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Chromatic and dynamic characteristics of some photochromes in the components of bifunctional photochromic and electro-optical devices

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Abstract

This work is part of a research project whose final aim is to realise prototypes of bifunctional photochromic and electro-optical devices. The photochrome will be incorporated in films composed by nematic liquid crystals dispersed in a polymeric matrix or in fluid monomer emulsions. To choose suitable photochromic components, the behaviour of some compounds (four naphtho-spiro-indolino-oxazines and a nitromethoxy-spiropyran) was investigated in the components of the matrix (liquid crystals and monomers) and compared with that in organic solvents. The colour-forming and colour-bleaching kinetics were determined. The molecules investigated, while maintaining their photochromic behaviour, generally exhibited a better colorability in liquid crystals and monomers, due to decreasing of the bleaching rate. The results of this work indicate that two of the molecules investigated have the prerequisites of colorability, reversibility and durability to be used in the bifunctional devices. Preliminary tests on the behaviour of a prototype of bifunctional film are reported. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photochromes; Spiro-oxazines; Spectrokinetic study; Medium effects

1. Introduction

Inclusion of photochromic molecules in solid matrices may provide a route to optically switchable materials for different applications [1]. In such context, the behaviour of photochromic systems embedded in different homogeneous and heterogeneous matrices was investigated as a preliminary step to realise prototypes of new bifunctional films. These films should be able to modulate both the transparency, by means of an electric field, and colour, by light-inducing the reaction of the photochromic molecules.

Two different approaches will be followed in realising the films: using polymer dispersed liquid crystals (PDLCs) [2–5] or using photopolymerizable liquid-crystal fluid emulsions (EDLC) [6–8], both containing the photochrome(s).

The photochromic molecules on which attention has been focused are spiro-pyrans and spiro-oxazines that generally exhibit only thermal, not photochemical, reversibility and good colorability. Studies on photochromism of spiropyrans and spiro-oxazines (SOs) have been carried out in various organic solvents [9] as well as in different media, such as polymer matrices [10,11], liposomal membranes [12], monolayers [13–15], and bilayer-clay matrices [16].

In this work, a preliminary investigation on some photochromes was carried out in homogeneous solutions to choose the compound(s) offering the best compromise among the different requirements (high colorability, durability, absorption spectrum in the visible region) for potential applications. The photochromes were characterised by the optical properties of both the starting (closed form) and the photocoloured (open form) molecules and by the kinetics of their photochemical opening and thermal bleaching. Then, further investigation was carried out on the photochromic molecules included in the separate components of the matrices, that is, the monomers and the liquid crystals, to check the possible presence of undesired chemical and optical interactions which could interfere with the measurements.

The compounds chosen for this study were four naphtho-spiroindolino-oxazines and a nitromethoxy-spiropyran, the behaviour of which was previously investigated in organic solvents [17–23]. Their choice was based on their good colorability and capability to be activated by light in the visible spectral range. This last requirement was important in order to minimise filter effects by the matrix, which absorbs in the UV, and to take advantage of sunlight irradiation.

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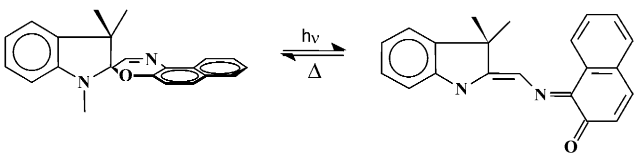


SO PM

Scheme 1.

The photochromism of these molecules, illustrated in Scheme 1, is due to photocleavage of the C–O spiro-bond of the SO upon irradiation, which leads to the coloured photomerocyanine (PM) by a thermoreversible reaction. Inclusion of these compounds in matrices can cause changes in the chromatic properties, as well as in the photokinetic behaviour; thermal- and/or photo-reactions may occur over different time scales and the photoproducts may be forced to assume preferred conformations.

Before investigating the photochromic behaviour in the bifunctional systems, preliminary studies have been carried out in various microheterogeneous media, such as micelles [24], microemulsions [24,25] and gels [25]. In this work, five photochromes were investigated in a solvent of polarity similar to that expected in the environment of the bifunctional films and in the separate components of the matrices.

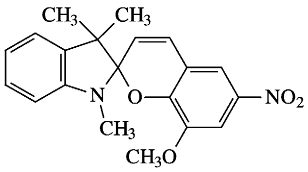
2. Experimental

2.1. Materials

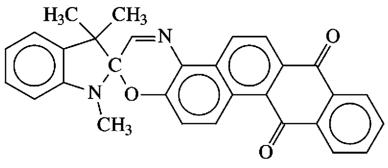
The photochromic molecules studied in this work (Scheme 2) were supplied by the Great Lakes Chemical Italia S.r.l. for previous investigations [17–19] and were used without further purification.

The solvents used were ethylacetate, EtAc (Carlo Erba, RS), acetonitrile, MeCN (Fluka, distilled before use) and toluene (Fluka).

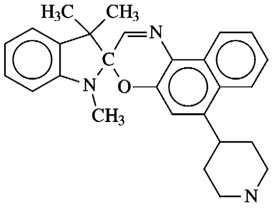
The components of PDLC and EDLC are nematic liquid crystals and polymerizable monomers. The nematic liquid crystals used in this investigation were E7, E49 and TL202 (Merk), eutectic mixtures of cyano-biphenyl and -terphenyl. Bisphenol A Glycerolate Diacrylate (Aldrich) was the monomer (indicated as BAGD in Table 2), inhibited with 4.5 ppm monomethyl ether hydroquinone.



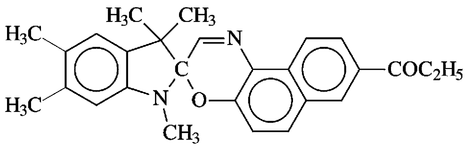
8’-methoxy-6’-nitro-1,3,3-trimethyl-spiro-(indolino-2,2’-benzopyran), ***1***



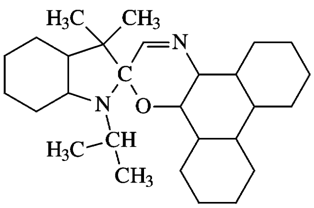
1,3,3-trimethyl-spiro-(indolino-2,3’[3H]anthraquinone-h[2,1-b][1,4]oxazine), ***2***



6’-piperidine-1,3,3-trimethyl-spiro-(indolino-2,3’[3H]naphtho [2,1-b][1,4]oxazine), ***3***



6’-propanoyl-1,3,3-trimethyl-5,6-dimethyl-spiro-(indolino-2,3’ [3H]naphtho[2,1-b][1,4] oxazine), ***4***



1-isopropyl-3,3-dimethyl-spiro-(indolino-2,3’ [3H]phenanthreno[2,1-b][1,4]oxazine), ***5***

Scheme 2.

The monomer matrices Mix 1 and Mix 2 were mixtures of BAGD and CN945B85 (an aliphatic urethane triacrylate, 85% in hexandioldiacrylate from Cray Valley-Total) or CN965 (an aliphatic urethane diacrylate, from Cray Valley-Total), respectively, both in the weight ratio 39:61. This composition was chosen in order to match the refractive indexes of the components.

2.2. Equipment and measurement conditions

Absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer and Beckman DU 7500 or HP 8453 diode-array spectrophotometers. The irradiating source, used to produce the metastable PM form, was a 150 W Xe lamp.

For measurements in solution, the light from the source was filtered by a Jobin-Yvon H10 UV monochromator and directed on the sample by a fibre optic, the appropriate excitation wavelength was chosen for each compound. The concentration of the starting SO was of the order of $5 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, corresponding to absorbances in the range 0.3–1.0 at the excitation wavelength. The irradiation of the sample (1 cm path cell, $1\,\mathrm{cm^3}$ of solution) was carried out in the spectrophotometer holder at a right angle to the analysis light. The intensity of the irradiating monochromatic light (typically, $10^{-6}\,\mathrm{Einstein\,dm^{-3}\,s^{-1}}$) was determined using potassium ferrioxalate actinometry. An Oxford Instruments cryostat was used for the temperature control.

Concerning the parameters reported in Table 1, the uncertainty can be estimated within 10% for k_Δ and 15% for $\varepsilon_{\mathrm{PM}}$, Φ, and E_a; that of the frequency factor, A, might reach one order of magnitude.

For measurements in the liquid crystals and monomers, a thin cell (0.1 cm path) was used to reduce light absorption by the turbid medium. The irradiation was carried out in a front-face geometry at an incident angle of about 30°, using all light emitted by the source at $\lambda > 350\,\mathrm{nm}$. The set up geometry did not allow using the thermostat, but temperature ($20 \pm 2°\mathrm{C}$), measured for each run, did not appreciably change during the time of experiment.

For all kinds of run, the colour-forming kinetics was followed by monitoring the visible PM absorbance under stationary irradiation as a function of time up to photostationary state attainment. Then, exposure to light was discontinued and the kinetic rate parameter of the thermal bleaching was determined from the decrease in absorbance. The activation energy of this process was only determined in solution from Arrhenius treatment of the bleaching rate parameters at various temperatures.

Table 1
Molar absorption coefficients at $\lambda_{\max}$, quantum yields, Φ, thermal bleaching rate parameters, k_Δ, and activation energies, E_a, of the coloured forms of **2**, **4** and **5** in EtAc solution and of **1** in MeCN

	1	2	4	5
$\lambda_{\max}$ (nm)	581	616	617	592
$\varepsilon_{\mathrm{PM}}$ ($\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$)	48000	21200	32000	110000
Φ	0.88	0.07	0.10	0.09
k_Δ ($\mathrm{s^{-1}}$) (293 K)	0.0052	0.013	0.020	0.19
E_a ($\mathrm{kJ\,mol^{-1}}$)	79	95	87	79
A ($\mathrm{s^{-1}}$)	8×10^{11}	7×10^{14}	5×10^{13}	5×10^{6}

3. Results and discussion

3.1. Measurements in solution

The kinetic investigation in solution was aimed at determining the photokinetic parameters of the colour-forming and colour-bleaching reactions of the photochromic molecules. The compounds were selected on the basis of their absorption spectra in a medium (ethylacetate) of polarity similar to that of the components of the matrices to be used for the bifunctional films. Preliminary experiments of photocoloration in various media allowed the polarity to be evaluated based on the solvatochromic effect on the colour band of the PM [17].

The time evolution of the PM absorbance (A_{PM} vs. time) under monochromatic steady irradiation (photocoloration) and at the end-of-irradiation (thermal bleaching) at various temperatures is shown in Fig. 1 as an example. The colour-forming and colour-bleaching kinetics are formally described by the monoexponential function of Eqs. (1) and (2), respectively,

$$A_{\mathrm{PM}} = A_{\mathrm{PM}}{}^{\infty}(1 - \mathrm{e}^{-\alpha t}) \tag{1}$$

$$A_{\mathrm{PM}} = A_{\mathrm{PM}}{}^{\infty}\,\mathrm{e}^{-k_\Delta t} \tag{2}$$

where $A_{\mathrm{PM}}{}^{\infty}$, α and k_Δ can be determined by a fit procedure. $A_{\mathrm{PM}}{}^{\infty}$ is the maximum absorbance of the coloured form attained at the photostationary state. The k_Δ parameter is the first-order kinetic constant of the bleaching process, while α contains experimental factors, like the intensity of the incident light, and properties intrinsic to the system,

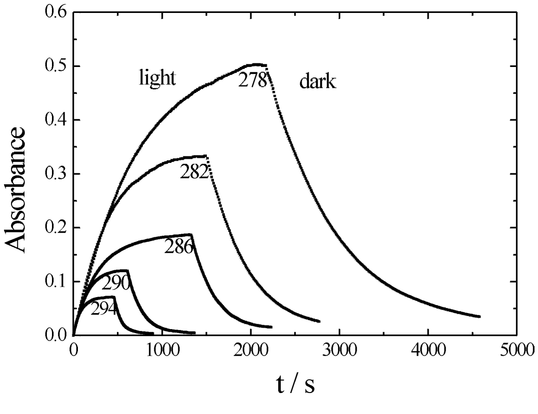


Fig. 1. Time evolution of the colour band of **2** in ethylacetate at different temperatures (K) under steady irradiation and in the dark.

like the quantum yield of the colour-forming reaction, Φ, and the molar absorption coefficient of the metastable photoproduct, $\varepsilon_{\mathrm{PM}}$. These parameters were determined by a photostationary method based on the temperature dependence of the bleaching rate [18,19]. In the kinetic rate equation of the colour-forming process (Eq. (3))

$$\frac{\mathrm{d}A_{\mathrm{PM}}}{\mathrm{d}t} = \varepsilon_{\mathrm{PM}}\Phi I^0 F A'_{\mathrm{SO}} - k_\Delta A_{\mathrm{PM}} \qquad (3)$$

where I^0 is the intensity of the monochromatic excitation light (Einstein dm^{-3} s^{-1}), A'_{SO} the SO absorbance at the exciting wavelength, λ_{exc}, and $F = [1 - \exp(-2.3A')]/A'$ represents the photokinetic factor [26–28] (A' is the total absorbance at λ_{exc}). Since the photokinetic factor is rigorously a time independent parameter only if the irradiation is carried out at an isosbestic point of the absorption spectra of the colourless and the coloured forms, preliminary experiments were performed in order to determine such point. Irradiation was then carried out at this wavelength. At the photostationary state, namely when $\mathrm{d}A_{\mathrm{PM}}/\mathrm{d}t = 0$, the PM absorbance attains its limiting value at the temperature of experiment ($A_{\mathrm{PM}}{}^{\infty}$) and the forward and back reactions proceed at the same rate, Eq. (4):

$$\varepsilon_{\mathrm{PM}}\Phi I^0 F^{\infty} A'_{\mathrm{SO}}{}^{\infty} = k_\Delta A_{\mathrm{PM}}{}^{\infty} \qquad (4)$$

By handling Eq. (4), the following relationship is obtained (Eq. (5)) [15,32]:

$$(A_{\mathrm{PM}}{}^{\infty})^{-1} = (\varepsilon_{\mathrm{PM}}c_0)^{-1} + (\varepsilon_{\mathrm{PM}}c_0)^{-1}(\Phi I^0 \varepsilon'_{\mathrm{SO}} F^{\infty})^{-1} k_\Delta \qquad (5)$$

which relates the experimental value of $A_{\mathrm{PM}}{}^{\infty}$, determined at different temperatures, with the corresponding bleaching rate k_Δ (c_0 is the starting concentration of SO). From the intercept of the plot $(A_{\mathrm{PM}}{}^{\infty})^{-1}$ vs. k_Δ, the molar absorption coefficient at the analysis wavelength, $\varepsilon_{\mathrm{PM}}$, was obtained and the Φ value could be determined from the intercept/slope ratio. An example of data treatment according to Eq. (5) is shown in Fig. 2 for **2** in EtAc: despite the very good correlation coefficient of the linear fit, $\rho = 0.997$, the intercept extrapolation implies a great uncertainty (±25%). The results obtained in EtAc for **2**, **4**, **5** and in MeCN for **1** are reported in Table 1. The activation energies of thermal bleaching reactions, obtained from Arrhenius plots (Fig. 3) in the temperature ranges appropriate for each molecule, are also reported in Table 1 together with the k_Δ values at 293 K.

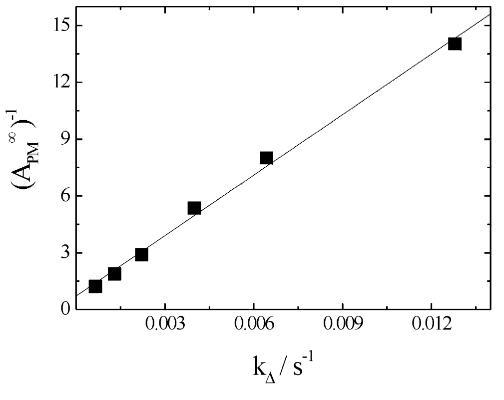


Fig. 2. Photocoloration data of **2** in EtAc treated according to Eq. (5) in the temperature range 274–294 K.

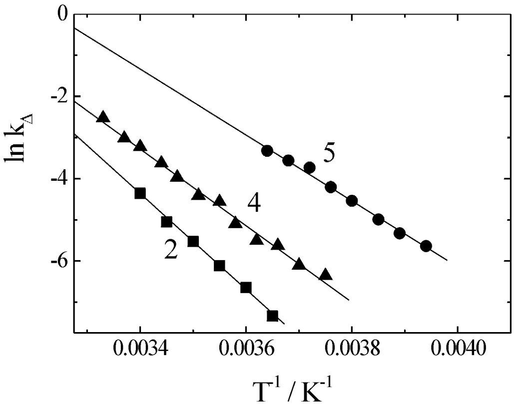


Fig. 3. Arrhenius plots for the bleaching processes of **2** (■), **4** (▲) and **5** (●) in EtAc.

The nitro-spiropyran, **1**, exhibited a peculiar behaviour since it was already deep blue coloured before irradiation in several solvents ($\lambda_{\max} = 525$–565 nm). Temperature and concentration did not affect the intensity of the colour band compared to that of the UV transition. Thus, thermal coloration can be ruled out. Increased hydrogen-bonding ability of the medium (ethanol, trifluoroethanol) increased the relative intensity of the colour band, while in a non-polar solvent (methylcyclohexane) fast coloration was followed by decomposition under steady irradiation. In a mixed, buffered aqueous solvent (acetonitrile/water, 2/1 (v/v)), the spectrum did not substantially change in the 4–11 pH range. For this molecule, the best photochromic response was obtained in a polar non-protic solvent (MeCN) where the initially pale yellow colour became blue-violet ($\lambda_{\max} = 581$ nm) under irradiation and underwent reversible thermal bleaching when irradiation was discontinued. Therefore, the kinetic study was carried out in this solvent. Temperature, concentration and solvent effects on the spectral behaviour indicate that the colour detected without irradiating is due to H-bonding interaction of the ground state molecule with the solvent and not to thermochromism or acid–base equilibrium.

Inspection of Table 1 shows that the colour bands appear in the 580–620 nm region with high absorption coefficients and very different quantum yields (0.09–0.9). For **5**, the $\varepsilon_{\mathrm{PM}}$ value was so high that extrapolation from the straight line of Eq. (5) gave very uncertain results and a graphical treatment at several analysis wavelengths was needed.

The colorability, that is the maximum colour intensity obtainable under fixed conditions, increased with decreasing temperature (Fig. 1). The greater are the Φ and ε values and the smaller is the bleaching rate, the greater is the maximum colour intensity obtainable. As a consequence, the colorability becomes markedly dependent on temperature due to the temperature dependence of the bleaching rate. At room temperature (293 K), colorability is better for **1**, **2** and **4** than for **5**, due to very fast bleaching rate and low photoreaction yield of the latter, despite its exceptionally high absorption coefficient.

3.2. Measurements in liquid crystals and monomers

The photokinetic study of the photochromes was then carried out in the separate components of the matrices to be used for the bifunctional films, that is, liquid crystals (E49, E7 and TL202) and the monomer (BAGD) or monomer mixtures (Mix 1 and Mix 2). All these media respond to the solubility requirements to obtain 10^{-3}–10^{-4} mol dm^{-3} photochrome solutions. Higher concentrations than in organic solvents were needed due to the necessity of using thin path cells (0.1 cm) to prevent that a large fraction of incident light was absorbed by the medium. The whole emission from the Xe source was used for irradiation. The experimental set-up did not allow the determination of the reaction quantum yields (see Section 2); however, the colour forming kinetics could be monitored and the fitting parameter, α (Eq. (1)), could be determined. The bleaching rates, k_Δ, were easily obtained from the absorbance decay in the dark.

The molecules analysed were **2**, **3**, **4** and **5**. Upon irradiation, all of them underwent photocoloration and exhibited good thermal reversibility, but with different dynamics and not in all media.

For one well-behaved compound, **2**, evaluation of colorability relative to an organic solvent (toluene) was carried out by measuring and comparing the ratio of the maximum absorbance of the colour band and the integral over the absorption spectrum of the closed form under identical conditions. The spectral evolutions of **2** in liquid crystal under irradiation and of the irradiated solution in the dark are shown in Fig. 4. The results for **2** reported in Table 2 show that the colour band shifts to lower energies in the monomers and much more in the liquid crystals compared to toluene; this red-shift of the maxima of the colour band indicates an increase of the medium polarity. The colour-forming kinetics are formally described by monoexponential functions in the monomers, but they are better described by biexponential functions (Eq. (6)) in the liquid crystals. Therefore, two rate parameters, α and β, were detected in this medium. These rate parameters have a simply mathematical meaning: they describe the best-fit curve for the experimental colour-forming absorbance/time data sets.

Table 2

Values of λ_{max} of the coloured form, colour forming (α, β) and thermal bleaching (k_Δ) rate parameters of **2** in liquid crystals and monomers compared with toluene solution under the same conditions (0.1 cm cell path, $T = 18°C$). In the last column a comparative evaluation of colorability is reported (see text)

Component	λ_{max} (nm)	α (s^{-1})	β (s^{-1})	k_Δ (s^{-1})	Colorability
E7 (LC)	629	0.12	0.014	0.0061	0.029
E49 (LC)	629	0.089	0.010	0.0050	0.035
TL202 (LC)	626	0.25	0.028	0.0090	0.030
BAGD	621	0.0099		0.0026	0.118
Mix 2	621	0.028		0.0035	0.073
Mix 1	621	0.013		0.0029	0.247
Toluene	615	0.041		0.0154	0.0008

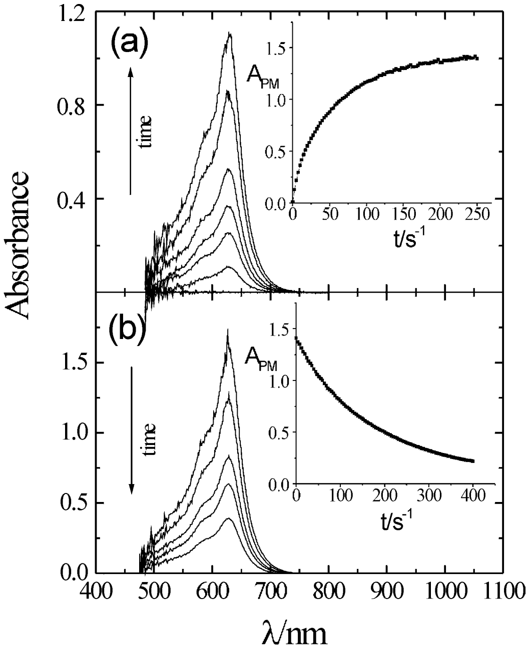


Fig. 4. Photochromic behaviour of **2** in E7. (a) Spectral evolution under irradiation; inset: colour-forming kinetics followed at the maximum absorption. (b) Spectral evolution in the dark; inset: kinetics of thermal bleaching.

$$A_{PM} = A_\alpha{}^\infty(1 - e^{-\alpha t}) + A_\beta{}^\infty(1 - e^{-\beta t}) \qquad (6)$$

The colour-bleaching rate constants, k_Δ, were determined from monoexponential fit of first-order kinetics (Eq. (2)); they were found to be slower than in toluene in both liquid crystals and monomers. Consequently, the colorability increases in all media by more than two orders of magnitude compared with the organic solvent. This photochrome also exhibited a fairly good reversibility, as can be seen from Fig. 5, where consecutive coloration–decoloration cycles are shown.

The results obtained with the other three photochromic compounds are reported in Table 3 (in liquid crystals) and Table 4 (in monomers). What was observed for **2** cannot be generalised for the other three molecules. For **4** and **5**, the bleaching rates are comparable or slowed down with respect to organic solvents. For the piperidine derivative (**3**), the process is faster in the monomer mixture ($k_\Delta = 0.12\,s^{-1}$) than in the liquid crystals ($k_\Delta = 0.02\,s^{-1}$). A similar difference was found for this molecule between ethanol ($k_\Delta = 0.58\,s^{-1}$) and toluene ($k_\Delta = 0.035\,s^{-1}$) at

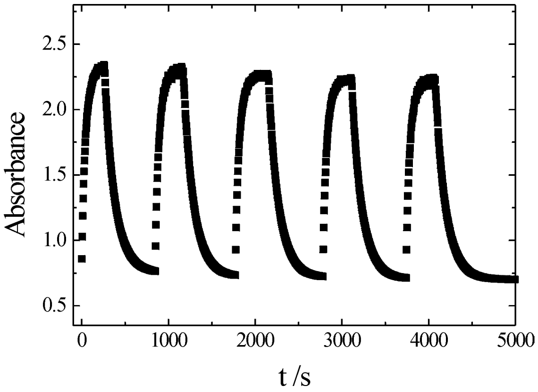


Fig. 5. Consecutive cycles of coloration and decoloration of **2** in E7 liquid crystal.

298 K [18,19]. However, in the present case, this behaviour cannot be assigned to a polarity effect, since, based on the solvatochromic effect, the liquid crystal is more polar than the monomer. Some other peculiar behaviours were also observed. The compound **4** yielded photochromic response in all media investigated, but exhibited non-exponential colour-bleaching kinetics in some of them. In E7 and TL202, a biexponential function (Eq. (7)) was more appropriate to describe the bleaching.

$$A_{\mathrm{PM}} = A_1^{\infty}\,\mathrm{e}^{-k_{1\Delta}} + A_2^{\infty}\,\mathrm{e}^{-k_{2\Delta}} \quad (7)$$

No sign of thermal equilibrium was observed in the spectra of **4** before irradiation, while the thermally equilibrated coloured form of **5** was detected in the liquid crystals. Furthermore, for this last molecule, the mixtures with the monomers were green coloured due to decomposition; therefore, the photocoloration and thermal bleaching could not be investigated.

Two factors are important in determining the matrix effect on the ring-opening and ring-closing rate: the structure variation from a globular (SO) to a *quasi*-planar (PM) shape and the change of dipole moment in the conversion SO ⇄ PM. Concerning the first factor, it is well known, from both thermodynamic [29] and spectroscopic [30] studies, that planar and/or linear molecules can be incorporated into liquid crystal matrices more easily than globular species. The thermal ring closure of PM to the thermodynamically stable SO is partially impeded by the nematic order of the liquid crystal environment; thus, k_{Δ} decreases. Considering the second factor, the greater is the difference in dipole moment between PM and SO, the greater will be the entity of the rearrangement of the solvent molecules, during the rotation of the two moieties leading to the transition state for closure. From previous studies on the solvatochromism of these molecules [17–19], we found that the red-shift due to solvent polarity is minimal for **2** (135 cm^{-1}) but greater for **4** and **5** (500 and 780 cm^{-1}, respectively) between MeCH and EtOH. This behaviour indicates that the ground states of these two molecules should approach configurations characterised by weakly polar quinoid forms more than the **2** ground state, in agreement with the character of the groups in the oxazine moiety. In fact, the positive solvatochromism is disfavoured by substituents which increase the contribution of zwitterionic forms to the resonance hybrid describing the ground state molecule, that is, by electron-attracting groups. Based on these considerations, the increase of activation entropy, due to disturbing the nematic order, is reinforced by the positive contribution due to solvent disorganisation around the less polar SO form. Both factors increase the barrier to rotation leading to a decrease in the bleaching rate. The polarity of **2**, greater compared with the other molecules, may be responsible for the non-exponential colour-forming rate, caused by interaction with the polar end of the liquid crystal molecules. This interaction can change depending on the inclusion site in the ordered nematic frame of the environment. In some cases, also the decays of the colour bands can fit biexponential functions, see Table 3. Non-exponential behaviour of bleaching has often been found in polymer matrices [10,11]. The fundamental reason of a more complex kinetic behaviour in matrices is that the initial distribution of the photochromic molecules in

Table 4
Values of $\lambda_{\max}$ (nm) of the coloured forms, rate parameters of the colour-forming (α) and thermal bleaching (k_{Δ}) processes of **3** and **4** in monomers (0.1 cm path cell, $T = 18°\mathrm{C}$)

Medium compound	Mix 1		Mix 2 (**4**)	BAGD (**4**)
	3	**4**		
$\lambda_{\max}$ (nm)	583	627	625	626
α (s^{-1})	0.125	0.016	0.016	0.012
k_{Δ} (s^{-1})	0.12	0.0073	0.0073	0.0037

Table 3
Values of $\lambda_{\max}$ of the coloured form and rate parameters of the colour-forming (α) and thermal bleaching processes ($k_{1\Delta}$, $k_{2\Delta}$) of **4** and **5** in liquid crystals (0.1 cm cell path, $T = 18°\mathrm{C}$). In the cases where two parameters are reported, the kinetics were described by biexponential functions

	E49			E7		TL202	
	3	**4**	**5**	**4**	**5**	**4**	**5**
$\lambda_{\max}$ (nm)	583	630	602	628	602	628	595
α (s^{-1})	0.051	0.031	0.147	0.033	0.251	0.062	0.13
$k_{1\Delta}$ (s^{-1})	0.020	0.018	0.054	0.021	0.237	0.037	0.13
$k_{2\Delta}$ (s^{-1})				0.003	0.005	0.002	0.003

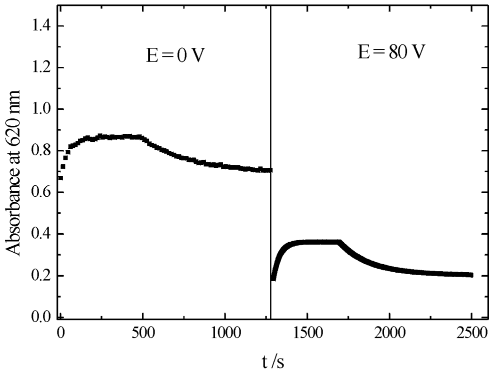


Fig. 6. Time evolution of the absorbance at 620 nm of **2** in a thin film of photopolymerizable liquid-crystal fluid emulsion (70% Mix 1/30% E49). Left side: photocoloration and thermal bleaching in the absence of electric field. Right side: photocoloration and thermal bleaching in the presence of a 80 V (AC, 1 kHz) electric field.

the medium is not random. In a condensed phase, where the relaxing species occupy a large number of different sites, there may be a more or less continuous distribution of the decay rates and/or energy barriers [10,11,31,32]. In these high viscosity media, PM molecules can find themselves in statistically different environments, due to the response of the medium which is slow compared to probe decay [33]. This may alter the local probability of decay.

3.3. *Prototype of a bifunctional film*

After the tests of the photobehaviour of some promising photochromes in the presence of the various components of the complex bifunctional system, a preliminary test of the latter was carried out in a photopolymerizable liquid-crystal fluid emulsion containing **2** as the photochromic component. An example of the time evolution of its absorbance at 620 nm under irradiation in the absence and in the presence of a 80 V (AC, 1 kHz) electric field is shown in Fig. 6. In the first run (left), the initial absorbance is relevant before irradiation because of the modest transparency of the matrix. The curve shows the increase of absorbance due to formation of the PM, until the attainment of the photostationary state under irradiation, and the thermal bleaching in the dark. In the second run (right), the initial absorbance is much smaller due to the field effect which increases the transparency of the matrix. Using the same procedure as in the first run, the increase (UV irradiation) and decrease (dark) of the PM absorbance were recorded. This preliminary result can be considered satisfactory since it indicates that the film displays both the expected functions. However, the reversibility of the photochromic process in the film is less complete than in the separate components as shown by the non-negligible residual absorbance present after the bleaching. This negative aspect, which can be caused by an increased degradation of **2** through specific interactions with the matrix or, more probably, to light scattering or similar optical problems, deserves further investigation.

4. Conclusions

The results obtained from the photokinetic study of five photochromic compounds in homogeneous solutions, liquid crystals and monomers indicate that the photocolorability generally increases in liquid crystals and monomers due to decreasing of the bleaching rate. Therefore, these systems are promising for the preparation of bifunctional materials. However, not all of them are equally suitable to be used as additive to PDLC and EDLC. The spiropyran **1** exhibits fairly high photocolorability and favourable absorption spectrum in the closed form, but its behaviour is very sensitive to environment which can induce coloration in the dark and photo-decomposition under irradiation. Among the four SOs, the best candidates for bifunctional films are **2** and **4**, not only because of suitable absorption spectra and high colorability, but also due to compatibility with the matrix components; their spectra in fact do not substantially change in these media and the reversibility is good. The presence of double-exponential colour-forming and colour-bleaching kinetics does not affect the potential interest of the photochromic compounds for applications if reversibility is maintained. A preliminary test on a photopolymerizable liquid-crystal fluid emulsion showed that bifunctional electro-optical and photochromic devices can be realised.

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