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The Thermal *cis–trans* Isomerization of Azo Dyes Dispersed in Polymeric Blends as a Probe for Characterizing their Morphology

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ABSTRACT

The thermal cis–trans *isomerization of some 4-diethylaminoazobenzenes was studied kinetically as a function of temperature in various polymeric matrices. Blends of isotactic polypropylene mixed with various weight fractions of hydrogenated oligocyclopentadiene or oligo-β-pinene were used. Kinetics experiments confirmed that the isomerization reaction is a sound probe for characterizing the transition from rubbery to glassy state of the medium with the appearance of a multiplicity of first-order reactions. The isomerization rates were found to be dependent on the position of the substituents, but no marked influence of the composition of the polymeric blend was detected, even in the presence of considerable changes in the glass transition temperature or in the crystallinity of the samples. This behavior confirms that the isomerization reaction takes place essentially in the amorphous regions which appear to be quite similar for the various blends examined.*

1 INTRODUCTION

The thermal *cis–trans* isomerization of azobenzene derivatives in a polymeric matrix was previously used by us in order to characterize the morphological features of the amorphous phase of some polymers. We investigated films with different morphology made of poly(ethylene terephthalate) (PET), isotactic polypropylene (*i*PP), polycaprolactam (PCL) and cellulose matrices.[1–7] As azo dyes, some 4-diethylaminoazobenzenes and chrysophenine were used.

The kinetics of the *cis–trans* isomerization of aromatic azo compounds in polymeric matrices was found to be dependent on the free volume changes of the microstructure correlated to the morphology of the amorphous regions of the different polymeric samples.

Above the glass transition temperature (T_g) of the polymer, the thermal isomerization was always found to follow a single first-order kinetics. Under or around T_g, the kinetics is more complex and can be resolved as the sum of two or three simultaneous first-order reactions.

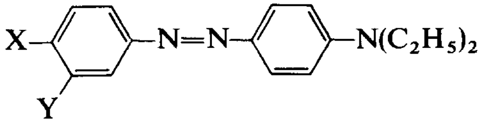
Blends of *i*PP and hydrogenated oligocyclopentadiene (*i*PP/HOCP) and of *i*PP and β-pinene (*i*PP/β-P) are miscible at molecular level in the melted state and give rise, during crystallization, to an amorphous phase in which both polymers are present with a single glass transition. This fact normally occurs in compatible blends in which the glass transition temperature follows the Fox law.[8] The *i*PP/HOCP blends were thoroughly characterized by Martuscelli and co-workers,[9–11] while the study of *i*PP/β-P blends is in progress.[12]

With the aim of improving the knowledge of the morphology of the amorphous phase of these blends, some kinetic studies on the isomerization of azo dyes dispersed in them were carried out and the results are reported in this paper.

2 EXPERIMENTAL

2.1 Materials

The azobenzene derivatives **I–IV** were supplied by ACNA SpA and purified by repeated crystallizations from 1-butanol. Isotropic (unoriented) films of binary blends of *i*PP (Moplen T30S, M_w 300 000, Himont) and HOCP (Escorez M_w 630, Esso Chemical; obtained from 1,3-cyclopentadiene monomer and consisting of a mixture of *cis-* and *trans*-isomers) were prepared by mixing the polymer in a microextruder and by extrusion at 280°C (0·04 mm thick, quenching in cold air stream). The weight mixing



I: X = OCH_3; Y = H
II: X = CN; Y = H
III: X = NO_2; Y = H
IV: X = H; Y = NO_2

ratios (*i*PP/HOCP) were 100/0, 95/5, 90/10 and 50/50. An isotropic film of binary blend of *i*PP and oligo-β-P (Zonarez β, 115, M_n 650) with a weight mixing ratio (*i*PP/β-P) equal to 90/10 was prepared by extrusion at 280°C.

Films obtained through nonisothermal crystallization were dyed in water starting at 40°C, raising the temperature up to 80°C in 45 min and keeping this temperature for 1 h. Film dyeing was carried out with 0·5–1·0% dyestuff calculated on the weight of the film.

The morphological characteristics of the samples are reported in Table 1. The values of the crystallinity index (α) and T_g were obtained with a Perkin–Elmer DSC-4 scanning calorimeter. The samples (5 mg) were heated starting from 40°C at a scanning rate of 10°C min^{-1}. The temperature and apparent enthalpies of fusion of the samples (T_m and ΔH^*, respectively) were obtained from the maximum and the area of the endothermic peaks. Indium was employed to calibrate the temperature scale and the heat of transition. The values of α were calculated from the equation $\alpha = \Delta H^*/\Delta H_{iPP}$, where ΔH^* is the apparent enthalpy of fusion of the blend under investigation and ΔH_{iPP} (55 cal g^{-1}) is the heat of fusion of 100% crystalline *i*PP used as reference.

The glass transition temperatures were determined by heating the samples from −33°C to 77°C at a rate of 40°C min^{-1}. The values of T_g were taken at the temperature corresponding to 50% transition.

TABLE 1

Morphological Characteristics of the Films Obtained from *i*PP/HOCP and *i*PP/β-P Blends

Sample		*Melting temperature (°C)*	*Crystallinity index*	*Glass transition temperature (°C)*	
				Experimental	*Fox equation*
*i*PP/HOCP	100/0	164	0·43	−14	
	95/5	163	0·40	−8	−8·8
	90/10	162	0·36	−3	−4·0
	50/50	158	0·21	+19	+27·0
	0/100		0·0	+53	
*i*PP/β-P	90/10	161	0·37	+5	−2·0
	0/100		0·0	+70	

2.2 Measurements

For the kinetic measurements, the polymer films, dyed as described above, were sandwiched between two quartz plates and exposed for 15 min in a thermostatted system to the light of a 100-W tungsten lamp, a time long enough to reach a photostationary state.[13] After irradiation the film was quickly introduced into the cell compartment of a Beckman DU7 spectrophotometer thermostatted at the same temperature as the irradiation. The thermal return was monitored as the change in absorbance at a wavelength corresponding to the absorption maximum of the *trans*-isomer.

3 RESULTS AND DISCUSSION

Blends of *i*PP and HOCP and blends of *i*PP and β-P exhibit in every case a single T_g value depending on their composition; this fact and other experimental data previously reported[9-12] reveal the presence in the blends of a single homogeneous amorphous phase. The T_g values of the blends considered (Table 1) increase with HOCP or β-P concentration and are in most cases in good agreement with those evaluated from the Fox equation.[8] The uniqueness of the amorphous phase in the blends under examination is due to the miscibility at molecular level of the polymers in the melted state.[11] Such a phase is constituted by the amorphous fractions of crystallizable polymer *i*PP and noncrystallizable glassy polymers HOCP or β-P.

The thermal *cis–trans* isomerization of dyes **I**–**IV** dispersed in polymer films of various compositions has been studied kinetically in the temperature ranges reported in Table 2, which also shows the corresponding rate constants at 20°C and the activation parameters obtained according to the Eyring equation.

Apart from the cases of pure HOCP and *i*PP/HOCP 50/50 blend, all the samples were examined at temperatures higher than the T_g values of the corresponding blends. Thus, as expected, a single first-order kinetics was observed. On the other hand, for pure HOCP the temperature range explored was lower than the T_g value of the polymer. Consequently, the kinetics of the thermal *cis–trans* isomerization could be well resolved only by considering the process as the resultant of two simultaneous first-order reactions (indicated as 'slow' and 'fast' in the following text), according to a procedure previously described.[1,2] The data relative to these two reactions are reported in Table 2.

The T_g value of the blend *i*PP/HOCP 50/50 falls within the explored temperature range, so that two different behaviors were observed for all the dyes dispersed in this matrix: a single reaction and a complex process

TABLE 2

Thermal *cis–trans* Isomerization Rate Constants at 20°C (k)[a] and Activation Parameters (ΔH^* and ΔS^*) for Dyes **I–IV** in Films of Pure *i*PP, Pure HOCP and Their Blends

Dye	*Polymeric matrix*	*Single or slow reaction*[b]				*Fast reaction*[b]			
		Temperature range (°C)	10^3k (s^{-1})	ΔH^* ($kcal\,mol^{-1}$)	ΔS^* (*e.u.*)	*Temperature range (°C)*	10^3k (s^{-1})	ΔH^* ($kcal\,mol^{-1}$)	ΔS^* (*e.u.*)
I	Pure *i*PP	15–40	5·2	21·8 ± 2·3	5·9 ± 7·8				
	*i*PP/HOCP 95/5	15–40	6·0	30·1 ± 0·8	33·8 ± 2·7				
	*i*PP/HOCP 90/10	13–40	4·6	24·1 ± 1·3	13·0 ± 4·4				
	*i*PP/HOCP 50/50	13–40	3·9	25·4 ± 1·9	17·3 ± 6·5	13–20	50·0	31·6 ± 6·8	44·1 ± 23·5
	Pure HOCP	15–40	9·8	23·7 ± 1·3	13·1 ± 4·4	15–40	164·5	23·6 ± 1·3	18·6 ± 4·5
	*i*PP/*β*-P 90/10	13–40	4·1	26·6 ± 1·2	21·2 ± 4·0				
II	Pure *i*PP	15–40	18·4	21·0 ± 0·6	5·0 ± 1·9				
	*i*PP/HOCP 95/5	15–40	12·9	23·3 ± 3·7	12·4 ± 1·4				
	*i*PP/HOCP 90/10	5–40	12·4	24·2 ± 0·9	15·4 ± 2·0				
	*i*PP/HOCP 50/50	13–40	10·0	23·5 ± 1·2	12·7 ± 4·1	13–20	85·4	20·5 ± 0·6	6·6 ± 2·1
	Pure HOCP	15–40	19·0	20·7 ± 1·5	4·3 ± 3·8	15–40	194·2	12·1 ± 4·9	−20 ± 16
	*i*PP/*β*-P 90/10	5–40	12·7	23·4 ± 0·6	12·6 ± 2·0				
III	Pure *i*PP	15–40	151·6	18·7 ± 1·3	1·8 ± 4·3				
	*i*PP/HOCP 95/5	15–40	154·1	18·4 ± 0·6	0·4 ± 1·9				
	*i*PP/HOCP 90/10	13–40	174·1	15·8 ± 1·2	−8·2 ± 4·1				
	*i*PP/HOCP 50/50	13–40	155·4	18·0 ± 0·8	−0·8 ± 2·8	13–20	1495	11·7 ± 1·1	−17·7 ± 3·7
	Pure HOCP	15–40	73·4	12·3 ± 0·1	−21·9 ± 3·0	15–40	536·1	16·3 ± 0·5	−3·9 ± 0·8
	*i*PP/*β*-P 90/10	13–40	210·2	15·3 ± 1·6	−9·7 ± 5·3				
IV	Pure *i*PP	15–40	7·1	25·2 ± 0·4	17·5 ± 1·3				
	*i*PP/HOCP 95/5	15–40	4·4	23·0 ± 1·4	8·6 ± 4·8				
	*i*PP/HOCP 50/50	15–40	4·2	26·4 ± 0·9	13·6 ± 3·0	15–22	60·7	23·7 ± 0·9	17·2 ± 3·1
	Pure HOCP	15–40	2·0	19·5 ± 0·3	−4·6 ± 1·0	15–40	21·4	12·2 ± 0·1	−24·7 ± 0·4
	*i*PP/*β*-P 90/10	15–40	5·7	26·3 ± 3·3	20·7 ± 9·0				

[a] Calculated according to the Eyring equation.

[b] For definition of fast and slow reaction see text.

resolved in two simultaneous first-order reactions were obtained above and below the T_g value, respectively; the corresponding kinetic parameters are collected in Table 2.

The Arrhenius plots of the two cases aforementioned are shown in Fig. 1 for dye **II**, chosen as an example. It is evident that the values of the logarithm of the rate constants (k) of the slow reaction in *i*PP/HOCP 50/50 blend align with those of the single reaction measured above T_g, namely in the first part of the diagram. This indicates that, on going from temperatures higher than T_g to temperatures lower than T_g, there is not a complete discontinuity of the free volume distribution in the amorphous phase. The appearance of the 'fast' reaction reflects the intervention of further constrictions of the dye due to unequal microenvironment and different free volume availability of the disperse dyes in the amorphous region of the glassy polymeric matrix. Similar results were obtained with all the other dyes.

In Fig. 2 are reported the Arrhenius plots for the *cis–trans* isomerization of dye **II**, chosen again as an example, in all the blends studied here (without considering the fast reactions in the case of pure HOCP and *i*PP/HOCP 50/50 blend).

The more reliable experimental data (namely those not involving the

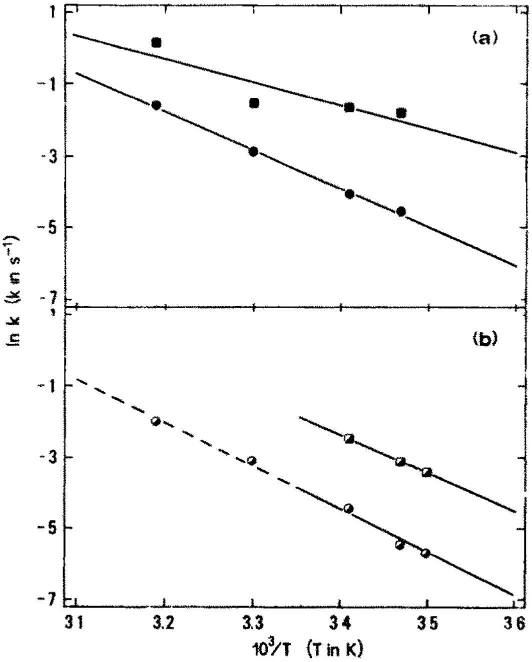


Fig. 1. Arrhenius plots for dye **II** in (a) pure HOCP, (b) *i*PP/HOCP 50/50 blend. ■ and ●, as well as ◪ and ◑, refer to 'fast' and 'slow' reactions, respectively. (—, below Tg; – – –, above Tg.)

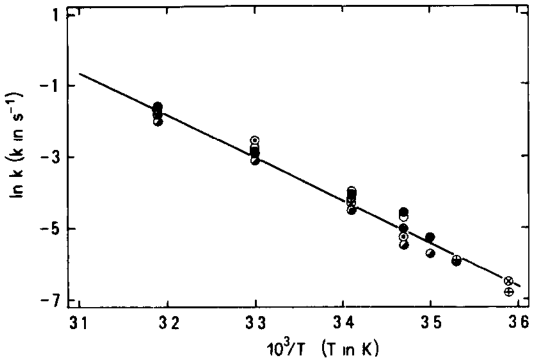


Fig. 2. Arrhenius plots for dye **II** in (a) pure HOCP (●), (b) *i*PP/HOCP 50/50 (◑), (c) *i*PP/HOCP 90/10 (⊕), (d) *i*PP/HOCP 95/5 (⊙), (e) pure *i*PP (○), (f) *i*PP/*β*-P 90/10 (⊗).

splitting of the process in slow and fast reactions) show that in most cases, for the same dye, the kinetic behavior of thermal *cis–trans* isomerization does not significantly change on going from films of pure *i*PP to films of blends with increasing concentrations of HOCP or *β*-P. In other words, the variations of the kinetic parameters brought about by changing the concentration of the components and the composition of *i*PP blends were found to be within the experimental error involved in kinetic measurements on films, often with a hardly reproducible morphology of the microzones.

These results indicate that the behavior of dyes in the amorphous phase of the blends is not affected by any modification of the crystalline phase. The independence of the dye isomerization kinetics on the nature and concentration of the matrix is reasonably due to the compatibility and solubility of HOCP and *β*-P with *i*PP, which gives rise to homogeneous mixtures. Moreover, these polymers present similar chemical structures and polarities and possess no groups able to give specific interactions with the dye, such as hydrogen bonds, that strongly affect the isomerization kinetics here considered.[14] Previous studies on the solvent effect on the kinetics of the thermal *cis–trans* isomerization have shown that, as an example, the rate constant of dye **III** at 25°C is $5{\cdot}0 \times 10^{-3}\ \mathrm{s}^{-1}$ in cyclohexane and $7{\cdot}1 \times 10^{-3}\ \mathrm{s}^{-1}$ in *n*-heptane.[15] Therefore it is not surprising also that similar chemical structures of the polymer matrices lead to similar isomerization rates.

Considering now the 4′-position of 4-diethylaminoazobenzene, the substituent effect on the reaction under examination can be evidenced by the sequence of kinetic coefficients at 20°C (i.e. $k_{\mathrm{I}}{:}k_{\mathrm{II}}{:}k_{\mathrm{III}} \approx 2{:}5{:}70$) where the numerical values come from averaging the rate constants of the considered dye in all the investigated blends. This series is in line with that observed in *n*-hexane for the same dyes.[16]

As far as the influence of the different position of the substituent on the aromatic nucleus of the azo dye is concerned, one can compare the kinetic coefficients relative to compounds **III** and **IV**. As expected, the values for the 4′-substituted dye were found to be higher than those for 3′-substituted dyes, in this case by a factor of about 30. Such a difference is analogous to that observed for the same reaction of the same dyes in cyclohexane solution, where a ratio of $k_{III}/k_{IV} \approx 50$ was obtained.[14,15]

The above results show that, even if solid systems usually lower the substituent effects, these phenomena are still clearly evident in this case.

4 CONCLUSION

The results show evidence that the kinetics of the thermal *cis–trans* isomerization of azobenzenes dispersed in polymeric matrices is a sound probe for characterizing the transition from rubbery to glassy state of the medium with the appearance of a multiplicity of first-order reactions. However, within the temperature range of the rubbery state, no significant variation of kinetic rates has been observed for the four azo dyes considered in the different isotropic blends of *i*PP/HOCP and of *i*PP/β-P, even in the presence of marked changes of the T_g values.

This behavior supports the hypothesis that the kinetics of the *cis–trans* isomerization is essentially determined by the microstructure of the polymer amorphous regions where the dye is sited in the dyeing process, and that these amorphous regions are quite similar for the various blends under examination.

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REFERENCES

1. Dubini-Paglia, E., Beltrame, P. L., Marcandalli, B., Carniti, P., Seves, A. & Vicini, L., *J. Appl. Polym. Sci.*, **31** (1986) 1251.
2. Beltrame, P. L., Dubini-Paglia, E., Marcandalli, B., Sadocco, P. & Seves, A., *J. Appl. Polym. Sci.*, **33** (1987) 2963.
3. Beltrame, P. L., Dubini-Paglia, E., Marcandalli, B. & Seves, A., *J. Appl. Polym. Sci.*, **38** (1989) 755.
4. Dubini-Paglia, E., Beltrame, P. L., Seves, A. & Prati, G., *J. Soc. Dyers Col.*, **105** (1989) 107.

5. Dubini-Paglia, E., Beltrame, P. L., Marcandalli, B. & Seves, A., *J. Appl. Polym. Sci.*, **41** (1991) 765.
6. Seves, A., Romanò, M., Dubini-Paglia, E. & Beltrame, P. L., *J. Appl. Polym. Sci.*, **43** (1991) 1821.
7. Beltrame, P. L., Dubini-Paglia, E., Seves, A., Pellizzoni, E. & Romanò, M., *J. Appl. Polym. Sci.*, **44** (1992) 2095.
8. Fox, T. G., *Bull. Am. Phys. Soc.*, **2** (1956) 123.
9. Di Liello, V., Martuscelli, E., Ragosta, G. & Buzio, P., *J. Materials Sci.*, **24** (1989) 3235.
10. Martuscelli, E., Canetti, M. & Seves, A., *Polymer*, **30** (1989) 304.
11. Martuscelli, E., Silvestre, C., Canetti, M., De Lalla, C., Bonfatti, A. & Seves, A., *Makromol. Chemie*, **190** (1989) 2615.
12. Seves, A., unpublished results.
13. Marcandalli, B., Seves, A., Dubini-Paglia, E. & Beltrame, P. L., *Dyes & Pigments*, **14** (1990) 79.
14. Marcandalli, B., Beltrame, P. L., Dubini-Paglia, E. & Seves, A., *Dyes & Pigments*, **11** (1989) 179.
15. Schanze, K. D., Fleming Mattox, T. & Whitten, D. G., *J. Org. Chem.*, **48** (1983) 2808.
16. Marcandalli, B., Pellicciari-Di Liddo, L., Di Fede, C. & Bellobono, I. R., *J. Chem. Soc., Perkin II* (1984) 589.