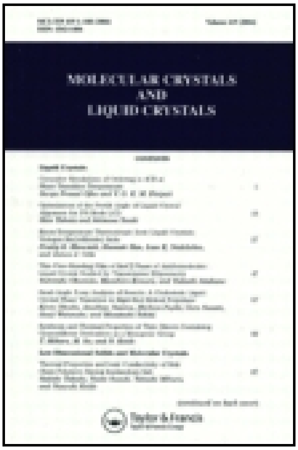

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

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Version of record first published: 24 Sep 2006.

To cite this article: Jean-Pierre Desvergne , Henri Bouas-laurent & Alain Deffieux (1994): Photochromism of Anthracene Derivatives in Fluid Solutions and Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 111-118

To link to this article: http://dx.doi.org/10.1080/10587259408037797

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 111–118
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Printed in the United States of America

PHOTOCHROMISM OF ANTHRACENE DERIVATIVES IN FLUID SOLUTIONS AND POLYMERS

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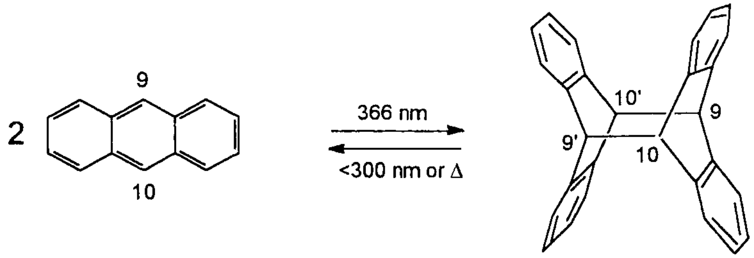
Abstract The photochemical behaviour of a new series of bisanthracenes in fluid solution and in polymer matrices is described. These systems which incorporate an acetal link undergo an efficient photocycloisomerization. Moreover, new polymers bearing anthracene pendant groups were described; they undergo at 366 nm an interchain anthracene photodimerization with a twofold increase of their average molecular weight ($\overline{M}_W$). Photodissociation easily proceeds at 270-280 nm in solution as well as in polymers.

A great number of anthracene derivatives are known to smoothly photodimerize ($\lambda >$ 300 nm) in a variety of solvents and in the solid state[1-4]. The reaction, which is photoreversible ($\lambda < 300$ nm), produces a large electronic absorption shift of the medium as shown in Figure 1. However, the photodimers, usually stable at room temperature, are scarcely soluble[5] in organic solvents or matrices which hinders their application to photochromic devices. Another drawback, related to the intermolecular nature of the reaction, is its dependence on the concentration and the medium viscosity; the latter is critical in polymers. In order to overcome these limitations, **bisanthracenes** and some **anthracenophanes** were used[3] as the intramolecular photoreactivity of these systems at low concentration is mainly controlled by the dynamics of the chain linking the chromophores.



We report herein recent results on new bisanthracenes whose photocycloisomerization efficiency is significantly increased in fluid solution and in polymers in comparison with precedent systems[3,6]. Further, the photochemistry of a new kind of polymers with pendant anthracene groups was also investigated.

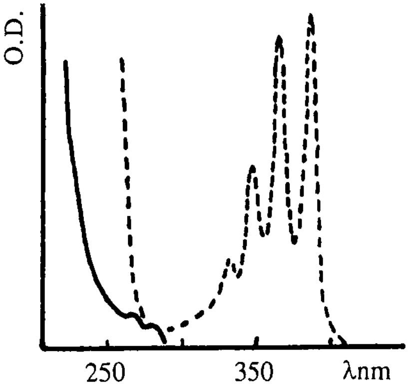
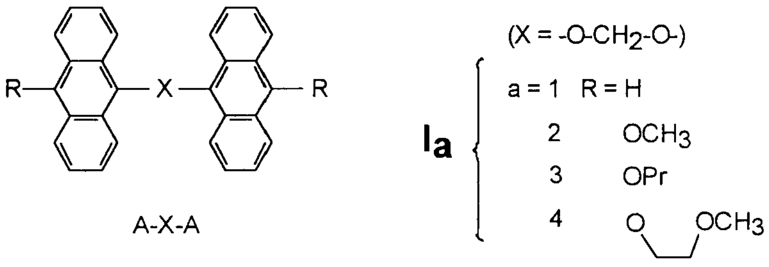


FIGURE 1 UV absorption spectra in cyclohexane at room temperature of bis(9-anthryloxy)methane I_1(-----) and its photoisomer (——)

I. BISANTHRACENES

Previous studies on bisanthracenes (A-X-A) have shown that the highest photocyclomerisation quantum yields (ϕ_R) from the singlet excited state are obtained with the short chains[2,3], especially for X = O-CH_2-O (ϕ_R=0.36) in methylcyclohexane[6] (I_1). To increase the solubility of this system and redshift the absorption spectrum some 10,10'-disubstituted derivatives were prepared (I_{2-4}). The photochromic properties of I_a were investigated. In Table I are listed, together with other properties, the photocyclomerization (ϕ_R) and photodissociation (ϕ_{diss}) quantum yields of the compounds in different media, at room temperature. A net enhancement of the reactivity is observed for R=H, OCH_3 and O-nPr in methanol[7] as compared with cyclohexane. The substitution on the meso positions by alkoxy groups decreases the efficiency of the reaction probably as a consequence of steric and electronic effects.



Besides, one notes that the photoproduct of the parent compound (R=H, I_a) is thermally stable at room temperature, whereas the substituted derivatives do not generate stable photoisomers as they slowly revert in the dark ($k_{diss} \leq 3x10^{-5}s^{-1}$) to the open form. The reverse process is sensitive to the nature of alkoxy groups as already recognized for other anthracenes[8]. Several cycles (closure at 366 nm, thermal opening) could be performed without any apparent damage to the material.

TABLE I Quantum yields of photocycloisomerization (ϕ_R) at 366 nm and photocycloreversion (ϕ_{diss}) at 270 nm of bisanthracenes I_a at room temperature. k_{diss} represents the first order rate constant for the thermal ring opening of the photoproduct in acetonitrile, at room temperature.

I_a	cyclohexane		acetonitrile		methanol		k_{diss} s^{-1}
	ϕ_R	ϕ_{diss}	ϕ_R	ϕ_{diss}	ϕ_R	ϕ_{diss}	
a=1	0.38	0.22	0.43	0.23	0.54	0.20	≈0
2	0.33	0.16	0.31	0.23	0.42	0.17	$0.6x10^{-6}$
3	0.24	0.11	0.22	0.10	0.27	0.10	$31x10^{-6}$
4	0.21	0.08	0.17	0.08	0.19	0.09	$15x10^{-6}$
4+Li+	0.22	0.08	0.18	0.09	0.18	0.10	≈0

The photodissociation leads to a photostationary state and its efficiency (ϕ_{diss}) is relatively low compared with other bisanthracenes[2,3] (for instance with R=H, $\phi_{diss}(ACH_2A)$ =0.76 and ϕ_{diss} (ACH_2O-CH_2A) = 0.64) and apparently not sensitive to the nature of the solvent. Interestingly, addition of Li^+ salt to a solution of I_4 does not change the photoreaction quantum yield ϕ_R but confers stability to the cyclomer (in CH_3CN, $k_{diss} \approx 0$ and $1.5x10^{-5}s^{-1}$ with and without Li^+, respectively).

This stabilization presumably involves a complex (II_4,Li^+) between the two ethylene-oxide arms and Li^+ after cyclomerization, the open form having a poor complexation ability for Li^+.

Although several consecutive light monitored cyclomerization-dissociation steps (366 and 270 nm) can be performed on the same A-X-A sample, degradation of the material is detectable by U.V. spectroscopy (Figure 2).

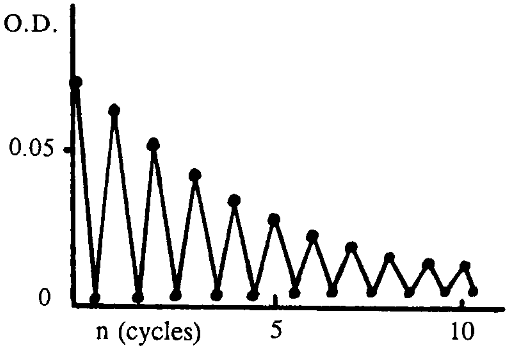
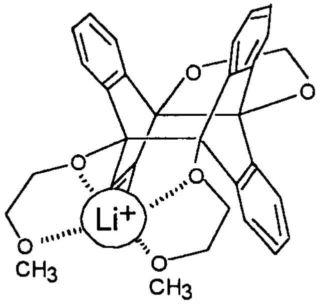


FIGURE 2 Photocycles of I_1 in degassed cyclohexane (conc.≈ 10^{-5} M, R.T.). The solution was first irradiated at 366 nm and at 270 nm to reach O.D.≈ 0.065; the following cycles consist of alternate irradiations (0.5 hour) at 366 and 270 nm.



II_4 (Li^+)

Besides, incorporated in various polymer matrices, I_a was also shown to smoothly photoisomerize as shown in Table II for I_1. In high molecular weight polymethylmethacrylate (PMMA), polystyrene (PS), poly α(methylstyrene) (PαS) and polyvinylchloride (PVC), which all exhibit glass transition temperature (Tg) ≥ 100°C, ϕ_R(20°C) is relatively low and close to 0.1. With a polybutadiene matrix, a polymer with a low Tg (≈-80°C), the photoisomerization efficiency is significantly higher (x2) in agreement with the possibility of local chain motion.

In the same polymer series (PMMA) ϕ_R is also dependent, as expected, on the average molecular weight of the polymer sample: ϕ_R increases with decreasing $\overline{M}_W$. This indicates a higher chain segment mobility in low molecular weight sample likely due to chain ends effect. These results suggest that I_a can be used as a probe to study the chains mobility and arrangement in polymeric materials.

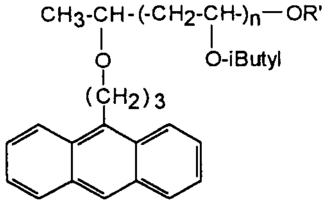
TABLE II Photoisomerization quantum yields (ϕ_R) of I_1 in different polymer matrices (bulk), conc.≈ 10^{-4}M, λ_{irra}=366 nm, R.T. (PMMA: polymethylmethacrylate, PS: polystyrene, PαS: polyα(methylstyrene), PVC: polyvinylchloride, PBD: 1,4-polybutadiene)

PMMA	d = 1 .2 Tg≈105°C	$\bar{M}_w$ 19,400 ϕ_R = 0.120	$\bar{M}_w$ 48,600 ϕ_R = 0.098	$\bar{M}_w$ 160,000 ϕ_R = 0.072
PS	d = 1.05 Tg≈100°C	$\bar{M}_w$ 250,000 ϕ_R = 0.102		
PαS	d = 1.07 Tg≈ 160°C	$\bar{M}_w$ 113,000 ϕ_R = 0.120		
PVC	d ≈ 1.4 Tg≈80°C	$\bar{M}_w \geq$ 100,000 ϕ_R = 0.087		
PBD	d ≈ 0.9 Tg = -80°C	$\bar{M}_w \geq$ 200,000 ϕ_R = 0.23		

II POLYMERS WITH PENDANT ANTHRACENE DERIVATIVES

The properties of these polymers are interesting for photophysical studies and technological applications such as photofabrication and information storage. Some studies were performed by other authors[9] on copolymers with pendant anthracenes, but the random nature of these materials makes the photocrosslinking difficult to govern; thus, for instance, in anthracene-derivatived polyesters[10], a significant level of intrachain photodimerization competes with photocrosslinking.

The new materials (P_A) presented here were obtained by functional initiation and/or functional termination of the living cationic polymerization of isobutylvinylether (IBVE) in the presence of HI/ZnI_2 initiating systems. To selectively introduce an anthracene group at the chain head, (9-anthryl) 3-propylvinylether (APVE) was first treated with HI, then the IBVE monomer was introduced and the polymerisation was triggered by adding ZnI_2. Termination of the polymerization was performed either by adding MeOH/NH_3 ($P_{0.3}$, $\bar{M}_n$ = 2000, $\bar{M}_w/\bar{M}_n$ = 1.17) or (9-anthryl) 3-propanol (APOH)/NH_3 to introduce an anthracene group at the chain end ($P_{0.6}$, $\bar{M}_n$ = 7000, $\bar{M}_w/\bar{M}_n$ = 1.5). The number of anthracenes fixed at each end is significantly lower than expected (0.3 and 0.6 for $P_{0.3}$ and $P_{0.6}$, respectively) likely due to remaining impurities in APVE. However, the photophysical properties of the polymers were investigated. These polymers were anticipated to favour interchain photoreactions rather than intrachain photoprocesses.



P_A

Irradiation (366 nm) of neat polymers or polymers in THF solutions induces a large change of the U.V. absorption spectrum: the ^1L_a structured band (300-400 nm) characteristic of anthracenes smoothly disappears and the NMR spectra indicate the formation of the classical 9,10-9',10' photodimer. Photoreversion process takes place upon irradiation at shorter wavelengths (280 nm). GPC chromatograms (THF) of the polymer before and after irradiation (366 and 280 nm) underline the dimerization process (signal corresponding to 2x$\bar{M}_w$) and the photoreversion capacity of the material (Figure 3).

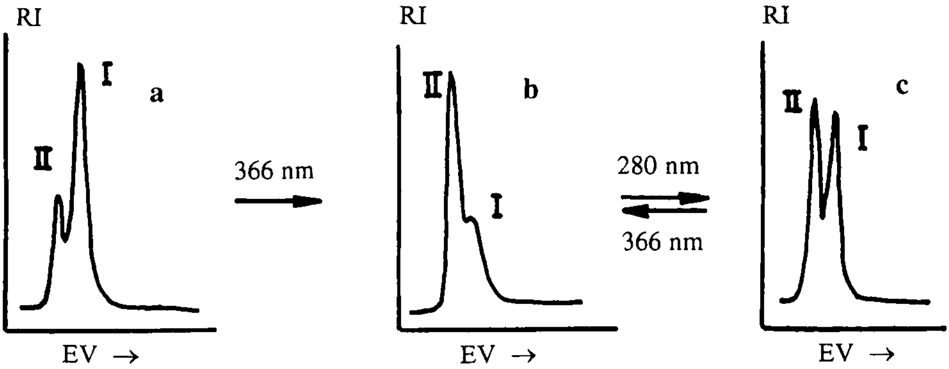


FIGURE 3 Variation of the GPC chromatograms of $P_{0.3}$ during the photoconversions a) before irradiation, b) and c) after subsequent irradiations at 366 and 280 nm (eluent THF, I: peak molecular weight = 2000(M_p), II: peak molecular weight = 4000(M_p), calibration Pstyrene, RI: refractive index, EV: elution volume).

As expected from the kinetic scheme generally accepted for anthracene derivatives photodimerization through the singlet state[2,3], plots of the reciprocal values of reaction quantum yields(1/ϕ_R) versus the reciprocal concentration of anthracene-bearing polymer (1/[P_A]) in THF give a straight line. From the intercept and the slope, the photodimerization quantum yield at infinite concentration ($\phi_R^{\infty}=k_R/k_2$) and the bimolecular interchain rate constants k_2 and k_R can be deduced (with $\tau \approx 5.5$-6 ns for all the P_A and (9-anthryl) 3-propylethylether (APEE) at R.T); the data are reported in Table III.

${}^1P_A \rightarrow P_A \quad (k_1)$ $P_A + {}^1P_A \rightarrow P_A{=}P_A \quad (k_R)$ $P_A + {}^1P_A \rightarrow P_A + P_A \; (k_{cq})$ $1/\phi_R = k_2/k_R + k_1/k_R[P_A]$	$k_1 = k_F + k_{nr}$ (monomolecular processes) and $k_1 = 1/\tau$. k_F and k_{nr} are rate constants for fluorescence and nonradiative pathways, respectively. $k_2 = k_R + k_{cq}$ (bimolecular processes).

The photodimerization process is not very efficient (Table III) as underlined by ϕ_R^{∞} and k_R values in spite of non negligible bichromophoric interactions in polymers following light absorption ($k_2 \approx k_{cq} \approx 6\text{x}10^9 M^{-1}s^{-1}$). k_R and ϕ_R^{∞} are lower than the relevant data recorded for the reference monomeric compound (APEE) in fluid solution or diluted in a polymer matrix (polyisobutylvinylether PIVBE, $\overline{M}_n$:13,500) and this is probably in relation to the low mobility of the polymer chain.

TABLE III Photodimerization quantum yields at infinite concentration (ϕ_R^{∞}) and bimolecular rate constants for polymers P_A and APEE in THF, at R.T.(λ_{irra}366 nm) $\phi_{diss.}$: photodissociation quantum yield (λ_{irra} 280 nm).

	APEE in THF	APEE in PIBVE	$P_{0.3}$	$P_{0.6}$
$\phi_R^{\infty} = k_R/k_2$	0.10	0.030	0.009	0.016
$k_2(10^9)M^{-1}s^{-1}$	10.3	4.6	6.3	5.9
$k_R(10^9)M^{-1}s^{-1}$	1.0	0.14	0.057	0.094
ϕ_{diss}	0.33	-	0.31	0.32

It is noticeable that the photodissociation efficiency (ϕ_{diss}) was found to be independent of the medium.

CONCLUSION

Bisanthracenes incorporating the three member link "O-CH_2-O" which display an efficient photocycloisomerization at 366 nm were studied for their photochromic properties in fluid solution and polymer matrices. The photoproducts dissociate into the open form by irradiation at shorter wavelength (270 nm) or by heating.

New photoactive polymers bearing anthracene pendant groups were designed and synthesized in order to get light modulated molecular weight ($\overline{M}_W$) materials. The interchain dimerization at 366 nm leads to a twofold increase of $\overline{M}_W$ and the reversible process (photodissociation) effected at 280 nm, partially restores the initial molecular weight distribution.

ACKNOWLEDGEMENTS

The technical assistance of C. Xavier, O. Palanque, M. Gotta and H.L. Tran Thanh are gratefully acknowledged. We also thank "La Région Aquitaine" and the Ministry of Education for financial support.

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