

Thermal Cis-Trans Isomerization and Photofading of Some Azo Dyes in Poly(ethylene Terephthalate) Matrices: A Kinetic Study

ERNESTINA DUBINI-PAGLIA,* PIER LUIGI BELTRAME, BRUNO MARCANDALLI, and PAOLO CARNITI, *Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, 20133 Milano, Italy*, ALBERTO SEVES and LOREDANA VICINI, *Stazione Sperimentale per la Cellulosa, Carta e Fibre Tessili Vegetali e Artificiali, 20133 Milano, Italy*

Synopsis

The thermal cis-trans isomerization of azo dyes $XC_6H_4N=NC_6H_4N(C_2H_5)_2$ (where X is H, OCH₃, CN, and NO₂) in poly(ethylene terephthalate) matrices, below the glass transition temperature, and in dibutylphthalate solutions has been studied kinetically in the temperature range 20–60°C. Kinetic behavior in the polymer is characterized by two or three simultaneous first-order processes with similar activation enthalpies. These processes reflect an unequal distribution of "tie-molecules," "folds," and "cilia" in the amorphous region of the polymer. Lightfastness of the dyes in poly(ethylene terephthalate) films has been investigated. Polymer morphology strongly affected the photofading, but no significant influence was observed in the kinetic experiments.

INTRODUCTION

The thermal cis-trans isomerization of azobenzene derivatives in a polymeric matrix below the glass transition temperature (T_g) proceeds in a way different from that is expected from its behavior in solution: the isomerization shows a deviation from linear first-order kinetics and can be described by two or more simultaneous first-order reactions.¹⁻⁵ The origin of this difference was attributed to the effects of restrictions in the mobility of the photochrome itself in the relatively rigid polymeric matrix and/or to the effects of different chain segmental mobilities of the polymer.^{4,5}

Moreover, in poly(ethylene terephthalate) (PET) films, a difference in dyeing and lightfastness was found depending on the different localization of the dye in going from a morphological structure of the polymer corresponding to a "free volume" model to a structure corresponding to a "pore" model.⁶

In this work we have carried out an investigation of the thermal cis-trans isomerization and on the fading of some azoderivatives in PET films below T_g since it seemed interesting to examine the behavior of a matrix of industrial interest dyed by a standard method.⁷ We have investigated the influence of the morphological structure of the film on the aforesaid re-

* To whom correspondence should be addressed.

actions and the effect of substituents present in the dye structure on the isomerization rates in a polymeric matrix.

The results of the kinetic study in PET films have been compared with the results obtained in dibutylphthalate, chosen as a suitable liquid model of PET films and for the expected significant substituent effect.^{8,9}

As models, 4'-acceptor or 4'-donor substituted 4-diethylaminoazobenzenes have been chosen.

EXPERIMENTAL

Materials

Spectrograde solvents were used throughout the experiments. The azobenzene derivatives were kindly supplied by ACNA S.p.A. Poly(ethylene terephthalate) films (viscosity average molecular weight, $M_v = 10,500$), extruded at 280°C (thickness, 0.04 mm), quenched in a cold air stream, were oriented by stretching with a ratio of 2.6 at 92°C. In order to obtain films at different degree of crystallinity, further thermal treatments were performed, at constant length, following these protocols: for PET/A, 3 min at 100°C and 3 min at 150°C; for PET/C, 3 min at 100°C, 3 min at 150°C, 3 min at 180°C, 3 min at 200°C, and 3 min at 210°C. Specific volume (V_s) measurements were carried out at 20°C by floatation in aqueous solutions of potassium iodide. The crystallinity index β was calculated assuming V_s (amorphous) = 0.750 cm³ g⁻¹ and V_s (crystalline) = 0.687 cm³ g⁻¹ according to de Daubeny et al.¹⁰ Wide-angle x-ray scattering was performed on a Siemens D-500 diffractometer equipped with a Ni-filtered CuK α radiation. The apparent crystal sizes in the directions perpendicular to the (100), (010), (105) crystal planes were calculated employing the Debye-Scherrer formula. The perpendicular direction to the (105) crystal plane was found by azimuthal scan according to the literature.¹¹ No correction for the lattice distortion was applied because the usually well detectable higher order reflections, necessary for this correction, were not observed.

The morphological characteristics of the two samples were as follows

	Specific volume (V_s , cm ³ g ⁻¹)	Crystallinity index β	Apparent crystal size		
			100	010	105
PET/A	0.7230	0.43	24	18	27
PET/C	0.7123	0.60	50	53	40

Dyeing experiments were carried out with 0.8–1.2% dyestuff calculated on the weight of the film. The process was started at 60°C, raising the temperature in 45 min to 125°C, and continuing at this temperature for 1 h. Film dye concentration was chosen to obtain an absorbance near 1 (about 0.01 mg of dye cm⁻² of polymer) for isomerization measurements. A proportionally lower amount of dyestuff was used in the case of films for lightfastness determination (absorbance < 0.3, mostly 0.1) in order to avoid a "filter" or "layer" effect.¹²

Measurements

Solutions of dyes ranging from 1×10^{-5} to 5×10^{-5} *M* were prepared by diluting a stock 10^{-3} *M* solution in dibutylphthalate. All operations were carried out in the dark. For slow cis-trans isomerization rates ($k < 10^{-2}$ s⁻¹) the solutions were exposed for 10 min in a thermostated glass cell to the light of a 100-W tungsten lamp, long enough to reach a photostationary state. After irradiation, the cell was quickly (<5 s) introduced in the thermostated cell compartment of a Cary 118 spectrophotometer, and the thermal return was monitored as the change in absorbance of the solution at a convenient wavelength. For the fast rates, a Nortech (Salisbury, England) model FPX1 flash photolysis apparatus was used. The transient signals were recorded by means of a Tektronix mode 5115 oscilloscope and a Polaroid camera.

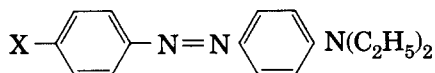
Non degased solutions were always used.

Adventitious catalytic action by traces of acidic impurities in the solvent was eliminated by adding a small amount of triethylamine (approximately 0.5% v/v) to the solution under investigation.¹³ A similar procedure was adopted for the films, but the samples were sandwiched between two quartz plates.

Lightfastness was evaluated after Xenotest (Hanau model 450) irradiation for a suitable time. The percentage of dye loss was determined from the absorbance values measured on films maintained 10 days in the dark after irradiation.

RESULTS

Four derivatives, (I)–(IV), were used:



(I) $X = \text{H}$

(III) $X = \text{CN}$

(II) $X = \text{OCH}_3$

(IV) $X = \text{NO}_2$

The first-order rate constants k at 25°C, and the activation parameters for the thermal cis-trans isomerization of the aforesaid compounds in dibutylphthalate are reported in Table I. The thermal cis-trans isomerization process in PET films was studied below the glass transition temperature of the polymer ($T_g = 77^\circ\text{C}$).

The kinetics could be resolved as the sum of two or three [in the case of (III)] simultaneous first-order reactions by extrapolating the linear portion of the curve $\ln(A_\infty - A_t)$ versus time t , where A_∞ and A_t are the absorbances at infinity time and time t , respectively, to zero time, by a least-squares fit with a correlation coefficient $r > 0.99$. In this way the way the rate constant of a first-order reaction was obtained. From the difference between the experimental curve and the extrapolated line, the linear time dependence of another first-order reaction was obtained ($r > 0.99$). This

TABLE I
Thermal Cis-Trans Isomerization Rate Constants at 25°C^a and Activation Parameters for
Azo Derivatives (I)–(IV) in Dibutylphthalate

Dye	k (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (u.e.)
(I)	1.0×10^{-4}	23.8 ± 1.5	2.8 ± 4.9
(II)	3.6×10^{-4}	21.7 ± 1.4	-1.6 ± 4.5
(III)	9.1×10^{-3}	14.7 ± 0.6	-18.7 ± 1.9
(IV)	4.5	11.0 ± 0.3	-18.8 ± 10.6

^a Calculated according to the Eyring equation.

procedure was extended to a third reaction in the case of (III). An example of this treatment of experimental data is reported in Figure 1. The results concerning the PET films are reported in Table II. The absorption maximum wavelengths for the azo compounds in dibutylphthalate and in PET films are listed in Table III. The fractions of dye that isomerize according to the simultaneous first-order reactions 1, 2, and 3, are in the ratios

$$r_1:r_2:r_3 = \frac{A_\infty - A_{0,1}}{A_\infty - A_0} \quad \text{to} \quad \frac{A_{0,1} - A_{0,2}}{A_\infty - A_0} \quad \text{to} \quad \frac{A_{0,2} - A_0}{A_\infty - A_0}$$

where the values $A_{0,i}$ were obtained by extrapolating the kinetic curve to zero time. The amplitude data referring to compound (III) are reported in Table IV. The fading curves are reported in Figure 2.

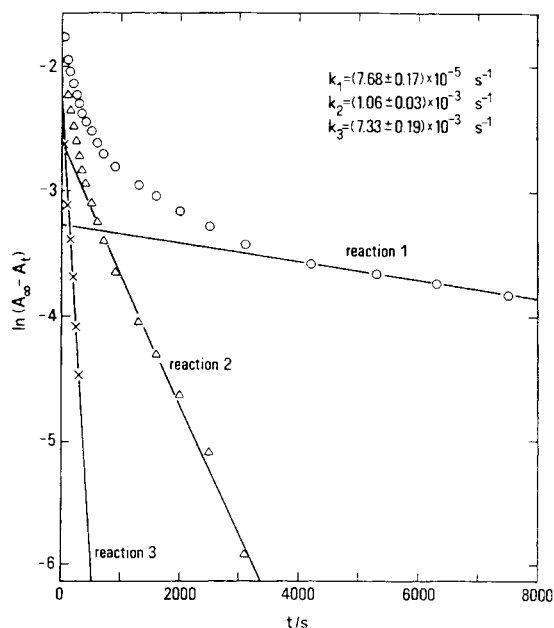


Fig. 1. Resolution of the thermal cis-trans isomerization of compound (III) in PET/C at 25°C using three first-order reactions; A_∞ , A_t , absorbances at 470 nm at infinity time and at time t . (O), experimental values; (Δ), X, values obtained according to the procedure described in the text.

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^b

Dye	Film	Reaction 1			Reaction 2			Reaction 3		
		$10^4 k$ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (u.e.)	$10^4 k$ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (u.e.)	$10^4 k$ (s ⁻¹)	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (u.e.)
(I)	PET/A	0.39	17.6 ± 2.5	-19.8 ± 8.2	5.4	11.6 ± 1.6	-34.4 ± 5.1			
	PET/C	0.51	12.4 ± 1.8	-36.5 ± 5.8	4.1	11.6 ± 1.6	-35.2 ± 5.2			
(II)	PET/A	0.28	14.5 ± 2.1	-31.3 ± 6.8	2.7	15.9 ± 2.9	-21.4 ± 6.3			
	PET/C	0.37	12.5 ± 1.1	-36.9 ± 3.6	3.0	14.2 ± 3.4	-27.0 ± 11.1			
(III)	PET/A	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/C	0.74	11.7 ± 0.5	-38.1 ± 1.5	11.3	11.0 ± 1.1	-34.9 ± 3.5	85	9.3 ± 1.9	-37.0 ± 6.0
(IV)	PET/C	9.7	—	—	205	—	—			

^a Calculated according to Eyring equation for (I), (II), and (III).

^b For definition of PET/A, PET/C, and reactions 1, 2, and 3, see text.

TABLE III
Solvatochromic Effect on the π - π^* Band for Azo Compounds (I)-(IV) in Dibutylphthalate and PET Films

Dye	E_{\max} (kcal mol ⁻¹) (dibutylphthalate)	E_{\max} (kcal mol ⁻¹) (PET)
(I)	68.4	67.4
(II)	68.9	68.1
(III)	61.6	60.8
(IV)	57.9	56.8

DISCUSSION

Kinetics

In all PET films and for all dyes, the thermal cis-trans isomerization reaction under T_g does not follow a simple first-order rate law as in solution, but it is well described as the sum of two or more relaxation processes characterized by the k_i values of Table II. These kinetic constants differ one from the other by about one order of magnitude, the highest value of the ratio k_2/k_1 being 21 for compound (IV).

In all the cases studied here, substitution in 4' position leads to a small but significant acceleration in going from electron donor to electron acceptor groups. This is a marked difference with respect to the behavior in solution, where as is well known^{13,14} and confirmed by our data in dibutylphthalate, these molecules show a characteristic V-shaped Hammett plot with a large acceleration for electron-withdrawing substituents.

A pronounced bathochromic shift of the charge-transfer absorption bands of compounds (I)-(IV) could be observed in going from dibutylphthalate solution to polymer films (see Table III). As suggested in a previous¹⁵ paper dealing with the solvent effect on the visible absorption spectra of some 4-diethylaminoazobenzenes, this may correspond to an enhanced polarity of the polymeric environment in comparison with dibutylphthalate. Even if cis-trans isomerization is expected to be strongly accelerated by increasing solvent polarity,¹³ the rate constants measured in solution (see Table I) have values comparable to the highest rate constants in PET films. Thus,

TABLE IV
Relative Amplitudes of the Observable Thermal Relaxation Processes of Dye (III) in PET Films at Various Temperatures^a

T (°C)	PET/C				PET/A			
	r_1 (%)	r_2 (%)	r_3 (%)	$\frac{A_\infty - A_0}{A_\infty}$	r_1 (%)	r_2 (%)	r_3 (%)	$\frac{A_\infty - A_0}{A_\infty}$
25	17.2	34.9	47.9	0.146	15.9	38.0	46.1	0.146
36	16.1	40.5	43.4	0.133	20.1	40.8	39.1	0.129
47	18.7	36.6	44.7	0.086	20.8	45.2	34.0	0.103
55	18.3	37.5	44.2	0.062				

^a For definition of PET/A, PET/C, r_1 , r_2 , and r_3 , see text.

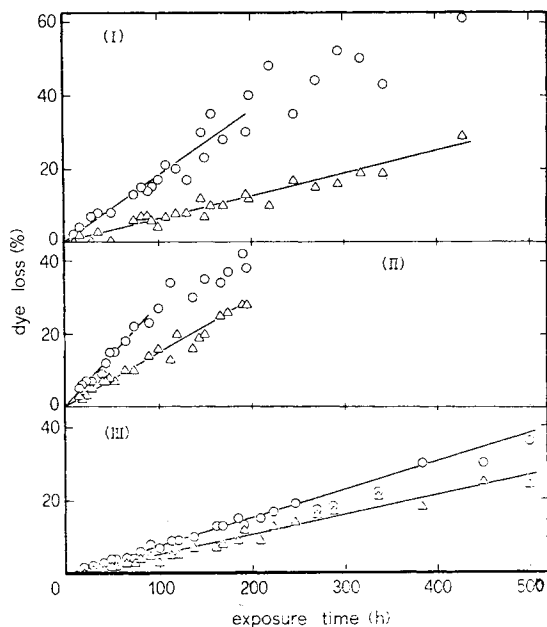


Fig. 2. Photofading time courses of compounds (I), (II), and (III) in free volume (PET/A, Δ) and in pore model (PET/C, \circ) poly(ethylene terephthalate).

under the aforementioned hypothesis on the polarity of poly(ethylene terephthalate), in these films it is possible to speak of "anomalously slow" processes, in opposition to the results obtained with other polymeric matrices, reported in literature.⁵ Moreover, ΔH^\ddagger and ΔS^\ddagger values in the polymer are always much lower than in solution for each dye. The considerable weight of the entropy 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.

The values of ΔH_1^\ddagger and ΔH_2^\ddagger for the same dye are substantially similar, with the exception of compound (I) (see Table II).

The small effect of substituents on activation parameters suggests the prevailing role of the polymer on the energetics of the isomerization reaction.

In a kinetic study on cis-trans isomerization of azo dyes in polyacrylate films under T_g , Eisenbach⁵ found two first-order processes: a fast one, characterized by an activation energy $E_a = 6.4 \text{ kcal mol}^{-1}$, which was attributed to a translational relaxation of the polymer chains, and a slow one ($E_a = 16.4 \text{ kcal mol}^{-1}$), which was correlated with a rotational mechanism. Our results are not easily rationalized on the basis of this model.

When considering PET films under T_g , the occurrence of a rotational mechanism can be ruled out, since no gauche-trans isomerization of this polymer has been observed under T_g .⁶ Thus, the cis-trans thermal isomerization of dye associated with a rotational change of the polymer cannot happen. In PET films only translational mechanisms are likely involved.

The observed k_i values (see Table II) seem to be only average values of a nearly continuous distribution of relaxations. In fact, in the case of compound (III), three processes could be detected, and in other cases there are some experimental hints of the presence of fast reactions that only the dead time of our experimental setup did not allow us to measure. Furthermore, the very low activation enthalpies of all the observed processes, and their similarity, cannot be reconciled with an interpretation in terms of translational and rotational ("crankshaft") chain segmental motions in the glassy polymer.

The present kinetic behavior, characterized by a multiplicity of first-order processes is in a better agreement with the hypothesis of Paik and Morawetz.⁴ Following these authors, the two or more processes detected in the experimental relaxation, reflect an unequal distribution of "tie-molecules," "folds," and "cilia" in the amorphous region of the polymer films. Therefore, the photoisomerization process in the glassy polymer will produce cis isomers in regions characterized by different local free volumes. If the free volume is greater than a critical size, the thermal reaction will proceed in solution, but for smaller free volumes, the cis isomer will be trapped in strained conformations from which it can return more easily to the trans form than the relaxed cis form.

Photofading

Makarewicz and Wilkes,¹⁶ in a study on the crystallization of PET, found that the maximum in the growth rate of PET spherulites occurs at about 180°C. Therefore it is possible to suppose different morphological features for samples crystallized below or above 180°C. Furthermore, the well-known minimum in the correlation dye uptake *versus* annealing temperature takes place at 180°C,¹⁷⁻²⁰ and Dumbleton et al.¹⁸ stated that this behavior can be ascribed to crystallinity and crystal size changes resulting from heat setting.

In a previous paper about morphological characterization of PET films,²¹ the dye-uptake phenomenon was interpreted as determined by two diffusion modes: (1) in accordance with the usual "free volume" model, and (2) in accordance with a "pore" model, previously described. Dye diffusion in the free volume model is considered to occur only because of the thermal motion of polymer segments in the amorphous phase, in observance of the semi empirical WLF equation. Diffusion of the dye molecules in the pore model is governed only by the porosity and tortuosity of the polymer matrix. The change from one to the other diffusion mode occurs at $\beta = 0.5$.

In the experimental section the characterization of PET films with two different models is reported. Sample A follows the dyeing free volume model: sample C, in spite of its higher crystallinity, shows an increase in dye uptake due to its higher porosity.

Light stability of the dye in a polymeric matrix is affected by several physical factors: some are external to the dye-matrix system, such as the spectral distribution of the light source and the atmospheric composition, humidity, and temperature; others are internal to the system and include the chemical structure of the dye, its physical state in the matrix, and the chemical and physical structure of the polymer matrix. In this study, ex-

ternal factors were controlled by selecting a standard procedure in evaluating the degree of lightfastness. For each dye, internal factors were limited to the influence of the polymer structure on the physical state of the dye molecule.

Plotting dye loss *versus* time of Xenotest irradiation, zero-order fading curves are obtained. There seems to be no doubt that the physical state of the dye is very important. A higher slope of fading curve was obtained for sample C having higher porosity. The increase of dye fading in going from A to C may be interpreted assuming that, in a pore model PET film, the dye in the large pores is not protected against external factors.

In Figure 2 the decreasing slope of the curves referring to dyes (I) and (II) in film C is due to a significant presence of degradation products as evidenced by a progressive shift in the absorbance maximum. The regression straight lines drawn in Figure 2 were obtained taking into account only measurements in the region where no shift in the maximum was observed.

It must be noted that the different behavior observed in photofading of A and C films is not paralleled in the *cis-trans* isomerization kinetics. This is because, in the latter case, only the dye in the amorphous region of the film is involved.

Under irradiation, a photostationary state is reached as a result of the competition between direct *trans-cis* photoisomerization and thermal processes. The *cis* isomer concentration is consequently determined by the intensity of light and by the temperature of the sample; as the thermal return is much more affected by temperature than the photochemical reaction, an increase in temperature reduces the *cis* isomer concentration at photostationary state. This is evidenced by the decrease of the overall amplitude of the thermal relaxation, as far as experimentally measurable. This is shown in Table IV, where the term $(A_{\infty} - A_0)/A_{\infty}$ is reported as a function of temperature. The weight of the single relaxation processes, expressed as a percentage of the whole absorbance change, is the same for PET/A and PET/C at any temperature (see Table IV). This behavior differs from that reported for poly(methyl methacrylate).⁵

It is interesting to note that the photofading rate is inversely related to the rate of the thermal *cis-trans* reaction. Photoisomerization and subsequent thermal isomerization is by far the main mechanism of dissipation of electronic excitation shown by these dyes.²² Therefore, the more efficient is this process in transferring excitation energy to the polymer medium, the greatest is the light stability.

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