).

	Refractive index (complex value)	
	633 nm	**785 nm**
uncolored	1.4295 -j 0.0002	1.4245 -j 0.0002
colored	1.4330 -j 0.0075	1.4275 -j 0.0002
discolored	1.4290-j 0.0006	----

CONCLUSION

To sum up, the synthesis and photochromic properties of sol-gel films containing dithienylethene molecules were investigated. Photochromism through absorption measurements and kinetic studies were performed on these materials. Thickness and optical index of the doped film irradiated either with UV or visible light can be easily deduced from ATR experiments. In the case of the methoxyphenyl substituted dithienylethene doped film the transition from the colored to the discolored state induces a large change in refractive index ($\Delta n \approx 3.10^{-3}$).

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