Effect of Polypropylene Morphology on Thermal *Cis-Trans* Isomerization and Photofading of Some Azo Dyes: A Kinetic Study

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Synopsis

Five polypropylene films were prepared having different crystallinity and morphology, the latter having been modified by stretching. They were colored with azo dyes $XC_6H_4N{=}NC_6H_4N(C_2H_5)_2$ (where $X{=}H$, OCH_3, CN, and NO_2). The kinetics of the thermal *cis-trans* isomerization of these dyes has been studied in the range 21–41°C, much above the glass transition temperature of the polymer. The isomerization process was found to be strictly first-order; the kinetic parameter values have been correlated with the free volume extent in the amorphous regions of the matrix. Lightfastness of the dyes in the polymer matrices has been also investigated: It appeared to be more important for the unoriented samples with respect to the stretched ones and substantially independent on the crystallinity degree.

INTRODUCTION

In previous works[1,2] we have investigated the effect of poly(ethylene terephthalate) morphology on the thermal *cis–trans* isomerization and photofading of variously substituted azo dyes dispersed in the polymer. When working below the glass transition temperature of the medium, the isomerization kinetics was characterized by a multiplicity of simultaneous first-order processes. Furthermore, significant interactions between the dye and the polymer matrix were observed as evidenced by the marked red shift measured by comparing the absorption maxima of the dye in PET films with those obtained in aliphatic hydrocarbons. Examples of the dependence of the term $E_{max}(\pi{-}\pi^*)$ for azo dyes on the nature and polarity of the medium have been recently reported.[3,4]

In the presence of such complex kinetics and marked dye–polymer interactions, the entire role of the polymer morphology on the reaction might be partially masked. So, in order to further verify the influence of the polymer amorphous phase morphology on the azo dye isomerization, in this work we have carried out an investigation on the same reaction by choosing isotactic polypropylene as polymer matrix. This polymer cannot give rise to hydrogen bonds or other specific interactions with the azo dyes and exhibits a rubber

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structure in the explored temperature range, resulting in single first-order kinetics.

EXPERIMENTAL

Materials

The azobenzene derivatives and isotactic polypropylene (Moplen T30S, M_w = 300,000) were kindly supplied by ACNA S.p.A. and Himont S.p.A., respectively. Polymer films extruded at 240°C (thickness 28 μm) and quenched in a cold air stream were used. Isotropic unoriented films at various degree of crystallinity were obtained by performing further thermal treatments according to the protocols: for PP/ua, 60 min at 90°C; for PP/ub, 60 min at 100°C; for PP/uc, 60 min at 120°C. Anisotropic monooriented films PP/mc4 and PP/mc8 were obtained by means of a longitudinal stretch at 92°C with ratios of 4.0 and 8.0, respectively. Specific volume (V_s) measurements were carried out at 20°C by floatation in mixtures of alcohol and water. The crystallinity index β was calculated assuming[5] V_s (amorphous) = 1.17 cm^3 g^{-1} and V_s (crystalline) = 1.05 cm^3 g^{-1}. Wide-angle X-ray scattering was performed on a Siemens D-500 diffractometer equipped with a Ni-filtered Cu$k\alpha$ radiation. The apparent crystal sizes in the directions perpendicular to the (110), (040), (130) crystal planes were calculated employing the Debye–Sherrer "formula." The crystal orientation function f_c was obtained from the azimuthal scans of the (110) and (040) X-ray reflections according to Wilchinsky.[6]

The orientation of anisotropic polymer was characterized by the following relative function[7]:

$$f_{rel} = \frac{3\cos^2\vartheta - 1}{2} = \frac{(D-1)(D_{max}+2)}{(D+2)(D_{max}-1)}$$

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 a proper wavelength for parallel and perpendicular infrared spectrum, respectively. D_{max} is the dichroic ratio obtained for the sample subjected to the highest draw ratio (PP/mc8). For measurements, two bands at 1220 and 1256 cm^{-1} were chosen; it is generally agreed that the former is associated with the crystalline phase and the latter with both the amorphous and crystalline regions. The relative orientation functions $f_{rel,c}$ and $f_{rel,av}$ correspond to the measurements at 1220 and 1256 cm^{-1}, respectively. Their values allow only a qualitative characterization of the oriented films. According to Samuels,[8,9] the relative amorphous orientation function $f_{rel,a}$ can be determined from the relation

$$f_{rel,a} = \frac{f_{rel,av} - \beta f_{rel,c}}{1 - \beta}$$

The infrared dichroism characterization of the films was performed on a Perkin-Elmer Mod. 983 IR spectrophotometer equipped with a polarizer.

TABLE I
Morphological Characteristics of the Considered PP Films[a]

Sample	Crystallinity index β	Orientation functions			Birefringence Δn	Apparent crystal size		
		$f_{rel,c}$	$f_{rel,av}$	$f_{rel,a}$		110	040	130
PP/ua	0.48	nd	nd	nd	0.0	nd	nd	nd
PP/ub	0.57	nd	nd	nd	0.0	122	144	131
PP/uc	0.65	0.33	0.31	0.27	0.0	153	186	154
PP/mc4	0.64	0.70	0.80	0.98	0.0331	207	177	161
PP/mc8	0.64	1.0	1.0	1.0	0.0354	234	207	196

[a] For definitions and full details, see text.

Birefringence was obtained by optical means (Berek compensator). The morphological characterizations of the samples are reported in Table I.

Film dyeing was carried out in water with 0.8–1.2% dyestuff, calculated on the weight of the film, at 80°C during 1 h. Film dye concentration was chosen to obtain an absorbance near 1 for isomerization measurements.

Measurements

The polymer films dyed, as described under Materials, were sandwiched between two quartz plates and exposed for 10 min in a thermostatted 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 into the cell compartment of a Cary 118 spectrophotometer thermostatted at the same temperature of the irradiation. The thermal return was monitored as the change in absorbance (A) at a wavelength corresponding to the absorption maximum of the *trans* isomer.

Lightfastness was evaluated after Xenotest (Hanau Model 450) irradiation for 1–24 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 15 days in the dark after irradiation.

RESULTS

Four derivatives (I)–(IV) were used:

$$X-\langle\ \rangle-N=N-\langle\ \rangle-N(C_2H_5)_2$$
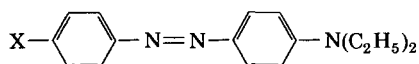
(I) X = H   (III) X = CN

(II) X = OCH_3 (IV) X = NO_2

These compounds were used to dye the films PP/ua, PP/ub, PP/uc, PP/mc4, and PP/mc8 described in the Experimental section.

TABLE II
Rate Coefficients (10^4 k/s^{-1})[a] of Thermal *cis–trans* Isomerization of
Dyes (I)–(IV) in Various PP Films

Dye	T (°C)	Polymer matrix				
		PP/ua	PP/ub	PP/uc	PP/mc4	PP/mc8
(I)	21	nd	17.1	11.0	1.0	1.3
	31	37.3	52.9	41.2	8.4	7.7
	41	76.8	97.9	64.4	56.4	50.3
(II)	31	49.8	nd	45.7	—	—
(III)	21	18.0	17.7	39.9	3.7	3.3
	31	50.2	49.2	73.0	16.6[b]	16.9
	41	62.5	108.0[b]	146.0	90.1	74.0
(IV)	31	316.0	nd	299.0[b]	—	—
	41	819.0	nd	903.0	—	—

[a]Sample mean deviations were ≤ 10%.
[b]Calculated according to Eyring equation.

TABLE III
Reproducibility of Rate Constant Values from Duplicate Kinetic Measurements
and Relative Amplitudes of the Observed Thermal Relaxation Process[a] of
Dye (I) in PP/uc Film at Various Temperatures

T (°C)	$10^4 k$ (s^{-1})		$\Delta A/A_\infty$ (%)	
	Run 1	Run 2	Run 1	Run 2
21	10.8	11.1	25.4	25.7
31	37.6	44.8	16.6	16.6
41	69.8	59.0	6.1	6.2

[a]See text.

The kinetics of thermal *cis–trans* isomerization of dyes (I)–(IV), studied much above the glass transition temperature of the polymer ($T_g = -10$°C), was found to be strictly first-order. The rate coefficients obtained in the temperature range 21–41°C are reported in Table II. The figures represent average values calculated from data of multiple kinetic runs carried out by using different pieces of the same died films. This procedure was suggested by the slight dishomogeneity observed in the distribution of dye in the PP films due to the scarce polymer–dye interaction.

In the case of dye (I) in PP/uc film, the values of the kinetic coefficients and of the term $\Delta A/A_\infty$, as obtained from duplicate kinetic measurements at various temperatures, are reported in Table III. The term $\Delta A/A_\infty$ measures the absorbance amplitude covered during the kinetic measurements relative to the absorbance at "infinity time" in order to take into account the different nature and concentration of dyes. This term is related to the extent of reaction kinetically followed.

The influence of the different polymer morphology on the activation parameters for the *cis–trans* thermal return of dyes (I) and (III) in PP films having the same crystallinity is shown in Table IV.

The time courses of dye loss under irradiation of dye (I) in the various polymer matrices are depicted in Figure 1. The values of fading rate obtained by a linear regression analysis in the time range 5–24 h, are collected in Table V.

TABLE IV
Activation Parameters of Thermal *Cis–Trans* Isomerization of Dyes (I) and (III)
in PP Films Having the Same Crystallinity ($\beta = 0.64$–0.65)
but Different Morphology

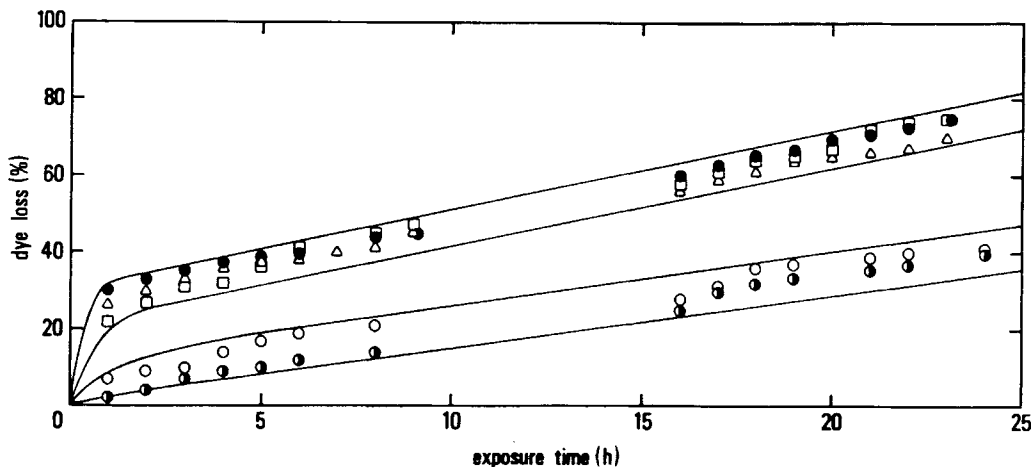| Dye	Polymer matrix	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)
(I)	PP/uc	15.2 ± 1.2	−19.9 ± 4.0
	PP/mc4	31.7 ± 1.9	31.4 ± 6.4
	PP/mc8	32.4 ± 1.2	33.4 ± 4.0
(III)	PP/uc	12.9 ± 2.2	−25.6 ± 7.2
	PP/mc4	28.1 ± 0.9	21.2 ± 2.9
	PP/mc8	27.4 ± 1.8	19.5 ± 5.9

Fig. 1. Photofading time courses of compound (I) in various polypropylene films: (□) PP/ua; (△) PP/ub; (●) PP/uc; (◐) PP/mc4; (○) PP/mc8.

TABLE V
Photofading Rate of Compound (I) in PP Films under Xenotest Irradiation

Polymer matrix	Photofading rate[a] (dye loss percent h^{-1})
PP/ua	2.02 ± 0.06
PP/ub	1.88 ± 0.03
PP/uc	2.12 ± 0.03
PP/mc4	1.59 ± 0.06
PP/mc8	1.30 ± 0.07

[a] Calculated in the time range 5–24 h.

DISCUSSION

In the temperature range under examination, isotactic polypropylene exhibits a rubber structure ($T_g = -10°C$). At the molecular level this structure is quite regular resulting in a facile crystallization; hence, all films of isotactic polypropylene here considered are characterized by an extended crystallinity (Table I). When using the most crystalline polymer ($\beta = 0.64$–0.65), three films were prepared, one unoriented (PP/uc) and two monooriented (PP/mc4 and PP/mc8), obtained with stretch ratios 4 and 8, respectively. The corresponding orientation functions relative to the most stretched film present low values, as expected, for PP/uc and high values for PP/mc4. Taking into account the function referring to the amorphous regions, it can be noticed that only a negligible variation is involved in changing the stretch ratio from 4 to 8. This is of particular interest if one considers that the behavior of dyed film is strictly determined by the features of the amorphous regions.

Birefringence (Δn) is another parameter that gives a reliable estimate of the supermolecular order of the polymer films. Also in this case the variation observed on going from PP/mc4 to PP/mc8 is rather small (Table I). Birefringence is a significant parameter since reasonably high Δn values are

associated with low free volume content that corresponds to compact packings of polymer chains in the film.

As to the apparent crystal size, an increase was observed with the increase of both crystallinity and stretch ratio, as expected.

With regard to the dyeing behavior of unoriented film, the dye uptake was found to increase with increasing crystallinity; however, the increase of absorbance of dyed films did not correspond to the higher decrease of absorbance of the dye in the dyeing bath. This fact suggests the occurrence of an agglomeration of dye in the film: Reasonably such an agglomeration is associated with the presence of microporosity in the polymer, just showing the prevailing role of the pore model with respect to the free volume model. The polymer microporosity enhances dye uptake whereas the absence of chemical affinity between dye and polypropylene does not promote the diffusion of dye in the free volume of the amorphous regions.

Kinetics

The time courses of the thermal *cis–trans* isomerization of azo dyes (I)–(IV) in PP films have shown that in every case the reaction is strictly first-order. This simple kinetics was expected since the measurements were carried out much above the glass transition temperature of the polymer and it is well known that complex kinetics usually occur only in glassy matrices.[1,2,10–12]

Due to the presence of diffuse microporosity, sometimes dyeing appeared uncompletely uniform and slight variations of kinetic results were observed when different pieces of the same film were considered. Thus, multiple measurements were generally carried out and results were averaged.

The first-order kinetic coefficients (k_i) for dye (I)–(IV) in the various films are reported in Table II. Examples of the reproducibility of duplicate kinetic measurements are shown in Table III, where a measure of the reaction extent experimentally followed ($\Delta A/A_\infty$) is also reported. This term represents the absorbance amplitude covered during the kinetic runs (ΔA) relative to the absorbance value measured at "infinity time" (A_∞); it generally decreases when temperature increases as, at similar "dead time," the fraction of the process experimentally followed is smaller.

Inspection of Table II reveals that the degree of crystallinity of the polymer matrix does not significantly affect the kinetics of compounds (I), (II), and (IV). Also in the case of compound (III), the variations of the coefficient k appear to be rather slight, by factors in the range 1.5–2.3, the highest values being measured at the highest level of crystallinity.

On the other hand, when considering how the different order degree in the polymer amorphous regions, obtained by different orientation of films at comparable crystallinity, influences the kinetics of *cis–trans* isomerization, significant results could be observed. In fact, as it is shown in Table II for compounds (I) and (III), on going from unoriented polymer matrix PP/uc with $\beta = 0.65$ to monooriented polymer matrices PP/mc4 and PP/mc8 with similar crystallinity ($\beta = 0.64$), the k values decrease by average factors 11, 5, and 1.5 at 21, 31, and 41°C, respectively. It is reasonable to argue that increasing temperature results in smoothing away the differences between the

two types of matrix, due to the increased thermal motion of the molecules of the rubber polymer. Thus, taking into a particular account the data at 21°C, the results in Table II clearly indicate a marked dependence of the *cis–trans* isomerization of the dyes under examination on the absence or the presence of a molecular orientation in the polymer.

Interestingly, no significant dependences appear between the two monooriented films obtained with the two different stretch ratios. This is probably due to the fact that most of the consequences of the stretching is already working at a stretch ratio close to 4.

The behavior above described supports the hypothesis that the kinetics of *cis–trans* isomerization is essentially determined by the microstructure of the polymer amorphous regions where dye is placed by dyeing process. Thus, the crystallinity has negligible effects on the reaction, whereas all the free volume modifications induced by stretching in the amorphous regions play a decisive role in determining the isomerization rate. The lower reactivity appears to be closely related to the lower extent of free volume.

With regard to the activation parameters of *cis–trans* isomerization, the higher reaction rate observed in the unoriented films in the temperature range 21–41°C can be ascribed to smaller $\Delta H^{\neq}$ values. In fact, as is shown in Table IV, the values of activation enthalpy for the reaction of dyes (I) and (III) in the unoriented polymer matrix are about one half of the corresponding values measured in the oriented films, while the values of activation entropy are lower by about 50 e.u.

The contrary was observed with the same dyes in the comparison between unoriented and bioriented poly(ethylene terephthalate) films. In that case the faster reactivity in the unoriented matrix was found to be due to entropic more than to enthalpic factors.[2]

The data of Table II at 31°C relative to unoriented films allow the evaluation of the dye substituent effect on the reaction rate. By averaging the values obtained in films at different crystallinity, one obtains the following ratios: $k_{OCH_3} : k_H : k_{CN} : k_{NO_2} = 47.8 : 43.8 : 57.5 : 308$. This corresponds to a V-shaped Hammett plot that is typical for the thermal *cis–trans* isomerization of these dyes in liquid solution and in other media.[2,13,14]

Photofading

A standard procedure in evaluating the degree of lightfastness was used to control external factors. Plotting dye loss of compound (I) vs. time of Xenotest irradiation, the fading curves drawn in Figure 1 were obtained. All these curves show two different trends: Initially (< 5 h) the increase of dye loss is rather fast, probably according to a first order kinetics; at higher exposure time such an increase becomes smoother and clearly obeys to a zero order law. Reasonably, these two different trends correspond to the two ways in which the dye can be associated to the polymer: either in an aggregated form physically bound to the matrix surface, or simply laid on the aggregate. In the latter case the dye behaves as a monomolecular layer giving rise to the first-order process.[15] On the other hand, for the aggregated dye the fading rate remains constant,[15] resulting in the linear portions of the graphs.

The above dichotomy, well evidenced in the case of isotropic samples, tend to vanish on going to stretched polymers. It can be suggested that stretching leads to a decrease of amount of the dye present as a monomolecular layer with respect to that of the aggregate, more tightly bound to the matrix.

The zero-order fading rates in the time range 5–24 h are collected in Table V. As it is also apparent in the figure, the dye loss is more important for the unoriented samples and is substantially independent of the crystallinity degree. When stretching is applied, the fading extent decreases and slower zero-order fading rates are obtained. These observations indicate that stretching induces compact packings in the amorphous regions of the polymer accompanied by a decrease of free volume extent, resulting in a higher protection of dye against external factors.

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