Bull. Chem. Soc. Jpn., 68, 1220—1225(1995)

Study of the Fatigue Process and the Yellowing of Polymeric Films Containing Spirooxazine Photochromic Compounds

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(Received July 7, 1994)

Photochromic polyurethane films containing 5-substituted 1,3-dihydro-3,3-dimethyl-1-alkylspiro[2*H*-indole-2,3′-[3*H*]pyrido[3,2-*f*][1,4]benzoxazine] and 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphth-[2,1-*b*][1,4]oxazine] were degraded under xenon light exposure. The loss of the photochromic response was monitored by spectrophotometry as a function of the irradiation time; meanwhile, the photoproduct formation and the amount of photochromic material still available were analyzed by chromatography after liquid–solid extraction. At the same time, the fade rates were monitored after flash-excitation photolysis or after the photostationary state during degradation. It was clearly demonstrated that the loss of photochromism was due exclusively to a photooxidation process of the initial dye, and not to an acceleration of the bleaching or a potential screen effect caused by the photoproducts.

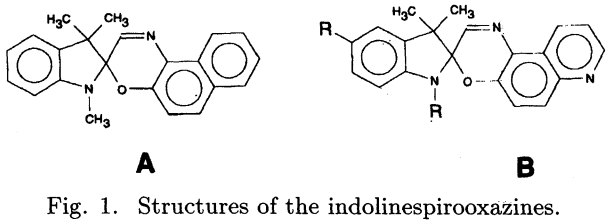
Spirooxazines are reversible dyes under UV light irradiation which exhibit photochromism in solution or as polymer matrix films.[1,2] The potentialities of their applications are numerous: for instance, optical switches, light filters, ophthalmic sunglass lenses[3] or cosmetics. For practical uses, these compounds can be employed in different kinds of polymers, such as cellulose acetate butyrate, polyurethanes, PVC, epoxies, acrylics[4] or, also, poly(vinyl butyral) and polyester.[5] One of the major limiting factors regarding their industrial applications is a fatigue phenomenon (photodegradation process) after long exposure to light. Despite the fact that this class of photochromic compounds is less degradable than indolinespirobenzopyran compounds,[6] its stability in the time (when no stabilizing agents are added) is not sufficiently acceptable for industrial purposes. Therefore, a study of the degradation of spirooxazines is of major importance in order to obtain a better understanding of the mechanisms involved, and to try to stabilize these compounds.

The photostability of the spirooxazines has not been very well studied in terms of degradation mechanisms. Most studies have concentrated mainly on the quantitative aspects by connecting structure-degradation relationships in solution by flash-photolysis techniques[7] or under continuous irradiation.[8] Recently, we began to study photodegradation processes of spirooxazines in solution in terms of qualitative aspects by fragment identification.[9,10] This work permitted us to propose mixed mechanisms for the photodegradation of photochromic molecules in spirannic series involving both radical processes and singlet oxygen intervention.[8,10,11]

As of this time, the photodegradation processes of these series in a polymer matrix have not been mentioned in the literature, but are of great importance because of the growing desire to use the spirooxazines in rigid media for all potential applications using the reversibility of the photochromes. In this work we studied the photodegradation of two compounds in a polyurethane matrix: 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazin] (**A**) and 5-substituted 1,3-dihydro-3,3-dimethyl-1-alkylspiro[2*H*-indole-2,3′-[3*H*]pyrido[3,2-*f*][1,4]benzoxazine] (**B**) (Fig. 1). The former compound (**A**) (for which the photodegradation scheme in solution is now well-known[8,9]) was chosen for a qualitative analysis of its photoproducts and, the latter one (**B**), for a quantitative analysis as a function of the irradiation time in order to monitor the kinetics of degradation.

Experimental

Photochromic Polymer. The 1,3-dihydro-1,3,3-trimethylspiro[2*H*-indole-2,3′-[3*H*]naphth[2,1-*b*][1,4]oxazine] (**A**) (Enichem Synthesis, Milan) or 5-substituted 1,3-di-



A **B**

Fig. 1. Structures of the indolinespirooxazines.

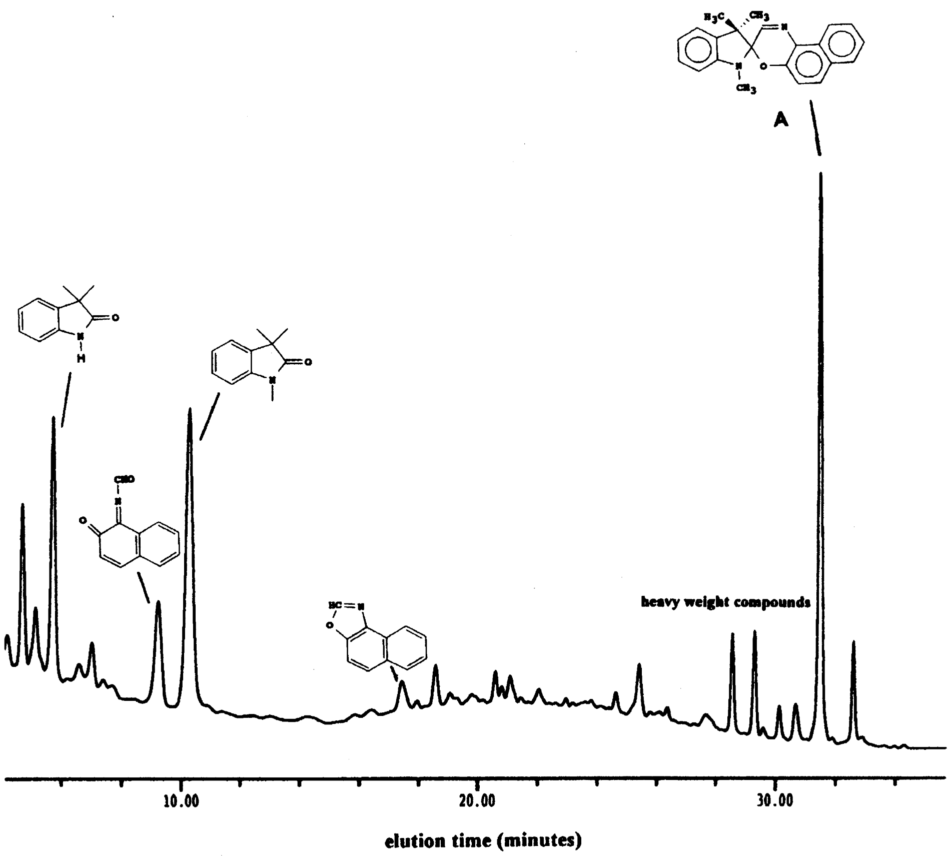


Fig. 2. Liquid Chromatography separation at 220 nm of the photoproducts of (**A**) after 100 h of suntest extracted from the polyurethane matrix. Column Hypersil 4.6 mm×25 cm C18 8 µm. Mobile phase: CH_3CN/H_2O: 40/60 (v/v) during 10 min, then 100% of CH_3CN within 30 min, flowrate 1.5 ml min^{-1}. Detection 200—450 nm. Scans 1 Hz. Temperature ambient.

hydro-3,3-dimethyl-1-alkylspiro[2*H*-indole-2,3′-[3*H*]pyrido-[3,2-*f*][1,4]benzoxazine] (**B**) (PPG Industries, Monroeville, USA) was mixed with the monomer components (polyols and isocyanates). The resulting monomer mixture was deposited on glass plates after soaking, and a polymerisation reaction was performed for three hours in an oven at 100 °C. Some coated polyurethane glasses were formulated without photochromes in order to obtain a blank extraction.

Photodegradation Experiments. Photochromic polymeric films were illuminated by a xenon lamp (suntest Heraeus 1.8 kW, $E_{UV}=3.5$ mW cm^{-2}, $E_{vis}=111$ klux, filter 300 nm) for degradation experiments. At fixed intervals of time, some samples were taken from the suntest. Colored lenses were completely bleached in the dark during 30 min in an oven at 80 °C (in order to accelerate the bleaching step); then, the absorbances were monitored at the photostationary equilibrium on a spectrophotometric optical bench (described below).

Photochromism Monitoring. The diminution of the absorbance was monitored on a home-built optical bench. This apparatus comprised a xenon photocoloration source (Oriel 200 W set at $E_{UV}=2$ mW cm^{-2} (measure centered on 365 nm) and $E_{vis}=50$ klux, filter KG2) irradiating the polymeric film in an air-regulated measure box set at 25 °C. After 30 min of excitation, the maximum of the absorbance (taken at the λ max of the photomerocyanine) and the bleaching kinetics were monitored as a function of time using a modified UV-visible diode array spectrophotometer (Zeiss, Germany). The discoloration rate was also measured for the same sample after flash excitation (50 µs, 150 joules) on another optical bench designed for this purpose.[12]

Extraction and Quantification of Irradiated Photochromic Compounds. Photochromes (**A**) or (**B**) and their photoproducts were extracted by refluxing the films for 45 min in acetone (SDS p.a., France) at 66 °C. Recovery of the extraction was quite quantitative (98%). The extracts were then evaporated to dryness under a soft stream of nitrogen, and were dissolved in acetonitrile (Carlo Erba, HPLC grade) for liquid-chromatography analyses. The HPLC system comprised a Beckman Gold system coupled with a 168 UV-visible diode array detector. The separation was carried out using a 4.6 mm×25 cm C18 8 µm reversed-phase column (Shandon Scientific, England). The mobile phase was a mixture of acetonitrile with water in the isocratic mode for the photochrome quantification, or with a linear gradient of CH_3CN in H_2O for photoproduct analyses (the exact analytical conditions were resumed in the corresponding chromatogramms). An analysis of the amount of (**B**) in the matrix was performed by an external calibration with the injection of known standards in acetonitrile (fixed volume); a quantitative determination of the extracted sample was made based on the peak area at 240 nm.

Results and Discussion

Photoproduct Analyses. Figure 2 represents the qualitative chromatographic separation of the photoproducts of (**A**) generated in the polyurethane matrix. The fragments had been previously identified by different hyphenated mass spectrometry techniques.[8,9] It can be seen that extraction from the polymer was relatively specific versus the involved photoproducts, thus leading to quite clean profiles. Indeed, a blank extraction of the polyurethane matrix did not show any significant interfering peaks (chromatographic profile not shown here).

The same kind of fragments were found when compared to degradation in apolar solvents, such as toluene or benzene. The main photooxidation products were the oxindols derivatives (trimethylated and dimethylated) corresponding to the indoline moiety of the initial molecule, the naphth[1,2-*d*]oxazole and 1-formylimino-2(1*H*)-naphthalenone corresponding to the naphthoxazine part of the pigment. Very few heavy weight compounds which could be generated by radical rearrangements of the initial molecule were found, their structures being not completely clear at this time; however, they appeared to certainly be close from the skeleton indicated in Fig. 3 as suggested by mass spectrometry analyses and X-ray data.[8,13]

Quantification of (B) during Degradation. Table 1 outlines the degradation kinetics of (**B**) in terms of the loss of photochromism (spectrophotometry) and the loss of photochromic material (chromatography) as a function of the irradiation time. It can be seen that the decrease in the absorbance is effectively due to a decrease in the photochromic material still available, as shown by the correlation between the two curves in the Fig. 4.

Thus, the degradation process is due almost exclusively to a photooxidation mechanism, and maybe, to a lesser extent, to rearrangement reactions. The yellowing phenomenon of the photochromic polymer matrix is undoubtly due to the apparition of absorbing fragments under irradiation. Indeed, a polymer irradiated without photochromes remains completly transparent; meanwhile, a photochromic one indicates absorption bands in the blue region (Fig. 5). The UV-visible absorption spectra obtained from the chromatographic separation of the fragments of (**B**) confirm this assertion (Figs. 6 and 7). The degradation products of (**B**) have not yet been identified. Nevertheless, the formation of absorbing species does not seem to act as a screen effect for the photocoloration reaction, because, in the case of this hypothesis, we should find by quantification, a large amount of (**B**) still remaining in situ. The results of the analyses confirm this idea (Table 1).

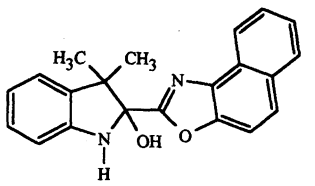


Fig. 3. Possible structure of one of the rearrangement products of (**A**).

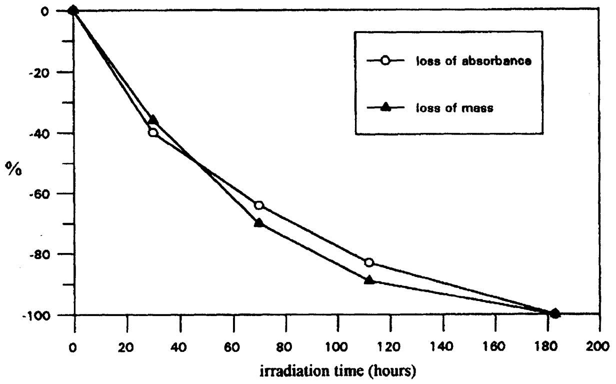


Fig. 4. Spectrophotometric and chromatographic monitoring of the loss of the photochromic response in function of the irradiation time.

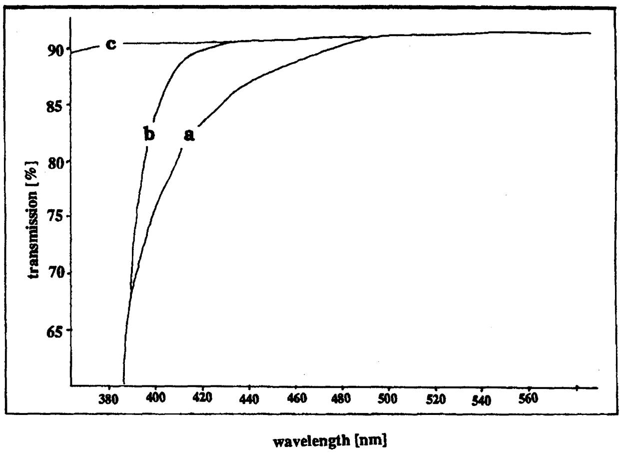


Fig. 5. Comparison of the transmission curves between a photochromic glass degraded (yellowish) [A], a photochromic one nondegraded [B], and a polyurethane control, containing no photochromes, irradiated 200 h in the suntest [C].

Bleaching Kinetics. The bleaching kinetics in the polymer were monitored after the photostationary state (Table 2) and after flash-excitation photolysis (Table 3) in order to determine whether an acceleration of the ring-closure rate occurs during degradation, as was found for spirooxazine compounds in toluene solution.[7,14,15] The discoloration reactions are described by a biexponential function, $A_{(t)}=A_1e^{-k_1t}+A_2e^{-k_2t}$, where k_1 represents a fast decay and k_2 a slow one. Tables 2 and 3 show that there is no variation of the kinetic constants for (**A**) and (**B**) before and during degradation. At the same time, the amplitudes of the fast and slow kinetics are of the same order during the degradation of the dye. The decrease in the pho-

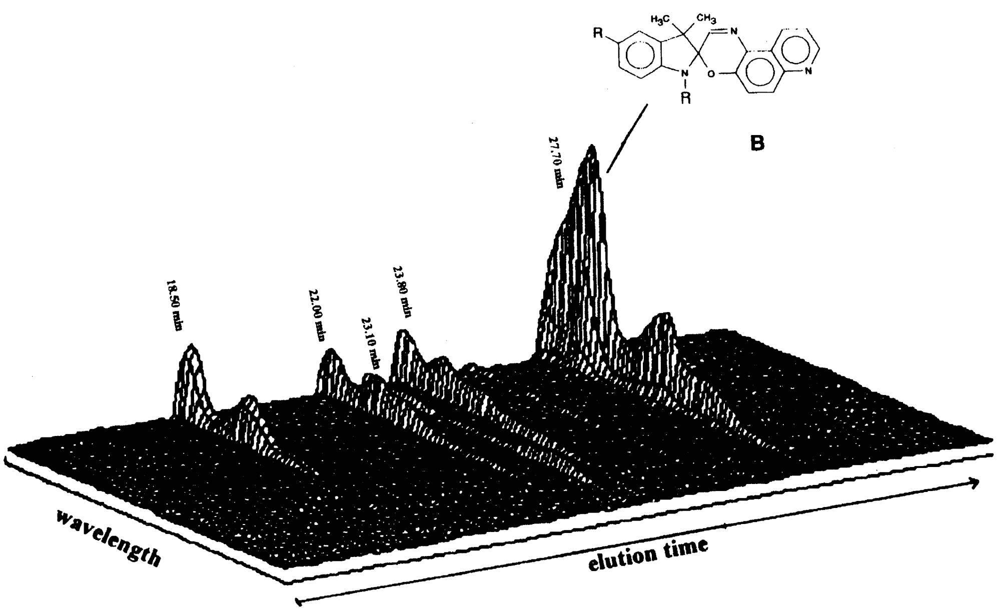


Fig. 6. 3D plot of the LC separation of the photoproducts of (**B**) extracted from the polyurethane matrix after 70 h of suntest exposure. Column Hypersil 4.6 mm×25 cm C18 8 µm. Mobile phase: CH_3CN/H_2O: 40/60 (v/v) during 10 min, then 100% of CH_3CN within 30 min, flowrate 1.5 ml min^{-1}. Detection 200—450 nm. Scans 1 Hz. Temperature 40 °C.

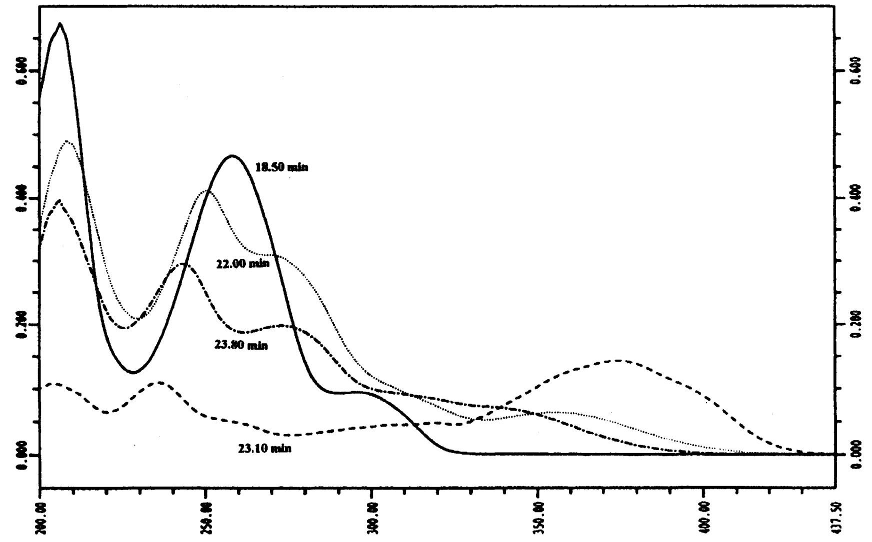


Fig. 7. UV-visible spectra of the photoproducts of (**B**) obtained from the LC separation of the Fig. 6.

Table 1. Analysis of the Amount of (**B**) (Chromatography) in the Matrix in Function of the Irradiation Time and Correlation with the Loss of the Photochromic Response (Absorbance Monitoring)

Irradiation time h	Absorbance (623 nm)	Loss of absorbance	Concentration mg/g	Loss of dye mass
0	2	0	0.98	0
30	1.21	−40%	0.63	−36%
70	0.72	−64%	0.3	−70%
112	0.34	−83%	0.11	−89%
183	0	−100%	0	−100%

tochromism during irradiation therefore cannot be attributed to an acceleration process of the fading, which could in part be responsible for the loss of the photochromic response.

Table 2. Bleaching Kinetics of (**A**) and (**B**) in the Polyurethane Matrix Measured after 30 min of Xenon Continuous Irradiation ($E_{\mathrm{UV}}=2$ mW cm^{-2}, $E_{\mathrm{vis}}=54$ klux, $^{*}E_{\mathrm{UV}}=0.5$ mW cm^{-2}, $E_{\mathrm{vis}}=14$ klux, $T=25$°C)

Compound	Irradiation time	Absorbance	Bleaching constants	Amplitudes
	h	(623 nm)	min^{-1}	
A*	0	0.17	$k_1=2.25$	$A_1=0.076$
			$k_2=0.17$	$A_2=0.08$
	200	0.072 (−57%)	$k_1=2.09$	$A_1=0.037$
			$k_2=0.14$	$A_2=0.03$
B	0	1.92	$k_1=0.81$	$A_1=0.44$
			$k_2=0.097$	$A_2=1.037$
	112	0.45 (−76%)	$k_1=0.87$	$A_1=0.12$
			$k_2=0.107$	$A_2=0.26$

Table 3. Biexponential Bleaching Kinetics of (**A**) and (**B**) in the Polyurethane Matrix during the Degradation Taken after Flash Photolysis Excitation ($E_{\mathrm{xenon}}=150$ joules, 50 µs, $T=33$°C)

Compound	Irradiation time	Absorbance	Bleaching constants	Amplitudes
	h	(623 nm)	s^{-1}	
A	0	0.41	$k_1=0.75$	$A_1=0.11$
			$k_2=0.09$	$A_2=0.23$
	200	0.122 (−70%)	$k_1=0.86$	$A_1=0.037$
			$k_2=0.093$	$A_2=0.065$
B	0	0.46	$k_1=0.17$	$A_1=0.12$
			$k_2=0.03$	$A_2=0.29$
	112	0.09 (−80%)	$k_1=0.16$	$A_1=0.036$
			$k_2=0.04$	$A_2=0.052$

Conclusion

This study of the fatigue process and the yellowing of polyurethane films containing spirooxazine photochromic compounds show that the photodegradation or loss of the photochromic response takes place mainly via a photooxidation process of the initial dye. Although this assertion seems to be more logical, we had to demonstrate that the other hypotheses were incorrect. Indeed, we must rule out the idea of a screen effect caused by yellowish photoproducts, which could potentialy affect the photocoloration process (300—400 nm).

Furthermore, during irradiation, an acceleration of the fade rate of the photomerocyanine form, which could deplete the photostationary state level, must also be eliminated.

This extraction procedure of indolinespiroheterocyclic photochromics and their photoproducts embedded in a polymer by liquid–solid extraction should allow, for routine analyses, one to study in detail the degradation processes of different series of photochromic compounds, or some molecules substituted in different ways. In particular, this technique could be helpful to study the degradation mechanisms of the photochromes by radical mechanisms[10] or singlet oxygen.[8,16] It will now be interesting to test whether supercritical fluid extraction (SFE) with carbon dioxide could be a good alternative for the extraction of these compounds; this work is now in progress at our laboratory.

References

1) N. Y. C. Chu, *Can. J. Chem.*, **61**, 300 (1983).

2) N. Y. C. Chu, in "Photochromism: Molecules & Systems," ed by H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam (1990), Chap. 10.

3) J. C. Crano, W. S. Kwak, and C. N. Welch, in "Applied Photochromic Polymer Systems," ed by C. B. Ardle, Chapman and Hall, New York (1992), Chap. 2.

4) N. Y. C. Chu, *Optical Energy Materials*, **14**, 215 (1986).

5) N. Y. C. Chu, "Optical Materials Technology for Energy Efficiency and Solar Energy Conversion VII, SPIE 1016," p. 152 (1988).

6) N. Y. C. Chu, "Proceedings of the 10th IUPAC Symposium on Photochemistry," Interlaken, Switzerland (1984).

7) R. Gautron, D. Eloy, P. Escaffre, R. Guglielmetti, E. Pottier, and P. Tardieu, *Bull. Soc. Chim. Belg.*, **100**, 315

(1991).

8) G. Baillet, Ph. D. Thesis, Marseille, 1993.

9) G. Baillet, G. Giusti, and R. Guglielmetti, *J. Photochem. Photobiol. A: Chem.*, **70**, 161 (1993).

10) G. Baillet, M. Campredon, R. Guglielmetti, C. Aubert, and G. Giusti, *J. Photochem. Photobiol. A: Chem.*, **83**, 147 (1994).

11) G. Baillet, V. Lokshine, R. Guglielmetti, and G. Giusti, *C. R. Acad. Sci. Paris*, **t. 319**, Serie II, 41 (1994).

12) R. Dubest, P. Levoir, J. J. Meyer, J. Aubard, G. Baillet, G. Giusti, and R. Guglielmetti, *Rev. Sci. Instrum.*, **64**, 1803 (1993).

13) V. Malatesta, M. Milosa, R. Millini, L. Lanzini, P. Bortolus, and S. Monti, *Mol. Crys. Liq. Cryst.*, **246**, 303 (1994).

14) G. Baillet, R. Guglielmetti, and G. Giusti, *Mol. Cryst. Liq. Cryst.*, **246**, 287 (1994).

15) D. Eloy and P. Jardon, *C. R. Acad. Sci. Paris*, **t. 315**, Serie II, 1325 (1992).

16) A. A. Firth, D. J. Mc Garvey, and T. G. Truscott, *Mol. Cryst. Liq. Cryst.*, **246**, 295 (1994).