

Effect of Poly(Ethylene Terephthalate) Morphology on Thermal *cis-trans* Isomerization and Photofading of Some Azo Dyes: A Kinetic Study

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Synopsis

Three poly(ethylene terephthalate) films were prepared having the same crystallinity but different morphology. They were colored with azo dyes $\text{XC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2$ (where X is H, OCH_3 , CN, and COOC_2H_5). The kinetics of the thermal *cis-trans* isomerization of these dyes has been studied below the glass transition temperature in the range 25–56°C. The isomerization process was found to be the result of a multiplicity of first-order reactions. The kinetic parameters have been correlated with the order degree at molecular level of the polymer. Lightfastness of the dyes in the polymer matrices has been also investigated: it appeared to be in relation with the supermolecular structure of the film.

INTRODUCTION

In a previous work¹ we have carried out an investigation on the thermal *cis-trans* isomerization and photofading of some diethylaminoazobenzenes in poly(ethylene terephthalate) (PET) films below the glass transition temperature (T_g). The kinetics of the reaction was characterized by the occurrence of a multiplicity of simultaneous first-order processes, as already observed by other authors in different polymeric matrices colored with other azocompounds.²⁻⁴ This fact was interpreted as deriving from the unequal microenvironment and different free volume availability of the disperse dyes in the amorphous regions of the glassy polymeric matrix.

The dye photofading was found to be strongly dependent on the crystallization conditions of PET, the lightfastness being a decreasing function of the film "porosity."⁵

In this work we have carried out an analogous investigation on PET films characterized by different order degrees in the amorphous regions but having equal crystallinity. The aim of this study was to attempt a correlation between the behavior of the dyes in the film and the morphology of the polymer.

EXPERIMENTAL

Materials

All the azobenzene derivatives were kindly supplied by ACNA S.p.A. Three different kinds of poly(ethylene terephthalate) films (viscosity average molecular weight, $\bar{M}_v = 10,500$), extruded at 280°C (thickness, 0.04 mm) and quenched in a cold air stream, were used: (i) isotropic, unoriented amorphous film (PET/u); (ii) longitudinally stretched film, with a ratio of 2.9 at 92°C (PET/m); (iii) two-way stretched film, longitudinally stretched as in (ii) and transversely stretched at 100°C with a ratio of 2.9 (PET/b).

In order to obtain films at equal degree of crystallinity, the thermal treatment was performed at constant length for 3 min at 100°C and 3 min at 150°C.

Specific volume (V_s) measurements were carried out at 20°C by flotation in an aqueous potassium iodide solution. The crystallinity index (β) was calculated assuming specific volumes V_s (amorphous) = 0.750 cm³ g⁻¹ and V_s (crystalline) = 0.687 cm³ g⁻¹, according to R. de Daubeny et al.⁶ The morphological characteristics of the samples are reported in Table I.

Infrared (IR) characterization of the films was performed on a Perkin-Elmer Mod. 983 IR spectrophotometer. For the evaluation of the "gauche"/"trans" ratio of the polymer, two bands at 898 cm⁻¹ and 973 cm⁻¹ were used. The *trans* index reported in Table I was obtained as the ratio of the heights of the aforementioned peaks.

As to the measurement of orientation of the polymer, Herman's function was calculated according to Samuels:⁷

$$f = \frac{3 \cos^2 \theta - 1}{2} = \frac{(D - 1)(D_o + 2)}{(D + 2)(D_o - 1)}$$

where θ is the average orientation angle between molecular axis and longitudinal stretching direction. The dichroic ratio D was determined as $D = A_{\parallel}/A_{\perp}$ with A_{\parallel} and A_{\perp} indicating the areas of the absorbance peak at 875 cm⁻¹ for the parallel and perpendicular spectrum, respectively. The dichroic ratio for a perfect orientation (D_o), that depends on the angle between the transition moment and the molecular axis, was obtained from the relation $D_o = 2 \cot^2 \alpha$ where α is the transition moment angle. For the calculation of f , the value $\alpha = 72.0^\circ$ was used.^{8,9} The 875 cm⁻¹ band was chosen because it is independent of conformational states.

TABLE I
Morphological Characteristics of the PET Films Considered^a

Sample	Specific volume $V_s/\text{cm}^3 \cdot \text{g}^{-1}$	Crystallinity index β	Molecular orientation in the direction of longitudinal stretching	<i>trans</i> Conformation index	Birefringence Δn
PET/u	0.723	0.43	0	0.86	0.005
PET/m	0.723-0.721	0.43-0.46	4×10^{-1}	2.02	0.140
PET/b	0.721	0.46	4×10^{-2}	2.88	0.009

^a For definitions and full details, see text.

All the infrared absorbance values were normalized by using the 795 cm^{-1} band in order to take into account the film thickness. Birefringence was obtained by optical means (Berek compensator).

Film dyeing was carried out with 0.8–1.2% dyestuff, calculated on the weight of the film. The process was started at 60° , raising the temperature to 125°C in 45 min and keeping this temperature for 1 h. Film dye concentration was chosen to obtain an absorbance near 1 for isomerization measurements. A proportionally lower amount of dyestuff was used in the case of films for lightfastness determinations (absorbance < 0.3 , mostly 0.1) in order to avoid a "filter" or "layer" effect.¹⁰

Measurements

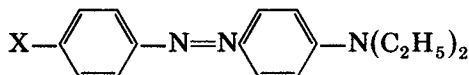
The polymer films dyed as described under Materials, were sandwiched between two quartz plates and exposed for 10 min in a thermostated compartment to the light of a 100-W tungsten lamp, a time long enough to reach a photostationary state. After irradiation the film was quickly introduced in the cell compartment of a Cary 118 spectrophotometer thermostated at the same temperature of the irradiation. The thermal return was monitored as the change in absorbance at a wavelength corresponding to the absorption maximum of the *trans* isomer.

Some kinetic measurements were carried out also in dibutylphthalate; solutions of the dye ranging from 1×10^{-5} to $4 \times 10^{-5}M$ were prepared by diluting a $10^{-3}M$ stock solution, operating in the dark. Adventitious catalytic action by acidic impurities in the solvent was eliminated by adding a small amount of triethylamine (ca. 0.5% v/v).¹¹ Nondegassed solutions were always used.

Lightfastness was evaluated after Xenotest (Hanau model 450) continuous irradiation for ca. 200 h. The percentage of dye loss was determined from the decreasing absorbance values at the maximum wavelength of the *trans* isomer measured at room temperature on films maintained 10 days in the dark after irradiation.

RESULTS

Four derivatives (I)–(IV) were used:



(I) X = H (III) X = CN

(II) X = OCH₃ (IV) X = COOC₂H₅

These dyes were dispersed in the films PET/u, PET/m, and PET/b described in the experimental section.

The kinetics of the thermal *cis-trans* isomerization of compounds (I)–(IV) in PET films could be resolved as the sum of two or three simultaneous first-order processes according to a procedure previously described.¹ The

TABLE II
 Thermal *cis-trans* Isomerization Rate Constants at 25°C^a and Activation Parameters for Dyes (I)-(IV) in PET Films of
 Different Morphological Structures at Constant Crystallinity Index

Dye	Film	Reaction 1			Reaction 2			Reaction 3		
		$10^4 \cdot k/s^{-1}$	$\Delta H^\ddagger/kcal \cdot mol^{-1}$	$\Delta S^\ddagger/e.u.$	$10^4 \cdot k/s^{-1}$	$\Delta H^\ddagger/kcal \cdot mol^{-1}$	$\Delta S^\ddagger/e.u.$	$10^4 \cdot k/s^{-1}$	$\Delta H^\ddagger/kcal \cdot mol^{-1}$	$\Delta S^\ddagger/e.u.$
(I)	PET/u	0.58	16.2 ± 0.2	-23.6 ± 0.6	5.3	14.0 ± 1.3	-26.5 ± 4.3			
	PET/m ^b	0.39	17.6 ± 2.5	-19.8 ± 8.2	5.4	11.6 ± 1.6	-34.4 ± 5.1			
	PET/b	0.35	12.4 ± 0.2	-37.4 ± 0.5	2.1	13.9 ± 1.3	-28.7 ± 4.3			
(II)	PET/u	0.54	18.4 ± 1.6	-16.2 ± 5.2	6.5	14.5 ± 1.2	-26.4 ± 3.8			
	PET/m ^b	0.28	14.5 ± 2.1	-31.3 ± 6.8	2.7	15.9 ± 2.9	-21.4 ± 6.3			
	PET/b	0.47	9.4 ± 0.5	-49.9 ± 1.5	3.9	12.0 ± 1.1	-33.7 ± 3.7			
(III)	PET/u	0.67	12.2 ± 0.6	-36.6 ± 1.2	8.5	15.0 ± 1.0	-22.3 ± 3.1	85	11.9 ± 2.0	-28.1 ± 6.9
	PET/m ^b	0.74	10.9 ± 2.0	-40.6 ± 6.6	10.0	13.8 ± 2.3	-25.7 ± 7.4	74	13.1 ± 1.6	-24.2 ± 5.0
	PET/b	0.31	13.5 ± 0.2	-33.9 ± 0.6	8.2	9.8 ± 0.2	-39.9 ± 0.8	56	10.5 ± 1.5	-33.7 ± 4.6
(IV)	PET/u ^c	0.55			6.4			64		
	PET/m ^c	0.18			4.1			55		
	PET/b	0.28	14.9 ± 1.0	-29.3 ± 3.3	4.5	12.1 ± 0.2	-33.5 ± 0.8	41	10.7 ± 1.6	-33.4 ± 5.0

^aCalculated according to Eyring equation.

^bFrom Ref. 1.

^cThe activation parameters were not calculated due to the limited range of temperature explored (25–34°C).

TABLE III
Average Weights of the Thermal Relaxation Processes of Dyes (I)–(IV)
in PET Films Observed in the Temperature Range ΔT and Extents
of the Absorbance Amplitudes Covered During the Overall Reaction

Dye	Film	\bar{r}_1^a	\bar{r}_2^a	\bar{r}_3^a	ΔT (°C)	$\Delta A/A_\infty$
(I)	PET/u	0.50	0.50		25–56	0.26–0.20
	PET/m	0.51	0.49		26–54	0.37–0.28
	PET/b	0.30	0.70		26–54	0.35–0.30
(II)	PET/u	0.31	0.69		25–56	0.15–0.10
	PET/m	0.22	0.78		25–53	0.21–0.15
	PET/b	0.23	0.77		26–55	0.27–0.16
(III)	PET/u	0.24	0.31	0.45	25–55	0.13–0.06
	PET/m	0.18	0.41	0.41	26–55	0.15–0.10
	PET/b	0.16	0.29	0.55	25–55	0.19–0.10
(IV)	PET/u	0.17	0.35	0.48	25–34	0.09–0.07
	PET/m	0.17	0.40	0.43	25–34	0.19–0.16
	PET/b	0.18	0.44	0.38	25–53	0.23–0.16

^aFor definition of \bar{r}_1 , \bar{r}_2 , \bar{r}_3 and $\Delta A/A_\infty$, see text.

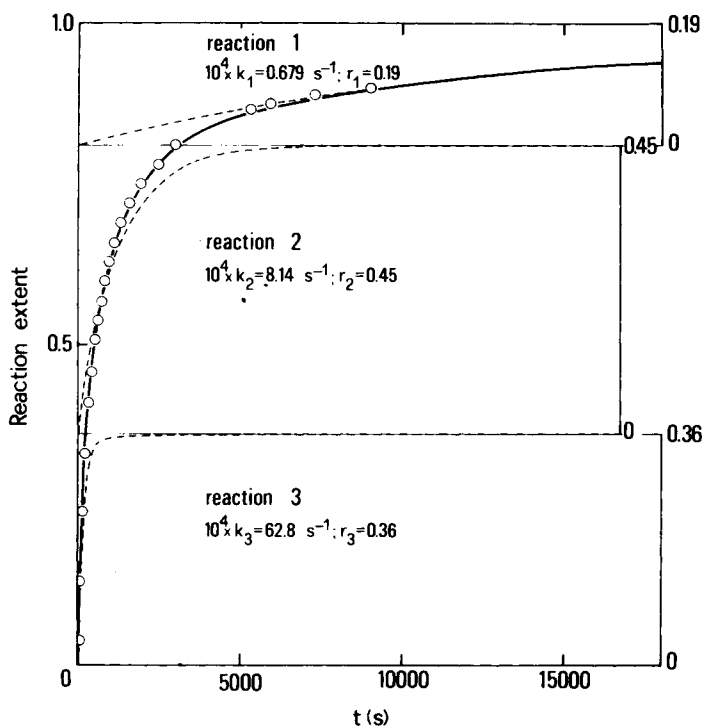


Fig. 1. Resolution of the thermal *cis-trans* isomerization of compound (IV) in PET/b at 34°C using three first-order reactions with weights r_i and constants k_i . (○), experimental values of the overall reaction extent; (---), calculated first-order reactions obtained by splitting the experimental time course.

TABLE IV
Relaxation Times at 25°C of the *cis-trans* Isomerization of Dyes (I)–(IV)
in PET Films ($\bar{\tau}$) and in Dibutylphthalate (τ)—Activation
Parameters ΔH^\ddagger and ΔS^\ddagger for the Reaction in Solution^a

Dye	Film	$10^{-4} \times \bar{\tau}/s$	Solvent	$10^{-4} \times \tau/s$	$\Delta H^\ddagger/kcal \cdot mol^{-1}$	$\Delta S^\ddagger/e.u.$
(I)	PET/u	0.96	Dibutylphthalate	1.0	23.8 ± 1.5	2.8 ± 4.9
	PET/m	1.40				
	PET/b	1.19				
(II)	PET/u	0.68	"	0.28	21.7 ± 1.4	-1.6 ± 4.5
	PET/m	1.08				
	PET/b	0.69				
(III)	PET/u	0.40	"	0.011	14.7 ± 0.6	-18.7 ± 1.9
	PET/m	0.29				
	PET/b	0.56				
(IV)	PET/u	0.37	"	0.098	15.9 ± 0.1	-18.8 ± 0.2
	PET/m	1.05				
	PET/b	0.75				

^aFor dyes (I)–(III) from Ref. 1.

first-order rate constants k_i at 25°C and the activation parameters of the single processes are reported for all dyes in Table II. The isomerization was studied below the glass transition temperature of the polymer ($T_g = 77^\circ C$) in the temperature range 25–56°C.

The average fractions of dye that isomerize according to the simultaneous first-order reactions 1, 2 and 3 (\bar{r}_1 , \bar{r}_2 , and \bar{r}_3) are collected in Table III. In the same table are reported the range values of the term $\Delta A/A_\infty$ that measures the absorbance amplitude covered during the kinetic measurements relative to

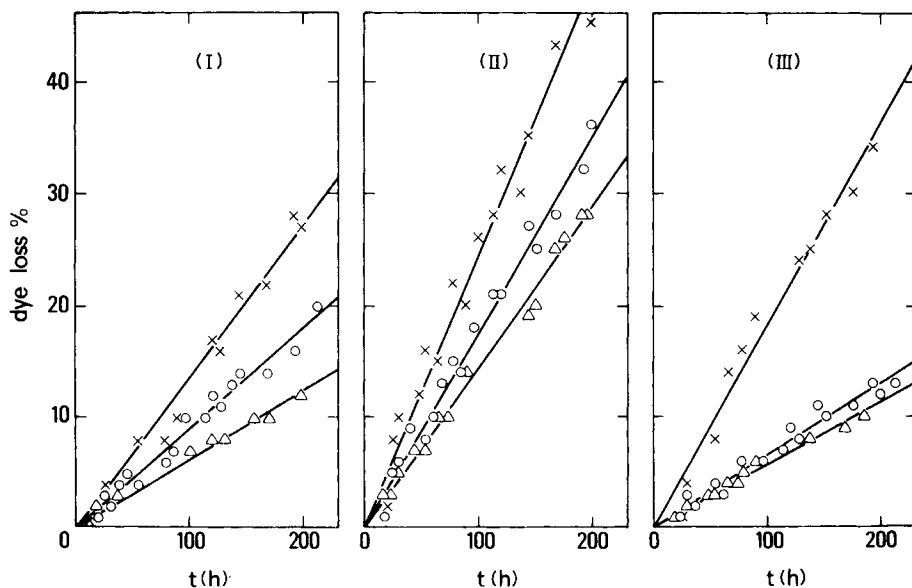


Fig. 2. Photofading time courses of compounds (I), (II), and (III) in poly(ethylene terephthalate). (x), PET/u; (o), PET/b; (Δ) PET/m.

TABLE V
Photofading Rate of Compounds (I)–(III) in PET Films Under Xenotest Irradiation

DYE	Photofading rate/dye loss percent $\cdot h^{-1}$		
	PET/u	PET/m	PET/b
(I)	0.136 \pm 0.004	0.063 \pm 0.002	0.090 \pm 0.002
(II)	0.243 \pm 0.006	0.144 \pm 0.002	0.175 \pm 0.003
(III)	0.182 \pm 0.005	0.057 \pm 0.001	0.065 \pm 0.002

the absorbance at infinity time in order to take into account the different nature and concentration of dyes. These values are related to the temperature range ΔT examined.

An example of the overall reaction extent *versus* time, together with its splitting into the three components, is shown in Figure 1. The reaction extent was evaluated as the ratio $(A_t - A_o)/(A_\infty - A_o)$.

The mean relaxation times $(\bar{\tau})^{12}$ evaluated at 25°C for the overall processes compared with the corresponding values obtained in dibutylphthalate are reported in Table IV. The activation parameters measured for the reaction in solution are also given.

The time courses of the dye loss under irradiation of dyes (I)–(III) are reported in Figure 2. The values of the fading rate obtained by a linear regression analysis, are collected in Table V.

DISCUSSION

Recently we examined some azo dyes in PET films equally oriented but having different crystallinity ($\beta = 0.43$ and $\beta = 0.60$, respectively).¹ It was found that polymer morphology strongly affects dye photofading but no significant influence was observed in the kinetics of the thermal *cis-trans* isomerization of the dyes. The latter fact was explained by considering that, for the same dye, kinetics depends only on the amorphous region of the polymer which was not different in the two cases examined. On the other hand, photofading, as well as tinctorial behavior, is affected by the crystallization conditions of the polymer: hence, a clear variation was expected, and experimentally found, in going from a "free volume" model to a structure corresponding to a "pore" model.

Three amorphous PET films with equal β values but morphologically different were prepared by modifying stretching conditions. In this way a more homogeneous comparison of the kinetic behavior and light stability could be carried out.

Film Morphology

In a quenched amorphous poly(ethylene terephthalate) the polymer chains are most likely coiled and/or folded and extremely tangled in a random structure. By using a stretch ratio approaching 3, a significant fraction of chain segments can be placed in the *trans* conformation and the microstructure of the polymer becomes more ordered than in the unoriented form. A subsequent transversal stretching of the longitudinally stretched film causes a

further rearrangement of the chain segments in the amorphous region of the polymer with a slight increase of the *trans* conformation content.

These situations occur in the three kinds of films PET/u, PET/m, and PET/b prepared for this study. These films show essentially the same crystallinity index β values (see Table I). The molecular orientation in the direction of longitudinal stretching is obviously zero for PET/u, very little for PET/b, and highest for PET/m. We also reported (Table I) two parameters that characterize in the best way the order degree of the polymer. The *trans* index is a good measure of the order at molecular level: such an order is increased by stretching that extends the molecular chain converting some *gauche* PET into *trans* PET in the amorphous region of the polymer. The highest value of *trans* index occurs, as expected, in the case of the twofold stretched PET/b film which appears to be consequently the more micro-ordered one. On the other hand, birefringence (Δn), as well as molecular orientation, gives a reliable estimate of the supermolecular order of the polymer film. The PET/m film exhibits the highest Δn value, followed by PET/b and PET/u. Reasonably high birefringence is associated to low "free volume" content that corresponds to compact packings of polymer chains in the film. This is the case of the stretched films even if biorientation partially disrupts tightness.

Kinetics

In every case, the time courses of the thermal *cis-trans* isomerization of dyes have evidenced that the overall process results from the sum of two, or more, simultaneous relaxation reactions. The corresponding first-order kinetic constants (k_i) are reported in Table II; they differ one from the other by about one order of magnitude, confirming our previous results.¹ This multiplicity of reactions reflects an unequal distribution of "tie molecules," "folds," and "cilia" in the amorphous region of the polymer films.

Taking into account, in the first instance, the two limiting cases represented by the polymer films PET/u and PET/b, the following observations can be made: (i) in all the cases, for each dye and for each relaxation process, the kinetic coefficients at 25°C in PET/u are higher than those in PET/b; (ii) the higher rate in the unoriented film is due to entropic more than to enthalpic factors. In fact, most ΔS^\ddagger values are higher for the unoriented film while most ΔH^\ddagger values are lower for the bioriented film. This situation corresponds to higher energy levels of the *cis*-reactants and lower entropies of the activated complexes in the case of the "micro-ordered" polymer PET/b, likely due to steric constraints.

The kinetic coefficients and activation parameters measured for the mono-oriented film are randomly distributed around the corresponding values of the other aforementioned polymers: probably, its behavior is intermediate but the numerical variations are of the same order of the experimental errors.

The relative weights of the single thermal relaxations were found to be little scattered in the temperature range here observed and were averaged (see Table III). Generally, the contribute \bar{r}_1 is the smallest one and \bar{r}_2 is less than \bar{r}_3 , indicating the prevailing weight of fast reactions. The term $\Delta A/A_\infty$ decreases when temperature increases as, at constant "dead time," the frac-

tion of process followed experimentally is smaller. The $\Delta A/A_\infty$ value is lower for PET/u than for PET/b in line with the lower *cis*-isomer content at the photostationary state due to the faster thermal return in the unoriented film: in this case the intermediate behavior of PET/m is evident.

In general, when the number of relaxation times exceeds two, the occurrence of a continuous relaxation spectrum cannot be unambiguously ruled out and the uncertainties in the determination of the single τ_i become more serious. Even if the resolution of the reaction courses in two or three relaxations was always satisfactory enough, a treatment in terms of mean relaxation time $\bar{\tau}$ ¹² was deemed useful. The mean relaxation time is defined as:

$$\bar{\tau} = \int_0^\infty (r_i e^{-k_i t}) dt$$

and corresponds to:

$$\bar{\tau} = \sum r_i / k_i$$

This term is an adequate kinetic measure of the overall process (see Table IV).

As far as the comparison of the different polymer films is concerned, $\bar{\tau}$ values in PET/u are always lower than in PET/b in line with the above observations made on the basis of k_i values. It is interesting to remark that a V-shaped Hammett plot is obtained by using $\bar{\tau}$ values. This behavior is typical for these dyes in the thermal *cis-trans* isomerization in liquid solution,^{11,13} and in particular in dibutylphthalate, as the inspection of Table IV reveals. On the other hand, the corresponding trend shown in the polymer by k_i values is not unequivocal at all. Likely, the integrated value averages out all the possible uncertainties related to the consecutive extrapolation method used in the splitting of the single rate coefficients.

This new approach to the analysis of the experimental data can be applied to our previous results¹ with analogous conclusions.

As it is shown in Table IV, the isomerization reaction proceeds faster in dibutylphthalate solution than in the polymer. Since specific interactions in the solvent and polymer here chosen are reasonably similar, as suggested by the comparison of values, the higher reaction rate is essentially due to entropic effect. The considerable weight of the entropic term in polymeric matrices may be easily explained taking into account the large molecular reorientation of neighboring chain segments necessary to create room for the isomerization process.

Photofading

As is well known, light stability of a dye in a polymeric matrix is affected by factors either external to the dye matrix system, such as the spectral distribution of the light source, the atmospheric composition, humidity and temperature, or internal to the system, including the chemical structure and physical state of the dye and polymer.

In this study a standard procedure in evaluating the degree of lightfastness was used to control external factors. Plotting dye loss vs. time of Xenotest

irradiation, the zero-order fading curves drawn in Figure 2 were obtained; the slopes of the corresponding straight lines are reported in Table V.

For each dye the lightfastness in PET/m was always the greatest followed by that in PET/b. This sequence parallels the trend observed for the birefringence and molecular orientation in the direction of longitudinal stretching (see Table I). Such behavior is clear evidence that light stability is essentially governed by the supermolecular order of the polymer matrix, which is not the case of the kinetics of the thermal *cis-trans* isomerization. It should be noted that the stretching process employed to give PET/m film leads to tighter packing of the polymer, and consequently to a smaller free volume content. Among the films observed herein, the unoriented isotropic one represents the situation with the largest free volume while, from this point of view, PET/b is an intermediate case.

The nature of the dye appears to be important, dye (II) being markedly less stable. Electronic factors are likely to play a role as this compound is characterized by the presence of a strong electron-donating group.

The origin at molecular level of photofading appears to be the result of many intertwined factors that, at the present stage of research, cannot be easily discriminated. Further work on this topic is in progress.

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