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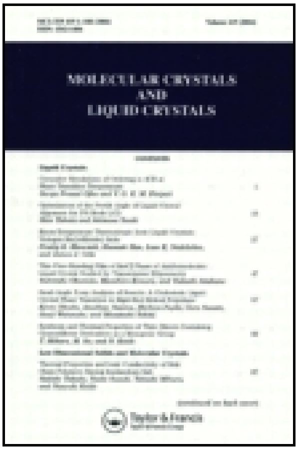

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Photodegradation Study of a [2H]-Naphtho [1,2-b] Pyran Derivative in Solution and in Polymer Matrix

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Version of record first published: 24 Sep 2006

To cite this article: R. Demadrille, M. Campredon, R. Guglielmetti & G. Giusti (2000): Photodegradation Study of a [2H]-Naphtho [1,2-b] Pyran Derivative in Solution and in Polymer Matrix, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 1-8

To link to this article: http://dx.doi.org/10.1080/10587250008023886

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Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 1-8
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Photodegradation Study of a [2*H*]-Naphtho [1,2-b] Pyran Derivative in Solution and in Polymer Matrix

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This paper deals with the investigation of the photodegradation of (2,2-(4,4 '-dimethoxyphenyl)-5,6-dimethyl-[2H]-naphtho-[1,2-b]pyran in toluene solution and in polyurethane matrix. With the aim of proposing mechanisms for the photodegradation processes, a complete determination of the photoproducts' structures has been carried out using HPLC, GC/MS and direct introduction MS techniques. The different techniques allowed us to detect the production of well-known photoproducts but also the formation of new high molecular weight oxygenated derivatives. Our investigations also underline the detection of new photo-induced products that are produced by secondary oxidative pathway.

Keywords: photochromism; photodegradation; photooxidation; polymer; chromene

INTRODUCTION

Photochromism of [2*H*]-chromenes is a phenomenon based on the absorption of U.V light irradiation by an uncoloured form, which leads

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after the scission of the C-O bond of the closed pyranic moiety to a coloured species. After isomerisation the coloured form can revert back to the initial molecule thermally or photochemically.

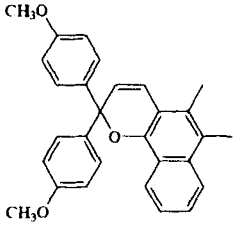
Recent interest in the photochromism of benzo and naphthopyrans has been increased by the commercialisation of photochromic plastic lenses in the early 1990's. However photodegradation processes still constitute significant restriction in the applications of these dyes.

Until now, degradation studies of organic photochromes were focused on indolinospironaphthoxazine[1-2-3], indolinospiropyran[3], and [3H]-naphtho-[2,1-b]-pyran[4] series in solution and more recently in polymer matrix[5]. These different studies have stated that molecular and singlet oxygen was mainly responsible for the loss of the photochromic properties during the degradation.

In order to extend these observations to [2H]-naphtho-[1,2-b]-pyran series, the photodegradation of the 2,2-(4,4'-dimethoxyphenyl)-5,6-dimethyl-naphtho-[2,1-b]pyran derivative has been performed under continuous irradiation in toluene solution and in polyurethane matrix.

EXPERIMENTAL DETAILS

Scheme 1: studied compound (I).



The studied compound 2,2-(4,4'-dimethoxyphenyl)-5,6-dimethyl-naphtho-[2,1-b]pyran (compound I) is available from James Robinson Ltd.

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The polymer matrix used in this study is a copolymer polyester-polyurethane available from Aldrich: poly(4,4'-methylenebis(phenyl-isocyanate)-*alt*-1,4-butanediolpoly-(butylene adipate)). The Tg value of the matrix is −18°C (measured using Differential Scanning Calorimetry).

Polymer samples are 14µm thick and contain 2.10^{-5} Mol/g (dye/polymer); the concentration of the toluene solution is 10^{-4} Mol/L.

All degradations were performed in a Sun Test (Atlas) equipped with a 1500W Xenon lamp and a 290 nm filter at 25°C. The photodegradation in solution is carried out in a quartz reactor under stirring.

The loss of optical density is followed with a spectrophotometer (diode array detector) at the Photostationary State that is reached after 10 min of irradiation with a 150W Xenon lamp at 20°C (analytical wavelength 493nm in toluene and 501nm in polymer matrix).

After degradation photo-induced fragments are extracted from the coating with acetonitrile at 60°C and injected in the different chromatographic systems.

The chromatographic systems are consisted of GC/MS (6890 HP GC system and 5973 MSD)(EI 70ev) equipped with a short column (optima 0.2µm, 12m x 0.2mm). The high performance liquid chromatograph consists in a Beckman HPLC Gold system coupled with a 168 diode array detector (LC/DAD). The separation system is composed by a C18 nucleosyl (25cm x 4.6mm, 5µm) reverse phase column with a gradient of acetonitrile in water from 30% to 100% during 45min set at 1ml/min. The structures of the by-products are mostly determined by analysis of the GC-MS chromatograms. Synthesis of the real material and

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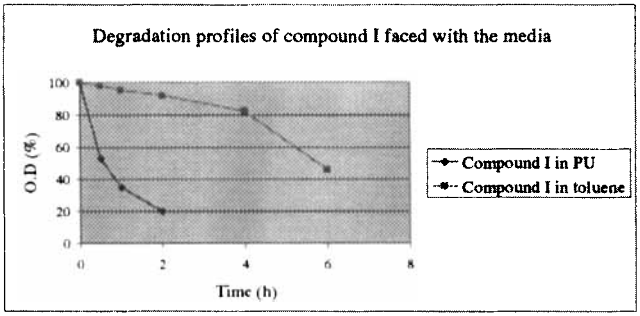
comparison of the mass spectra, the retention time and the U.V spectra can help us to confirm the structures of the photo-induced fragments.

RESULTS AND DISCUSSION

The degradation profiles are obtained by looking regularly at the loss of the optical density at the Photostationary State after irradiation performed with a Xenon lamp. Scheme 2: degradation profiles



From the degradation profiles (scheme 2), it clearly appears that the compound is less stable under irradiation in polyurethane matrix in spite of the fact that this polymer is stable thermally and photochemically in this range of exposure. During the degradation, a yellowing is also observed in both media. In order to explain this observation a HLPC coupled with diode array detector analysis allowed us to underline the formation of several by-products revealing strong absorption band between 400 and 430nm. These products may be responsible for a

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screen effect observed at the end of the degradation when the compound is studied in polymer matrix.

Previous studies carried out on various series such as spiroindolinonaphthoxazine[2] and [3H]-naphtho-[2,1-b]pyran[4], have shown that $^1O_2$ reacts on diene systems obtained after the photochromic interconversion. Concurrently molecular oxygen can react with the biradical species form after the scission of the C-O bond of the pyran moiety to lead to oxidised fragments.(chart I)

Recently we have demonstrated that these fragments can undergo secondary oxidative reactions. (4,4'-dimethoxy)-β-phenylcinnamaldehyde (P5) is converted into carboxylic acid derivative (P6) that can lead after decarboxylation to (4,4'-dimethoxy)-diphenylethylene (P7). We have also demonstrated that this fragment reacts with singlet oxygen to produce corresponding benzophenone derivative (P4). As P5, 3,4-dimethyl-2-formyl-naphthol, which can be formed either directly from the compound (I) or from the photodegradation of the naphthofuran derivative (P1), is converted to the corresponding carboxylic acid (P3) leading to 3,4-dimethylnaphthol (P0) after decarboxylation. It is important to note that carboxylic acids have been detected with the GC/MS system after derivatisation performed with bis(trimethylsilyl)trifluoroacetamide.

The next chart also presents the structures of new high molecular weight by-products. These epoxidised products are produced from the addition of oxygen on the diene system obtained after photochromic interconversion. According to the review of E.L.Clennan[6] we suppose that the bi-epoxidised fragment is formed after a [4+2] reaction between

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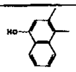
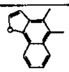
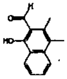
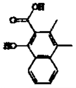
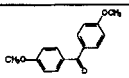
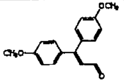
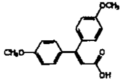
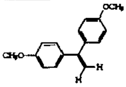
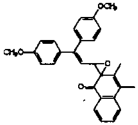
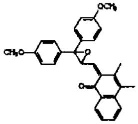
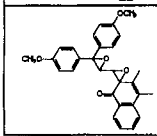
Attributed Structures	Molecular Weight	Toluene	Polyurethane	Code
	172	X	X	P0
	196	XX	X	P1
	200	XX	XX	P2
	216	X	X	P3
	242	XXXX	XXXX	P4
	268	XXX	XXX	P5
	284	XX	XX	P6
	240	X	XX	P7
	438	XX	XX	P8
	438	XX	XX	P9
	454	X	ND	P10

Chart 1: Detected by-products : X traces, XX quite important, XXX important, XXXX very important, ND non detected.

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singlet oxygen and the cis isomer of the open form of the photochrome. The resulting endoperoxide leads after rearrangement to the product P10. The observation of the mono-epoxidised products can be explained by the reaction involving molecular oxygen and the biradical species of the open form. The hydroperoxide intermediates can after the loss of hydroxyl radical undergo a cyclisation leading to the mono-epoxides.

CONCLUSION

In this work, we have shown that similar oxidation processes are responsible for the loss of the photochromic properties in toluene solution and in polyurethane matrix.

We also underline the fact that several photoproducts are unstable and undergo secondary oxidative reactions. In addition to previous studies we have determined new high molecular weight by-products resulting from the addition of molecular or singlet oxygen on the diene system of the open form.

These observations could help us to determine efficient stabilisers to use, such as hindered amines light stabilisers or phenolic antioxidants, in order to increase the fatigue resistance of these class of photochromic dyes.

ACKNOWLEDGMENTS

The authors would like to thank ESSILOR Int. (France), PPG Industries (USA), TOI (USA) and Conseil General 13 for financial support and Dr Claude AUBERT (Université de la Méditerranée) for his fruitful advice

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