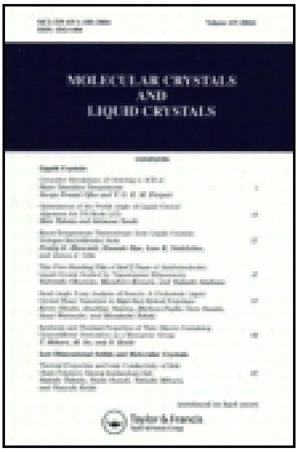


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photodegradation of Organic Photochromes in Polymers - Naphthopyrans and Naphthoxazines Series -

Gilles Ballet [a]

[a] Essilor International, 57, avenue de Condé, 94100, Saint-Maur des Fossés, FRANCE

To cite this article: Gilles Ballet (1997): Photodegradation of Organic Photochromes in Polymers - Naphthopyrans and Naphthoxazines Series -, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 298:1, 75-82

To link to this article: http://dx.doi.org/10.1080/10587259708036145

Mol. Cryst. Liq. Cryst., 1997, Vol. 298, pp. 75–82
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTODEGRADATION OF ORGANIC PHOTOCHROMES IN POLYMERS - NAPHTHOPYRANS AND NAPHTHOXAZINES SERIES -

GILLES BAILLET
Essilor International, 57, avenue de Condé, 94100 Saint-Maur des Fossés, France

Abstract The natural solar and artificial induced photodegradation of naphthopyran and naphthoxazine series was investigated in PMMA and in a polyurethane network. The degradation profiles through the depth of the coatings were monitored by Raman spectroscopy in function of the cumulated UV-A doses. The analyses of the formed photoproducts in each series were carried out by different off-line hyphenated chromatographic techniques. The detected products are clearly oxidized species and are similar to those found in apolar solvents. Moreover, the mechanisms of degradation seem to be of the same order between natural solar exposure and artificial solar simulation (suntests) that allows to use Xenon arc sources for accelerated degradation tests. The use of an oxygen barrier layer above the photochromic coating allows to demonstrate the formation of the naphtho[1,2]furan, which is the precursor of the 2-hydroxy-1-naphthaldehyde formation, in the naphthopyran series.

INTRODUCTION

The photodegradation of photochromes in the indolinospiropyran(1,2) and indolinospironaphthoxazine series in terms of analytical studies, has been now widely studied in solid state(3) or in solvent solutions(4-6), especially at the beginning of the 90's. As the main fields of applications for these dyes are their use in polymer matrices (ophthalmic lenses, light filters,...)(7) we are focusing now on the light induced degradation aspects in thermoplastics or in thermoset polymeric networks(8). The aim of these studies is to assess how the degradation takes place through a polymer coating depending on the depth of the coating and the concentration of the incorporated photochromic dyes. Another important aspect is to evaluate if there are different mechanisms of degradation in function of the medium (solvent, solid matrix) and in function of the irradiation sources (artificial versus natural). The goals being that, degradation experiments conducted under artificial accelerated tests, have to be as close as possible against the natural solar exposure.

QUANTITATIVE ASPECTS OF THE PHOTODEGRADATION

In a previous study(8), we showed that the loss of the photochromic response of an indolinospiroxazine derivative in a polyurethane (PU) matrix was only due to the loss of the photochromic material still available in the coating. Indeed, an acceleration of the bleaching rate (increase of kΔ) during the degradation was not observed when compared with the degradation in solvent solutions (9). Moreover, the hypothesis of some potential screen effect induced by the formed photoproducts was discarded, assuming that the UV-A irradiance (2 mW/ cm^2 /s) was sufficient to activate the photochromic response through the depth of the coating (15 μm). However, we did not know how the photooxidation process took place inside the depth of a polymer coating.

Depth profiling with confocal microscopy-Raman spectroscopy

Samples of 3,3-diphenyl-[2H]-Naphthopyran (**A**) and 1,3,3-trimethylspiro[indoline-naphthoxazine] (**B**) (Figure 1) in PMMA (5% w/w, 30 μm thickness) were exposed to outdoor sunlight and in a suntest (Xenon arc source). The cumulated UV-A doses were recorded with a radiometer. At different intervals of exposure time, the concentration profiles of the photochromes from the surface through the depth of the coating were recorded by Raman spectroscopy equipped with a confocal microscope that allows to investigate small volumes (e.g., 1 μm^3). The figure 2 shows the Raman spectra of a degraded samples (photochrome A) after a cumulated UV-A dose of 1500 j/ cm^2. The figure 3 summarizes an example of the obtained concentration profiles for B in function of the UV-A dose. The profiles were determined by taking the ratio of the main Raman scattering band of the photochrome at 1568 cm^{-1} versus the C=O stretching band of the PMMA at 1727 cm^{-1}.

It is clearly seen that the degradation of the photochromic compounds is not homogeneous through the depth of the polymer coating, the outside layers being first degraded. This can be explained by a gradient of the UV irradiance from the surface through the depth of the coating. Despite this inhomogeneity, the global photochromic response (activation) is not affected by this gradient of concentration for a punctual UV-A irradiance of 2 mw/cm^2/s $^{(8)}$ (an averaged value obtained for the sun at midday for instance).

The natural and artificial degradation of both A and B conducted to the same kind of degradation profiles, although, under natural exposure, the samples are exposed to different modes of irradiation (light and darkness).

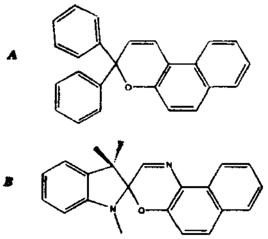


Figure 1: Structures of the studied compounds

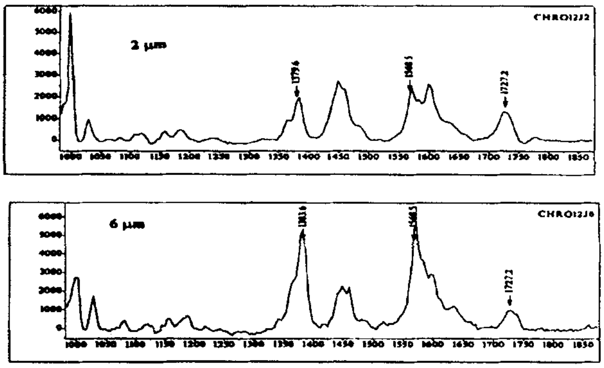


Figure 2: Raman spectra of A degraded in a PMMA coating taken at 2μm from the surface and at 6 μm of depth after a cumulated UV-A dose of 1500 j/cm^2

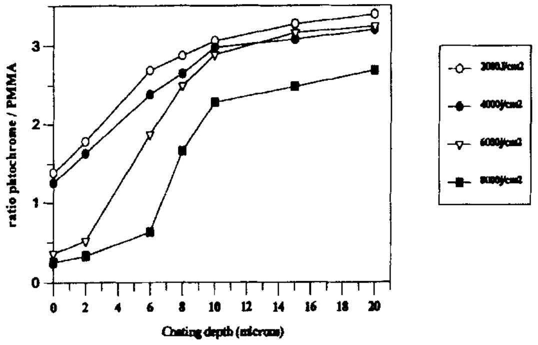


Figure 3: Exemple of concentration profiles of **B** through the depth of the coating in function of the received UV-A dose. For example, the daily averaged UV-A dose in Paris in summer (horizontal mode, south exposed) is 180 j/cm^2 for a clear sky and 80 j/cm^2 for an overcastweather.

ANALYSES OF THE FORMED PHOTOPRODUCTS

The light (natural and artificial) induced degradation products were extracted from the photochromic coatings (PMMA and PU) and were analyzed off-line by different hyphenated chromatographic techniques (see experimental part). The structures of the formed fragments were attributed by mass-spectrometry. The results for the two series are summarized in the tables 1 and 2. For comparison the photoproducts detected in toluene and in acetonitrile are also depicted.

In the diaryl-[2H]-naphthopyran series (Table 1), clearly, we are dealing with an oxidation process as stated before in the spirooxazine and spiropyran series in solution(4). The major fragment is the benzophenone (C1) the corresponding product of the oxindoles (O1) in the indolinospiroheterocyclic series. When compared to the spiroindoline series we found many aldehyde derivatives (C2, C4, C6, C7) (their corresponding acids were not found). Here, we were able to detect traces of the naphtho[1,2]furan (C5) the corresponding product of the naphthoxazole (O4) in the spirooxazine series. The naphtho[1,2]furan had not been found during the degradation of the indolinospironaphthopyran in solution(4). Few products, corresponding to the degradation of C5: C9 (phthalic anydride), C10 (1[3H]-isobenzofuranone) and C11 ([2H]-1-benzopyran-2-one) are also detected. Some high molecular weight products are also detected (C13, C14) and benzoyl like derivatives: Cx1 and Cx2 which structures have not been clearly elucidated. Globally, we found the same degradation patterns with natural and artificial exposure in PMMA. In the polyurethane network, the photodegradation profiles seem to be of the same nature than in PMMA. Between acetonitrile and toluene, the latter solvent seems to conduct to the closest degradation patterns to the polymer matrices, although we found a specific product (C12) which formation could be explained by recombinations with aryl and benzyl radicals.

With the 1,3,3-trimethylspiro[indolinenaphthoxazine] **B** (Table 2) we found again the same low molecular weight derivatives as described before(4). Many high molecular weight products are detected (O11-O16). These products can be considered as intermediate products and, likely, precursors for the formation of some of the low molecular weight compounds (O1-O10). Here again, we have the same photodegradation profiles between the toluene, the PU coating and the PMMA coatings. The degradation mechanisms seem appreciably different in acetonitrile solution by taking in account the relative ratio of each product.

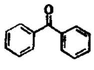
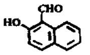
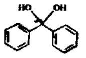
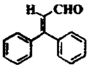
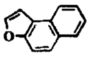
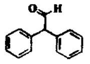
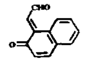
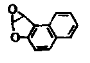
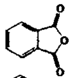
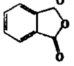
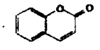
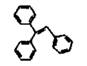
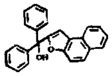
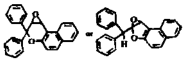
Attributed structure	Mw	code	toluene suntest	CH_3CN suntest	PU suntest 2000j/cm²	PMMA suntest 6000j/cm²	PMMA solar exposure 5000 j/cm²
	182	C1	xxxx	x	xxxx	xxxx	xxxx
	172	C2	x	x	x	nd	x
	200	C3	x	x	nd	x	x
	208	C4	xx	x	x	x	x
	168	C5	x	x	x	x	x
	196	C6	x	x	nd	nd	nd
	184	C7	x	xx	x	x	x
	184	C8	x	x	x	x	x
	148	C9	xx	xx	x	x	x
	134	C10	x	x	x	x	x
	146	C11	x	x	nd	x	x
	256	C12	xxx	x	nd	nd	nd
	350	C13	nd	x	x	x	x
	350	C14	nd	nd	x	x	x
undetermined	278	Cx1	x	nd	x	x	x
	264	Cx2	x	nd	nd	x	x

TABLE 1: Comparison of the formed photoproducts for the 3,3-diphenyl-[2H]-naphthopyrane **A** in function of the medium (xxxx = major compounds, x = traces, nd < limit of detection)

Finally, the main characteristic of this study is that there are no major differences between degradation experiments conducted under solar exposure and artificial simulation (Xenon arc) for the two studied compounds. So, the mechanisms of degradation being of the same order, one can use confidently suntests as accelerated degradation tests for photochromic dyes in polymer matrices. It will be interesting to conduct the same study with other irradiation sources like fluorescent lamps or Mercury arc lamps, although these sources do not emit in the visible region.

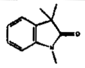
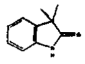
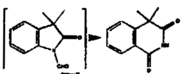
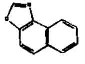
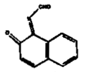
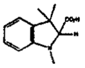
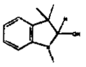
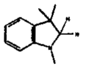
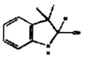
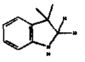
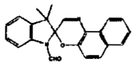
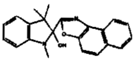
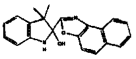
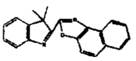
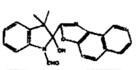
Attributed structure	Mw	code	toluene suntest	CH_3CN (*) suntest	PU suntest 2000j/cm^2	PMMA suntest 6000j/cm^2	PMMA solar exposure 5000 j/cm^2
	175	O1	xxxx	x	xxxx	xxxx	xxxx
	161	O2	xx	xx	xx	xx	xx
	189	O3	xx	xxxx	xx	xx	xx
	169	O4	xxx	xx	xxx	xxx	xxx
	185	O5	xx	x	x	xx	xx
	205	O6	x	x	x	x	x
	177	O7	x	x	nd	x	x
	161	O8	x	x	nd	x	x
	163	O9	x	x	nd	nd	nd
	147	O10	nd	x	nd	x	x
	342	O11	x	x	x	x	xx
	344	O12	xx	x	x	xx	xx
undetermined	344	O13	xx	x	x	xx	x
	330	O14	xx	x	x	xx	x
	312	O15	x	xxxx	x	x	x
	358	O16	xx	x	x	xx	x

TABLE 2: Comparison of the formed photoproducts for the 1,3,3-trimethylspiro[indolinenaphthoxazine] **B**

(*) other products were detected at traces level. (xxxx = major compounds, x = traces, nd < limit of detection)

EFFECT OF AN OXYGEN BARRIER COATING

As it was clearly demonstrated that the degradation processes took place essentially via an oxidation process, it was interesting to assess the role of an oxygen barrier above the photochromic polymer coating. The hydrosoluble Carboxymethylcellulose, being known for its barrier properties (10), was tested for degradation experiments. It was found that this coating was able to increase the photofatigue resistance time with the naphthopyran and naphthoxazine series by a factor of about 1.5-2 time (11). An investigation of the formed photoproducts in the 3,3-diphenyl-[2H]-naphthopyran series (**A**) and 1,3,3-trimethylindolinospironaphthopyran series (**C**) showed for the first time the evidence of the formation of the naphthofuran product in high yield. We suspected this derivative to be an intermediate for the 2-hydroxy-1-naphthaldehyde formation (C2) but without proof for this mechanism. A control experiment by irradiating reference compounds of naphthoxazole (O4) and naphthofuran (C5) in PMMA showed no significative degradation of these compounds after a cumulated UV-A dose of 500 j/cm^2 in a suntest (figure 4). On another hand, if we make a mixture of these reference compounds with rose bengal (Φ_Δ $^1O_2 = 0.76$) (12) (ratio sensitizer/dye: 1/10) in the PMMA, we were able to check the complete degradation of the naphthofuran (C5) with only 50 j/cm^2. The irradiation of C5 induced the formation of the salicylaldehyde derivative (C2) as the major product, plus the formation of C9, C10 and C11. We had no sensitized degradation of the naphthoxazole derivative (O4), even with an UV-A dose ten times higher (500 j/cm^2).

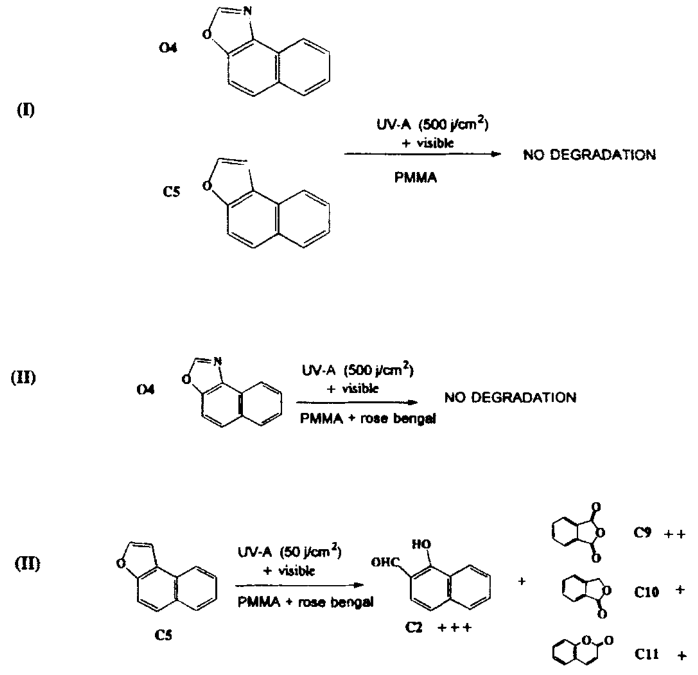


Figure 4: Irradiation of the naphthoxazole and the naphthofuran in PMMA in presence of air (**I**) and photosensitized $^1O_2$ (**II**) (+++ = major compounds, + = minor compounds.)

These experiments demonstrate unambiguously the fact that the naphthofuran is indeed formed during the photodegradation of the diaryl-[2H]-naphthopyran and indolinospironaphthopyran series, but this derivative is rapidly oxidized, generating other underproducts, including the salicylaldehyde derivative.

DISCUSSION

The photooxidation mechanisms of the photochromic compounds in the naphthopyran and naphthoxazine series are complex and could be governed by competitive oxidation reactions. Some hypotheses involve the reaction of the molecular oxygen with the diradical species induced during the opening of the C-O bond(6, 13). The reaction with the superoxide anion $O_2^{-\circ}$ has been suggested by Malatesta et al.(5) as the sole possible oxidation process leading to the intermediate (O12) in the spiroxazine series. From our experiments, in solvents and in polymers, we were able to detect other high molecular weight products. The experiment with the sensitized irradiation of the naphthofuran shows that the singlet oxygen is able to induce the formation of the salicylaldehyde derivative, but we do not know what could happen with the superoxide anion. A more recent study(14) using a specific singlet oxygen chemical trap (α,α'-dimethylstilbene) shows that, during irradiation, the photochromic molecules are able to induce the formation of a specific hydroperoxyde product from the α,α'–dimethylstilbene precursor. It is not clear whether the photomerocyanine or the degradation products of the photochromes are able to generate singlet oxygen, but it seems that this pathway has to be taken in account. The chemistry of the dioxygen being rather complex(15), more academical works are to be done in order to explain the oxidation pathways during the light induced degradation of photochromic molecules. Moreover, as we are studying here simple parent compounds (to the point of view of their chemical structures) we do not know what could happen with highly conjugated systems (i.e. fused heterocycles) which could induce the formation of highly conjugated photoproducts.

EXPERIMENTAL

The photochromes **A** (3,3-diphenyl-[3H]-naphtho[2,1-b]pyran) from Japan Kemix, **B** (1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1b][1,4]oxazine] from Aldrich and **C** (1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,2'-[3H]naphth[1,2b]pyran (synthesized according to (16)) were incorporated in PMMA (Aldrich), (Mw = 996.000, Tg = 100°C (DMA, 1Hz)) at 5 % w/w and deposited by spin on mineral glass plates. For the 5% w/w photochromic polyurethane networks (Tg = 35°C, DSC), the coatings were prepared according to (8). The Carboxymethylcellulose (Aldrich) coatings were deposited in water solution at 4% w/w by dip and were evaporated to dryness 1h in an oven at 100°C (final thickness 1-2 µm). The naphtho[1-2] furan was synthesized by Dr. Dauzonne (Institut Curie, France) and the naphthoxazole was synthesized according to (4). The samples were exposed to the natural daylight in Paris on an horizontal plane south exposed. The UV-A doses (J/cm^2) were recorded simultaneously by integration of the punctual UV-A irradiance (W/cm^2/s) with a research radiometer equipped with an outdoor UV-A SUD 033 probe (IL 1700, Ealing, France). Tne simulation experiments were conducted in a 1800 w suntest (Heraeus, France) equipped with a 290 nm filter. The Raman experiments were performed with a Labram system (Dilor S.A., France) equipped with a confocal hole and an Olympus microscope (hole 100 µm, grating 1800 g/mm, cooled CCD detector and 15mW 632.8 nm HeNe laser). The photoproducts analyses were performed by dissolving the PMMA in cold acetone and by injecting an aliquot fraction into the different hyphenated chromatographic systems. For the polyurethane networks, the extractions were carried out with supercritical carbon dioxide at 200 atm and 80°C ($\rho_{CO2} = 0.6$ g/cm^3) during 30 minutes in the dynamic mode. Methanol was added as polar modifier (20% v/v) in order to extract the polar fragments. The photoproducts were trapped on a C18 cryogenic trap at 0°C, eluted with methanol and injected into the different chromatographic systems. The chromatographic systems consisted of a GC-MS (EI 70 ev) (Trio 1000, Fisons Inst., France) equipped with a J&W DB5MS column (15m x 0.32 mm, film 0.25 µm). The HPLC (Jasco, Prolabo, France) was coupled with UV-visible diode array detection (Waters 996, France) and with Mass spectrometry (Trio 1000 Fisons Inst., France) equipped with an API interface. For the API$^+$ experiments, the sampling cone was fixed at 20 volts and the skimmer cone at 10 volts in order to get the [MH]$^+$ ion. Then, the sampling cone was fixed at 50 volts to get the fragmentation patterns by chemical induced dissociation. The needle voltage was fixed at 3600 volts and the nebulizer temperature fixed at 600°C. The column was a 4.6 mm x 25 cm Rx C18 5µm Zorbax (Rockland Technologies, Interchim, France) and the mobile phase consisted of a linear gradient of 30% CH_3CN in water to 100% within 30 min at 1 ml/min.

ACKNOWLEDGMENTS

I would like to thank P. Tardieu, A. Thuillier and N. Lelard (Essilor Int.) for their great help.

REFERENCES

1. P. Fruit, R. Gautron and C. Audic, Bull. Soc. Chim. Fr., 5, 2237 (1968)
2. G. Baillet, V. Lokshine, R. Guglielmetti and G. Giusti , C. R. Acad. Sci. Paris, t. 319, Série II,41 (1994)
3. T. Yoshida and A. Morinaka, J. Photochem.Photobiol., 63, 227 (1992)
4. G. Baillet, G. Giusti and R. Guglielmetti, J. Photochem. Photobiol., 70, 157 (1993)
5. V. Malatesta, M. Milosa, R. Millini, L. Lanzini, P. Bortolus and S. Monti, Mol. Cryst. Liq. Cryst., 246, 303 (1994)
6. G. Baillet, M. Campredon, R. Guglielmetti, C. Aubert and G. Giusti, J. Photochem. Photobiol., 83, 147 (1994)
7. J. C. Crano, W. S. Kwak and C. N. Welch in « Applied Photochromic Polymer systems », edited by C. B. Mc Ardle (Chapman and Hall, N. Y., 1992) chap. 2, pp. 31-77
8. G. Baillet, G. Giusti and R. Guglielmetti, Bull. Chem. Soc. Jpn., 68, 1220 (1995)
9. G. Baillet, R. Guglielmetti and G. Giusti, Mol. Cryst. Liq. Cryst., 246, 287 (1994)
10. K. Petrak, J. Appl. Polym. Sci., 23, 2365 (1979)
11. P. Tardieu, Essilor Int. Personnal communication
12. K. Gollnick and G. O. Schenck, Pure Appl. Chem., 9, 507 (1964)
13. R. Gautron, Bull. Soc. Chim. Fr., 8, 3200 (1968)
14. C. Salemi-Delvaux, B. Luccioni-Houzé, G. Baillet, G. Giusti and R. Guglielmetti, Tetrahedron Lett. 37 (29), 5127(1996)
15. M. Chanon, M. Julliard, J. Santamaria and F. Chanon, New J. Chem., 16, 171 (1992)
16. E. Fisher and Y. Hirschberg, J. Chem. Soc., 5422 (1952)