

Influence of Polycaprolactam Morphology on Thermal *cis*-*trans* Isomerization and Photofading of Azo Dyes Differently Dispersed in It: A Kinetic Study

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Synopsis

Two polycaprolactam films were prepared characterized by different crystallinity degrees, the free volume model being prevalent in the former and the pore model in the latter. 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 and COOH), the latter of which gives specific interactions with the polymer. The kinetics of the thermal *cis*-*trans* isomerization of these dyes has been studied below and above the glass transition temperature of the polymer (T_g) in the range 20–80°C. In every case, the isomerization process was found to be the result of a multiplicity of first-order reactions and the dependence on temperature exhibited a break at the T_g value. Lightfastness of the dyes in the polymer matrices has been also investigated. The isomerization and fading kinetics are discussed in terms of polymer structural features as well as of the nature of the dye.

INTRODUCTION

Morphological features of the amorphous phase of a polymer affect the kinetics of the thermal *cis*-*trans* isomerization of azo dyes dispersed in it.^{1,2} This was shown in our previous work by considering solid poly(ethylene terephthalate) (PET) and isotactic polypropylene (PP), variously dyed.³⁻⁶

In the case of PET, the isomerization was kinetically followed below the glass transition temperature of the polymer ($T_g = 77^\circ\text{C}$). Under these circumstances the thermal return of azo dyes was not found to follow a simple first-order rate law, as usually occurs in solution as well as in molten or rubber polymers. The kinetics was then resolved as the sum of two or three simultaneous first-order reactions, according to a reported procedure.⁷ On the contrary, in the case of PP, the thermal return appeared strictly first order as the kinetic study was performed on the polymer in the rubbery state, namely above its T_g value (-10°C).

In the course of our investigation, we used oriented and unoriented films prepared by stretching, as well as films with different degree of crystallinity

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prepared by appropriate thermal treatments. In the latter case structures were obtained in which either pore model or free volume model prevailed.⁸

For both polymer matrices, the isomerization kinetics was found to be likely dependent on the free volume changes induced in the amorphous regions by stretching. On the other hand, no significant modifications were observed in the kinetic behavior on varying the crystallinity of the samples.

In the present study we have examined the thermal *cis-trans* isomerization of two azo dyes in films of Nylon 6, i.e., polycaprolactam (PCL) of different morphology, at temperatures below and above the glass transition temperature of the polymer. Polymers PCL with a water content of 3.5% exhibit a T_g of 50°C, a suitable value for our purposes.

Furthermore, in order to emphasize possible variations between the kinetic behavior of dyes differently associated with the polymer, we used two disperse dyes, only one of which able to give chemical bonds with the matrix. Differences of this nature have been reported by Eisenbach,² who also found in one case the presence of two simultaneous first-order isomerization reactions even slightly above the T_g value of the polymer considered.

Lightfastness of the dyes in the polymer matrices has been also investigated.

EXPERIMENTAL

Materials

The azobenzene derivatives were kindly supplied by ACNA S.p.A. Nylon 6 (polycaprolactam) having $\eta_{rel} = 2.3$ (from viscosimetry in 1% H₂SO₄ aqueous solution), extruded at 250°C, quenched in a cold air stream was used (film PCL1). In order to obtain films at higher degree of crystallinity, an additional thermal treatment was performed at constant length for 20 min at 190°C (film PCL2). The crystallinity index (β) was calculated assuming specific volumes V_a (amorphous) = 0.923 cm³/g and V_c (crystalline) = 0.813 cm³/g.⁹ Specific volume measurements were carried out at 21°C by floatation in xylene-carbon tetrachloride mixtures. Birefringence was obtained by Berek compensator. Differential scanning calorimetry data for T_g determination were obtained with a Perkin-Elmer DSC-4.

The morphological characteristics of the samples are reported in Table I.

Film dyeing was carried out with 0.8–1.2% dyestuff calculated on the weight of the film. The process was started at 40°C raising the temperature to 98°C

TABLE I
Morphological Characteristics of the PCL Films

Sample ^a	Specific volume V_s (cm ³ /g)	Crystallinity index	Birefringence Δn	Glass transition temperature ^b T_g (°C)
PCL1	0.876	0.43	0.004	50
PCL2	0.870	0.48	< 0.001	50

^a Both samples melted at 220°C.

^b Observed when the samples contained 3.5% by weight of water.

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

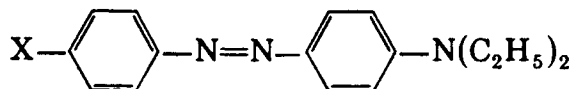
The polymer films dyed as described in the preceding section were maintained in the dark at room temperature in a desiccator at least for 30 days up to a water content of 3.5% by weight. Before every irradiation and kinetic measurement, they were heated at 60°C for 2 h and subsequently kept in the dark at 20°C for 24 h at 65% relative humidity. This treatment ensured a reproducible behavior of the samples, restoring them as fresh ones, i.e., canceling all their modifications occurred with time. These phenomena of ageing and restoring of the films are further discussed in the following sections.

For the measurements, the samples 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 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.

Lightfastness was evaluated after Xenotest (Hanau model 450) continuous irradiation for ca. 100 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

Two derivatives (I) and (II) were used:



(I) X = H and (II) X = COOH. These compounds were used in dyeing the films PCL1 and PCL2 described in the experimental section.

The kinetics of the thermal *cis-trans* isomerization of azo dyes (I) and (II) in PCL films, studied in the temperature range 20–80°C, could be resolved as the sum of two simultaneous first-order processes according to a reported procedure.⁷

The average fractions of dye that isomerize according to the simultaneous first-order reactions 1 and 2 (\bar{r}_1 and \bar{r}_2) below and above 50°C (the glass transition temperature of the polymer with a water content of 3.5% by weight) are collected in Table II.

The first-order rate contents k_i at 25, 50, and 75°C and the activation parameters of the single processes below and above 50°C are reported for the two

TABLE II
Average Weights of the Thermal Relaxation Processes of Dyes (I) and (II) in PCL Films
Observed below and above 50°C in the Temperature Range 20–80°C

Dye	Film	T (°C)	\bar{r}_1^a	\bar{r}_2^a
(I)	PCL1	< 50	0.12	0.88
		> 50	0.06	0.94
	PCL2	< 50	0.14	0.86
		> 50	0.06	0.94
(II)	PCL1	< 50	0.17	0.83
		> 50	0.07	0.93
	PCL2	< 50	0.09	0.91
		> 50	0.08	0.92

^a For definition of \bar{r}_1 and \bar{r}_2 see text.

dyes in the two aforementioned films PCL1 and PCL2 in Table III. In the same table are also reported the mean relaxation times (τ)¹¹ defined as

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

and corresponding in the present case to $\tau = r_1/k_1 + r_2/k_2$. This term is an adequate kinetic parameter of the overall process.

TABLE III
Thermal *cis-trans* Isomerization Rate Constants^a and Relaxation Times^b at Various
Temperatures and Activation Parameters below and above 50°C
for Dyes (I) and (II) in PCL Films

Dye	Film	T (°C)	Reaction 1			Reaction 2			τ/s^b
			$10^4 \cdot k$ (s ⁻¹)	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (e.u.)	$10^4 \cdot k$ (s ⁻¹)	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (e.u.)	
(I)	PCL1	25	0.898	7.5 ± 0.3	-51.7 ± 0.8	21.6	9.0 ± 0.3	-40.7 ± 1.1	1744
		50	2.53	12.5 ± 1.8	-36.4 ± 5.4	74.7	13.0 ± 1.3	-28.2 ± 3.7	478
		75	11.2			356.			80
	PCL2	25	0.789	5.3 ± 1.0	-59.7 ± 3.3	4.58	13.2 ± 1.0	-29.6 ± 3.2	3652
		50	1.69	9.9 ± 3.4	-45.3 ± 10.2	30.1			891
		75	5.65			> 400 ^c			< 111
(II)	PCL1	25	0.136	10.0 ± 3.5	-47.2 ± 11.2	20.3	10.4 ± 3.9	-36.1 ± 12.3	12909
		50	0.530	25.1 ± 3.5	-0.5 ± 10.5	76.7	23.8 ± 4.3	5.1 ± 12.9	2379
		75	9.17			1046.			85
	PCL2	25	0.932	18.2 ± 2.1	-15.8 ± 6.9	20.7	10.7 ± 1.2	-34.8 ± 3.8	1405
		50	9.56	29.8 ± 4.6	19.4 ± 13.7	96.9	23.3 ± 2.5	4.4 ± 7.5	183
		75	244.			1493.			9

^a Calculated according to the Eyring equation.

^b Calculated using values \bar{r} of Table III (for T = 50°C, the two \bar{r} values at lower and higher temperature were averaged).

^c The rather scarce extent of reaction followed in this case allowed only an indicative evaluation of the rate coefficient relative to the faster process (k_2).

The trends of $\ln k_i/T$ vs. $1/T$ for the considered cases in the whole explored temperature range are shown in Figure 1.

The kinetics of the dye loss of dyes (I) and (II) under Xenotest irradiations appeared of first order. The values of the fading rate obtained by a linear regression analysis are collected in Table IV.

DISCUSSION

The polycaprolactam under investigation is a semicrystalline polymer in which the ordered regions are constituted by parallel segments bound by hydrogen bonds and electrostatic interactions between amino and carboxyl groups. The microstructure of the polymer film presents tightly packed radial elements, the spherulites, that form during solidification.

The polymer amorphous phase, which, at variance with the crystalline one, has a high water absorption capacity, is characterized by a variable glass transition temperature depending on the water content. The absorbed water acts as a plasticizing agent and lubricates the polymer chains of the amorphous regions lowering the T_g value.

Furthermore, increasing the water content of the polymer results in an enhanced polarity of the medium. This was clearly evidenced by the decrease of the $E_{\max} (\pi-\pi^*)$ values of the dyes (I) and (II) dispersed in the polymer, observed when the latter was in contact with boiling water. As is well known, the polarity of the medium can markedly affect the kinetics of the reaction occurring in it.

Thus, in order to carry out reproducible measurements, a standard procedure was followed capable of conditioning the dyed polymer films to a constant water content (see Experimental). The conditioned polymer contained 3.5% by weight of water and showed, at 20°C and 65% relative humidity, a T_g value of 50°C.

Another difficulty that arose during the experimental work was associated with the observed "ageing" of the sample. This is substantially due to the fact that the free volume contraction occurring during the rubber to glass transition does not reach the equilibrium value in short times, so that it continues with time. As a consequence at long times the dyed polymer film progressively entraps the dye, thus hindering its isomerization. In fact it was found that the isomerization reaction that could be experimentally followed gradually decreased with the increase of the age of the conditioned polymer film. This was observed by Victor and Torkelson in the case of polystyrene.¹² A dyed film used for kinetic measurements 500 h after conditioning showed no isomerization reaction. In order to avoid the "ageing" effect and to carry out significant and reproducible measurements, a procedure of "restoring" was always followed before using the dyed films (see Experimental). This procedure ensured a behavior of an aged sample analogous to that of a freshly conditioned one.

The morphological characteristics of the two polymer films under investigation (Table I) show only a slightly higher crystallinity for PCL2. This notwithstanding, ongoing from PCL1 to PCL2, there is a substantial change because from a system governed by a free volume model one comes to a system where a pore model holds. In fact the crystallinity degree over which the pore model

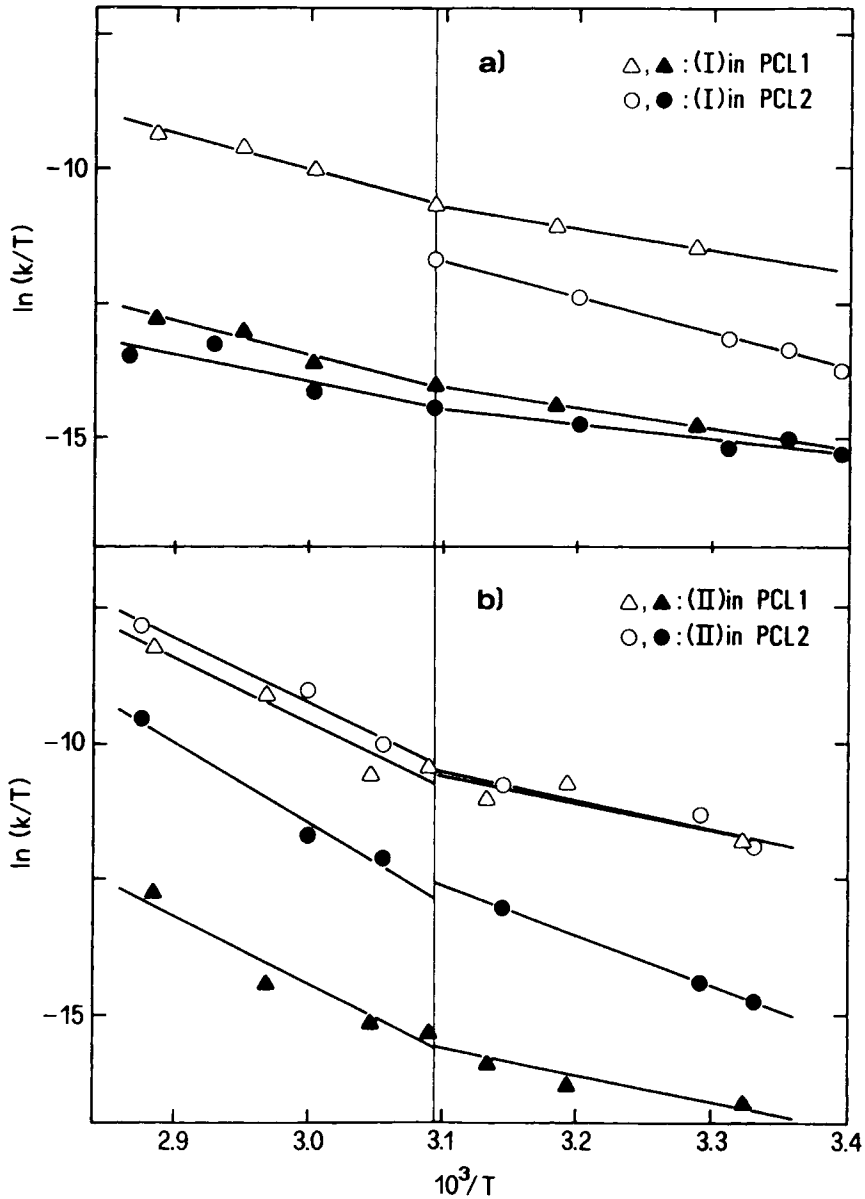


Fig. 1. Eyring plots of the rate constants k_1 and k_2 of the thermal *cis-trans* isomerization of azo dyes (I) (a) and (II) (b) in polymer films PCL1 and PCL2.

prevails was found to be $\beta = 0.44$, a higher value than that of PCL1 but less than that of PCL2. Such a value was obtained by a thermal treatment of film PCL1 with free ends at 190°C for 1 min, treatment that is known to induce a minimum dye uptake and that corresponds to the discriminating condition between the two models.¹³

Regarding the birefringence value Δn , films PCL do not show significant differences in their structural order, which in both cases appears rather low.

TABLE IV
Photofading Rate of Compounds (I) and (II) in PCL Films under Xenotest Irradiation

Dye	Photofading rate ^a (dye loss percent h ⁻¹)	
	PCL1	PCL2
(I)	0.214 ± 0.016	0.503 ± 0.046
(II)	0.394 ± 0.071	0.877 ± 0.131

^a $t_{\max} \approx 70$ h.

Kinetics

In the two polymer films and for both the dyes under investigation, the thermal *cis-trans* isomerization was not found to follow a simple first-order rate law, but it could be described as the sum of two relaxation processes characterized by the k_i values of Table III. This multiplicity of simultaneous first-order reactions was expected below the glass transition temperature since it is in line with our previous results³⁻⁵ and with those of other authors in different polymeric matrices colored with azocompounds.^{2,14,15} This fact was interpreted, as suggested by Paik and Morawetz,¹⁴ as deriving from the unequal microenvironment and different free volume availability of the disperse dyes in the amorphous regions of the glassy polymeric matrix.

On the other hand the occurrence of such a multiplicity, also slightly above the T_g value, already observed by Eisenbach,² needs some comment. Probably, the rubber structure of the polymer, for which a single process is usual, is not promptly achieved at temperatures higher than but still close to the glass transition temperature so that the consequence of the structural variation appears somewhat gradual.

A correct comparison between the kinetic results of PCL1 and those of PCL2 could be made in terms of k_1 , k_2 , or τ values as well, if the same reaction extent could have been followed in every case. Since this was not the case, significant conclusions can be shown only on the basis of k_1 values that refer to the slower reaction, surely monitored for all the samples.

With regard to dye (I), moderate differences of k_1 values, within a factor 2, can be observed in going from PCL1 to PCL2 (Table III). These results confirm that the different crystallinity shown by the two films does not markedly affect the kinetics of the isomerization reaction in the two media, i.e., this reaction essentially depends on the structural features of the amorphous phase of the polymer, as previously suggested.³

In the case of dye (II), the k_1 values are systematically higher in the more crystalline PCL2 film, by factors increasing with temperature from 7 to 27. This result does not contradict our findings as it refers to a dye that can give chemical bonds with the polymer matrix, thus representing a particular case. However, when dealing with a dye bearing a $-\text{COOH}$ group as dye (II), a catalytic effect can intervene whose importance increases with its concentration. Since the same overall amount of dye was employed in dyeing both PCL1 and PCL2 and since in the case of PCL2, where the pore model prevails, the concentration of (II) in the amorphous phase was consequently higher, an enhanced

catalytic effect should be expected in the latter case. This could explain the observed increase of the reaction rate in the case of the more crystalline PCL2 film.

The catalytic effect induced by the presence of a carboxyl group on the *cis-trans* isomerization was investigated by one of us considering the same dye (II) in various solvents.¹⁶ The substituent effect due to this group, independently of its catalytic power, was evaluated by carrying out some kinetic measurements at various dye concentrations and extrapolating the results to zero concentration. In this manner a ratio $k_{\text{COOH}}/k_{\text{H}} = 35.8$ was calculated in *N,N*-dimethylformamide. In the present case a comparison between (I) and (II) in the same matrix reveals a higher reaction rate for (I) in PCL1, by factors ranging from 6.6 at 25°C to 1.2 at 75°C, and a higher reaction rate for (II) in PCL2, by factors ranging from 1.2 at 25°C to 43 at 75°C. Again, in the case of the more crystalline PCL2, an enhanced catalytic effect can be invoked. It is noteworthy that all these observations can be qualitatively drawn also considering τ values instead of k_1 values.

As regards the dependence on temperature of the rate coefficients k_1 and k_2 , the occurrence of two different trends in the Eyring plots with a point of discontinuity close to the T_g value (Fig. 1) is of particular interest. As a consequence, the isomerizations carried out at temperatures higher than the T_g value are characterized by higher values of activation enthalpy and entropy. The higher values of ΔH^\ddagger above T_g , associated with an additional activation energy for viscous flow as suggested by Eisenbach,² are more than compensated by the entropic factor, which results in higher isomerization rates.

The presence of the two trends is much more marked in the case of dye (II), likely due to its higher sensitivity to morphological polymer changes, being chemically bound to it.

Photofading

A standard procedure in evaluating the degree of lightfastness was used to control external factors. Plotting the dye loss vs. time of Xenotest irradiation, zero-order fading curves were obtained; the slopes of the corresponding straight line are reported in Table IV.

For both dyes the lightfastness in PCL1 was found to be greater than in PCL2. Such a behavior is clear evidence that lightfastness is essentially governed by the supermolecular order of the polymer matrix and to a major extent by the structural model prevailing in the polymer. In the more crystalline PCL2 that exhibits a pore model behavior, the dye in the large pores is scarcely protected against external factors resulting in a higher photofading rate. However, inspection of Table IV reveals that dye (I) is significantly more stable than (II), just evidencing the importance of the nature of dye. Electronic factors as well as catalytic effects are likely involved in determining the lower lightfastness of dye (II).

CONCLUSIONS

The kinetics of the reactions here considered was characterized by the occurrence of a multiplicity of simultaneous first-order processes. This fact reveals

an unequal microenvironment and different free volume availability of the dyes in the amorphous regions of the glassy polymeric matrix.

Focusing our attention on dye (I), which cannot give chemical bonds with the polymer matrix, the comparison between the rate coefficients obtained in PCL1 and PCL2 indicates that crystallinity does not influence the kinetics of the isomerization process. This is in line with our previous results according to which this reaction essentially depends on the morphological features of the only amorphous phase of the polymer, as e.g., its structural order and free volume distribution.

Photofading proved to be able to evince the change from a system governed by a free volume model to one where a pore model holds.

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