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Photochromic Behaviour of Some Phenoxyanthraquinone Dyes in Solution and on Polyester Substrate

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ABSTRACT

The photochromic behaviour of four phenoxyanthraquinone dyes in solution and on polyester fabric has been investigated. It was found that the photochromism of the dyes resulted from 300 nm wavelength irradiation and in a nonpolar solvent. A photoisomerization pathway is involved. The sensitivity of phenoxyanthraquinone dyes to undergo photoisomerization to the respective ana-quinones depends on the irradiation wavelength and on the solvent polarity. In addition, from colour measurement data, it was found that the dyed polyester fabric exhibited similiar photochromic behaviour to that of the phenoxyanthraquinone dyes in non-polar solvents. © 1997 Elsevier Science Ltd

Keywords: photochromic, phenoxyanthraquinone dye, solvent, polyester fabric, colour assessment, photoisomerization.

INTRODUCTION

Photochromism is the phenomenon whereby the absorption spectrum of a molecule or crystal changes reversibly when the sample is irradiated by light of certain wavelengths [1, 2]. A colourless compound A, for instance, changes its molecular structure to a quasi-stable coloured structure B when irradiated by ultraviolet (UV) light; B can be returned to the colourless structure A by exposure to visible light or heating. A large number of organic and inorganic

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materials which exhibit photochromism have been known for many years, and such materials have found application in many areas [2–4] including dosimeter materials, light control filters, recording films in printing processes, decorative paints, architectural glass, automative and aerospace, and in textiles and cosmetics. In recent years, the synthesis of new photochromic compounds and the elucidation of their structures and photochemical properties have been the subject of active study. Certain spiropyran compounds are well known materials which are suitable for use as optical recording materials [5–7]. Many other photochromic compounds such as fulgide, dihydropyrene, thioindigo, aziridine, oxazine, azobenzene, salicylideneaniline, xanthene and polynuclear aromatic derivatives have been studied [8–10]. For application of these materials, the appropriate choice of a compound with the desired coloration wavelength, determined by the application, is important. In spite of extensive scientific investigations on organic photochromic compounds, very few synthetic methods and technical applications concerning photochromic compounds of anthraquinone have been reported. In this paper, a study of the effects of irradiation wavelengths and polarity of solvents on these dyes are described. In addition, dyeing polyester fabrics with the dyes to observe their photochromic behaviour were also examined.

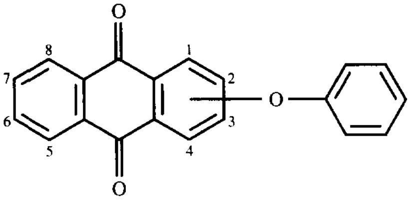
EXPERIMENT

Phenoxyanthraquinone dyes

Four photochromic dyes were synthesized in our laboratory and their structures were confirmed by the following apparatus. IR spectra (KBr) were recording on a JASCO Hc-2 FT-IF/IR-3. The ^{1}H NMR spectra were determined with a JUM-FX-100 (JEOL) FT-NMR spectrometer using TMS as internal standard. The mass spectra were determined on a Finnigan TSQ-700 mass spectrometer. Absorption spectra were recorded on a Milton Roy UV-1201 recording spectrophotometer. The structures of the dyes used in this study are shown in Fig. 1.

Determiuation of dye solution photochromism

We studied the ability of all the synthesized mono- and diphenoxyanthraquinones dissolved in various solvents to undergo reversible photoisomerization under the influence of UV and visible light. Solutions of dye in polar solvents (methanol and dimethylformamide) and in nonpolar solvents (benzene and carbon tetrachloride), solutions of the dyes (5.0×10^{-5} mol/l) were exposured at 35 ± 1°C using a Rayonet photoreactor equipped with a



Dye No.	Position of R
I	1
II	1 & 4
III	1 & 5
IV	1 & 8

Fig. 1. Structure of phenoxyanthraquinone dyes.

series of eight lamps with maximum emission at 254 and 300 nm, respectively. The kinetics of the colour change of the dyes were determined by measuring the maximum absorbance of the solution at suitable intervals. Then, fading the dye solutions by exposure to visible light (light of 13 W), and measuring the maximum absorbance.

Dyeing procedures [11] and colour measurement [12, 13]

The polyester fabrics were dyed in a rapid laboratory dyeing apparatus at a liquor ratio of 1:30 with 1.0% dye (calculated on the weight of the fabric). The pH was set to 4–5 with acetic acid. The dyeing method is shown in Fig. 2.

The CIE coordinates (L^*ab, a^*, b^*, C^*ab and H^*ab) and ΔE^* of the dyed fabrics before and after irradiation and fade by visible light exposure were determined on an applied computer system (model CS-5).

RESULTS AND DISSCUSSION

Structure of dyes and their photochromism

The data of characterization and spectral measurements for phenoxyanthraquinone dyes are shown in Table 1.

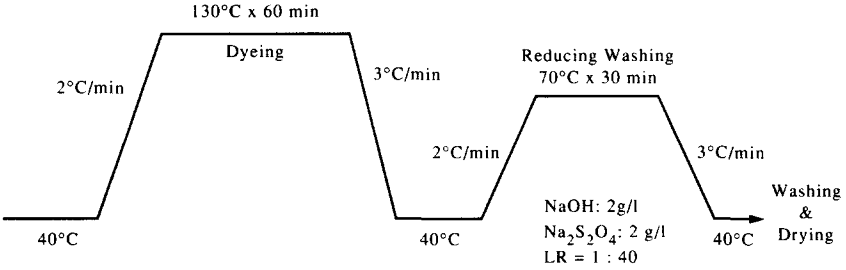


Fig. 2. Dying method used for phenoxyanthraquinone dyes on polyester fabrics.

TABLE 1
Characterization Data for Dyes I–IV

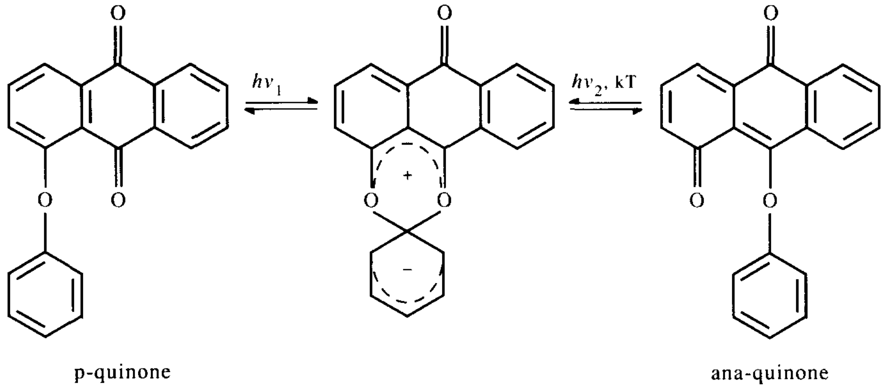
Dye no.	*Formula*	λ_{max} *(nm) in* C_6H_6		*Mass*	*IR* ν^{KBr} *(cm*$^{-1}$*)*	^{1}*H NMR (δ ppm)*
		Before irradiation	*After irradiation*			
I	$C_{20}H_{12}O_3$	363	470	300M$^+$	C=O: 1678 ArOAr: 1208–1253 Ar: 1490,1586	Aq: 8.28–7.66(7H) Ar: 7.40–7.05(5H)
II	$C_{26}H_{16}O_4$	378	472	392M$^+$	C=O: 1678 ArOAr: 1208–1246 Ar: 1490,1595	Aq: 8.18–7.72(6H) Ar: 7.39–7.03(10H)
III	$C_{26}H_{16}O_4$	368	474	392M$^+$	C=O: 1680 ArOAr: 1210–1256 Ar: 1506,1585	Ar: 8.06–7.63(6H) Ar: 7.41–7.06(10H)
IV	$C_{26}H_{16}O_4$	369	487	392M$^+$	C=O: 1680 ArOAr: 1207–1258 Ar: 1490,1586	Aq: 8.05–7.58(6H) Ar: 7.36–7.03(10H)

Aq: Anthraquinone, Ar: aromatics.

From Table 1, we found that all of the dyes solutions (in benzene) before irradiation were pale yellow and on irradiating at 300 nm, the pale yellow solutions became a deep yellow colour. Their colour change was slightly influenced by the position and the number of the phenoxy group of the dyes. The photochromic process of phenoxyanthraquinone dyes corresponds to the photoarylotropic transistion in the tautomeric system with a reversible structure rearrangement *p*-quinone$\rightleftharpoons$ana-quinone. Scheme 1

Spectral measurements confirmed the formation of the ana-quinoid structure. Figure 3 gives the IR spectrum of solution in CCl_4 of dye II before and after irradiation. In this case the intensity of the C=O stretching vibration band at 1678 cm^{-1} drops and a new band appears in a lower frequency region, 1635 cm^{-1}. As in the case of electronic absorption spectrum, changes in the infrared spectra are reversible.

Some support for this result comes from the works of Gerasimenko and Barachevskii [14, 15], who reported a comparison between the IR spectra of solutions of 1-phenoxyanthraquinone and of 6-phenoxy-5,12-naphthacenequinone in CCl_4 before and after irradiation. In both cases the intensity of the C=O stretching vibrations at 1685 and 1682 cm^{-1}, respectively, decreases



Scheme 1

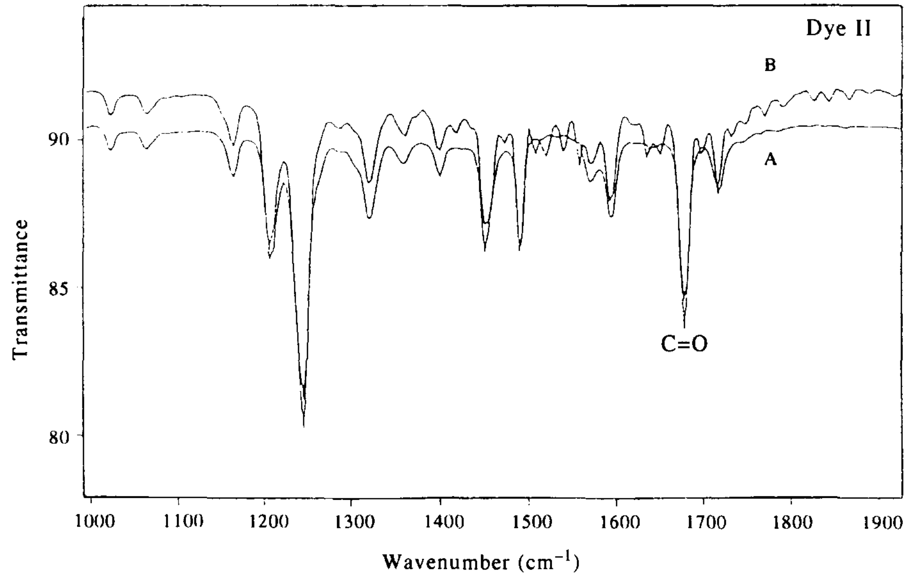


Fig. 3. The infrared spectrum of dye II in CCl_4. A, before irradiation; B, after irradiation by 300 nm wavelength.

and a new bond appears at lower frequency, namely 1635 and 1660 cm^{-1}, respectively.

Effect of UV wavelengths on photochromism

We examined the UV wavelength effects on the photochromism of the dyes in CCl_4 irradiated by 254 and 300 nm, respectively. For example, as observed for dye I, significant differences are apparent, there being a greater bathochromic effect and higher absorbance value resulting from irradiation at 300 nm than at 254 nm(see Fig. 4). We have concluded that the 300 nm

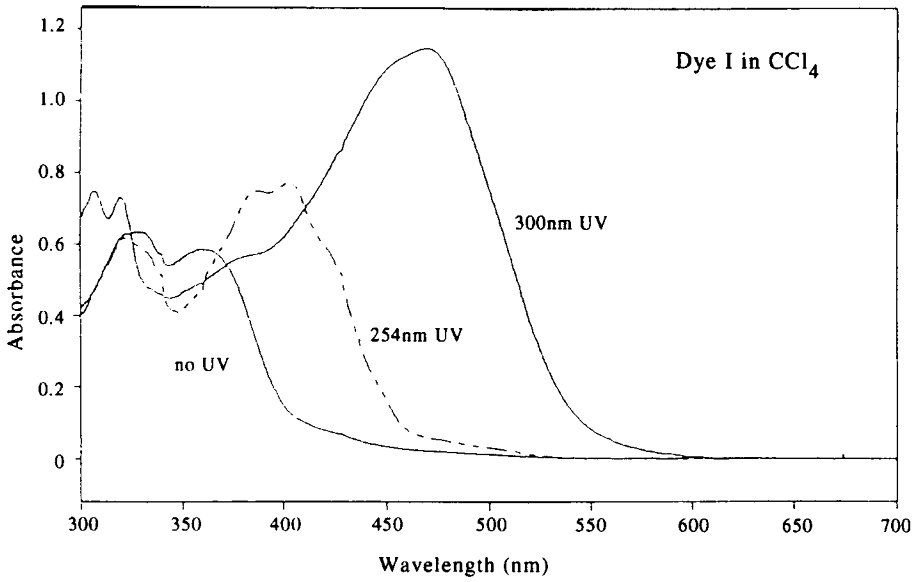


Fig. 4. Absorption spectrum of dye I in CCl_4 following UV lamp exposure for 4 minutes.

wavelength increases the photosensitivity of these dyes in CCl_4, which is the optimum energy for exciting the dye molecule from the ground state to the excited state. From Fig. 5, the rate of development of the deep yellow colour increases in the order 300 nm > 254 nm.

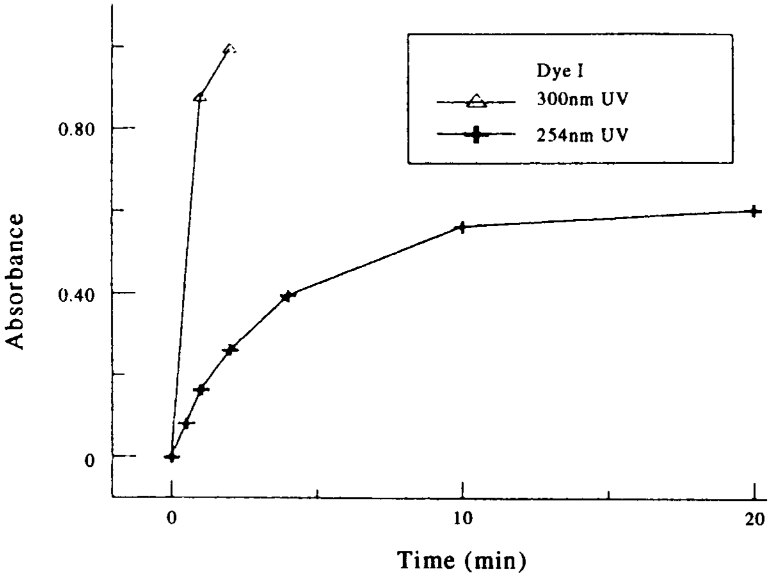


Fig. 5. Rate curves for coloration of dye I in benzene (5.0×10^{-5} mol/l).

Effect of solvent polarity on photochromism

Solvent effects are important in determing the photochromism of dye molecules in solution. Various dye molecules in solvents of different polarity have been measured by electron spectra. Table 2 gives the λ_{max} and absorbance values for the dyes (I–IV) in the solvents before and after 300 nm ultraviolet radiation.

We found that the λ_{max} values of the dyes in solvents showed slight change, except dye I in DMF, before irradiation, but there was significant change in the λ_{max} values after irradiation, and photochromism occurs in non-polar solvents. For instance, as can be seen from Figs 6 and 7, the

TABLE 2

The λ_{max} and Absorbance Values for Dyes I–IV in Different Solvents Before and After 300 nm Irradiation

	λ_{max} *(nm) & abs.*							
	MeOH irradiation		*DMF irradiation*		*C_6H_6 irradiation*		*CCl_4 irradiation*	
Dye no.	*Before*	*After*	*Before*	*After*	*Before*	*After*	*Before*	*After*
I	360 (0.52)	330 (0.67)	330 (0.68)	378 (0.54)	363 (0.54)	470 (0.99)	361 (0.58)	464 (1.14)
II	380 (0.49)	354 (0.41)	378 (0.55)	427 (0.60)	378 (0.50)	472 (1.20)	378 (0.53)	472 (0.99)
III	370 (0.81)	334 (0.26)	366 (0.71)	399 (0.69)	368 (0.75)	474 (1.28)	366 (0.86)	469 (1.10)
IV	370 (0.77)	330 (0.54)	366 (0.73)	398 (0.80)	369 (0.72)	487 (1.04)	367 (0.84)	484 (0.92)

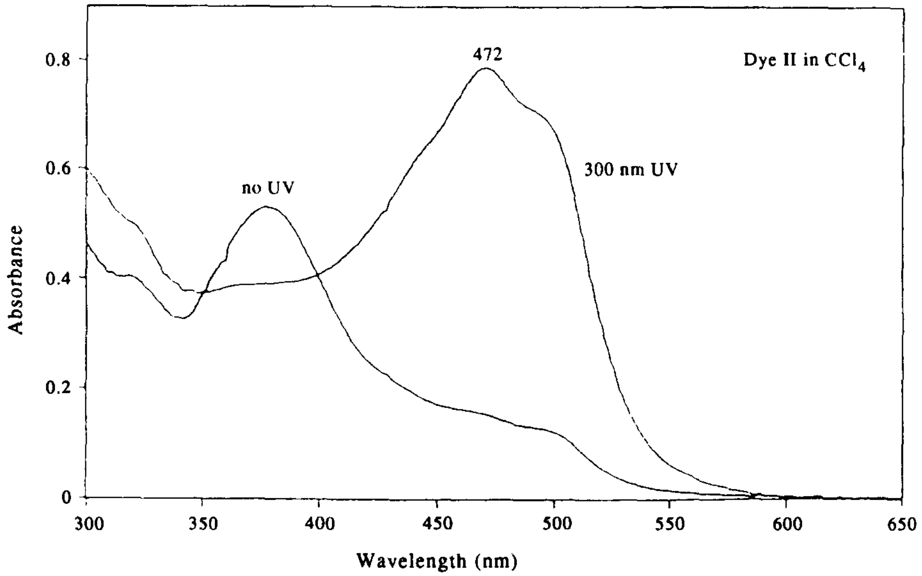


Fig. 6. Absorption spectrum of dye II in CCl_4 (5.0×10^{-5} mol/l) following 300 nm exposures for 4 minutes.

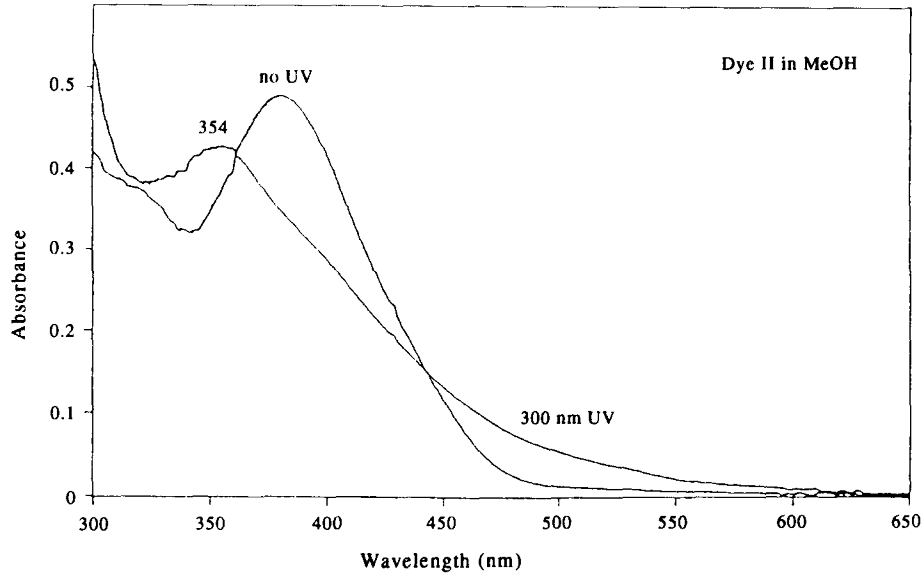


Fig. 7. Absorption spectrum of dye II in MeOH (5.0×10^{-5} mol/l) following 300 nm exposures for 4 minutes.

bathchromic effect was pronounced for dye II in the nonpolar solvent, the absorption shifting to 472 nm (Fig. 6), whereas in the polar solvent a hypsochromic shift occurs, the absorption being shifted to 354 nm (Fig. 7). This suggests that intermolecular hydrogen bonding occurs between dye II and methanol and, therefore, photochromism of dye II is limited.

Figure 8 shows the coloration rate curves of dye III in various polarity solvents, the rate of development of the deep yellow colour increases in the order: $C_6H_6 > CCl_4 >$ DMF > MeOH. These results appear to indicate that solvent polarity increases the photochromism of phenoxyanthraquinone dyes in solution.

Colour assessment

Dyed polyester fabrics underwent a significant colour change after 4 min of exposure. Table 3 shows the colorimetric data for dyed polyester fabrics before and after radiation and fade by visible light exposure. The L^*ab (lightness) and H^*ab (hue angle) of the fabrics show a significant decrease, from a pale yellow colour to an orange-reddish colour with 300 nm UV irradiation, and the colorimetric data of the faded fabrics are similar to those of the original samples. As regards the ΔE^*, the values for the dyed polyester fabrics before and after radiation, there is a very large difference in the 26.5–41.84 region, whereas comparing faded fabric with original dyed fabric, there

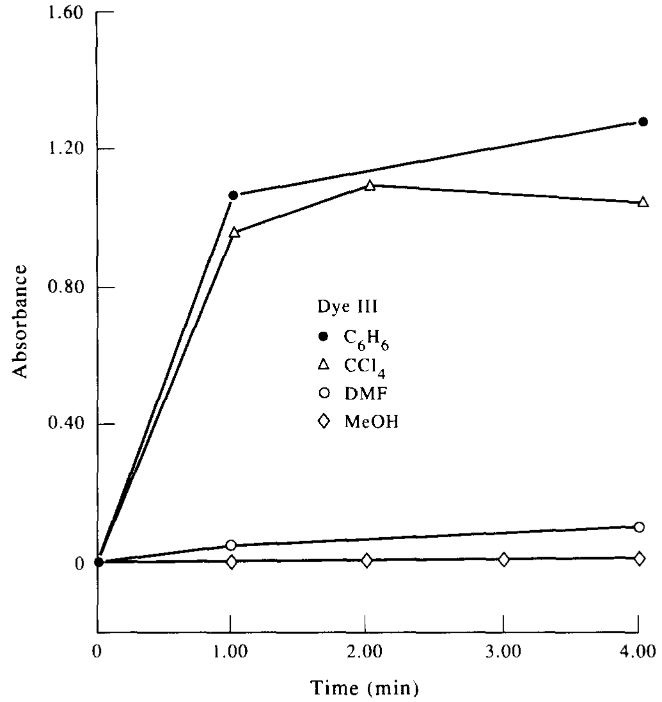


Fig. 8. Rate curves for coloration of dye III in solvents (5.0×10^{-5} mol/l) following 300 nm exposures.

TABLE 3

Colorimetric Data and ΔE^* for Dyed Polyester Fabrics Before and After 300 nm Irradiation and Fade by Visible Light Exposure

Dye no.		*Light* L*ab	a*	b*	*Chroma* C*ab	*Hue angle* H*ab	*Colour difference* ΔE*
I	A	86.27	−6.47	42.17	42.67	98.72	—
	B	65.70	27.39	28.13	39.26	45.77	41.84
	C	86.32	−6.87	41.23	41.80	99.47	1.02
II	A	77.75	14.32	63.73	65.32	77.33	—
	B	67.11	38.41	60.64	71.78	57.65	26.5
	C	77.65	15.03	63.27	65.03	76.63	0.85
III	A	84.49	−1.46	38.71	38.74	92.16	—
	B	67.24	30.84	45.68	55.11	55.97	37.28
	C	84.84	−2.61	38.22	38.31	93.91	1.29
IV	A	84.69	0.38	41.86	41.86	89.48	—
	B	71.67	26.45	53.23	59.43	63.58	31.28
	C	84.29	0.84	41.28	41.29	88.83	0.84

A: Before irradiation; B: after irradiation by 300 nm UV.
C: Fade by visible light exposure.
ΔE^*: relative to dyed polyester fabric before irradiation. $\Delta E^* = (\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2$

is only a very slight ΔE^*, in the 0.84–1.29 region. It is thus apparent that the colour development and fade of the dyes on polyester fabric are very significant.

CONCLUSIONS

From this study, we conclude that photochromism of phenoxyanthraquinone dyes in solvent is affected mainly by the UV wavelength to exposure and the polarity of solvent. The faster rate of and more significant colour development of the dyes results from 300 nm wavelength irradiation and in the nonpolar solvent, compared to 254 nm irradiation and in the polar solvent. The dyed polyester fabric exhibits similar photochromic behaviour to that of the phenoxyanthraquinone dyes in solvents.

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