

Cis-Trans Isomerization of Aromatic Azo Compounds Built in the Polyester Segment of Poly(ester urethanes)

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Summary

The photochemical and thermal cis-trans isomerization of 4,4 - (diamido)azobenzene derivative built in the polyester segment of a segmented poly(ester urethane) has been investigated.

The photoisomerization in bulk proceeds more slowly than in solution and lower fractions of cis-isomers are reached in the photostationary state. The thermal cis-trans isomerization follows first order kinetics in polymers with amorphous soft phase but can only be described by two simultaneous first order processes in annealed samples. This is attributed to restrictions in the chain segmental mobility; it is assumed that the isomerization behaviour reflects different molecular motions in the bulk polymer.

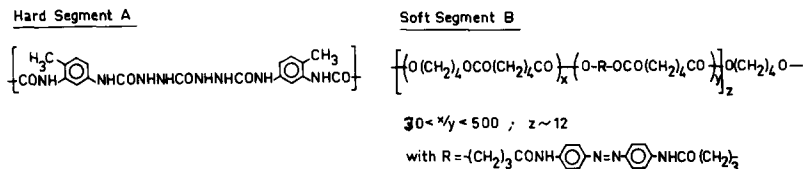
Introduction

The effects of an amorphous polymer matrix on the photochromic behaviour of a pendent or dissolved chromophore on a microscopic or molecular scale have been investigated and discussed in recent work¹⁻³). It was found that photochromic processes are controlled by the free volume and the segmental mobility. The temperature dependence of the thermal back reaction in the rubbery state can be described by the WLF-theory^{4,5}). In the glassy state it was concluded that the figures of the apparent energies of activation for these reactions reflect particular segmental (rotational or crankshaft and translational) motions of the polymer matrix needed for providing the free volume for the reaction.

The interesting question to which extent this is valid when the photochrome is built in the polymer backbone can only be studied when the chain segments are sufficiently flexible; in this case additional restrictions due to the binding of the chromophore to the polymer chain on both sides might be imposed. The only systems with photochromes in the polymer backbone studied so far were very stiff polyesters, polyamids or polyimide⁶⁻⁹). Due to the high glass transition temperature T_g and partially high degrees of crystallinity the photoisomerization process was suppressed completely or to a great extent. These restrictions should be overcome by incorporating the chromophore in a flexible chain which is part of a rubbery matrix, e.g. the polyester or polyether segment in segmented polyester- or polyether-urethanes.

In this paper the preliminary results on the cis-trans isome-

rization of an aromatic azo compound incorporated in the polyester segment of two poly(ester urethans) $\{A-B\}_n$ with random distribution of hard and soft segment length (PEUC 1: $x/y = 29$; PEUC 2: $x/y = 62$) are being reported.



Experimental

The aromatic azo chromophore 4,4'-di(4-hydroxybutyramido)azobenzene was synthesized following the procedure as given for the monosubstituted analog ¹⁾; mp 259 °C.

Copolyesters with terminal hydroxyl groups were prepared by copolycondensation of the azo chromophore with 1,4-butanediol and adipic acid in toluene ¹⁰⁾. The poly(ester urethanes) were synthesized by reacting the chromophoric polyesters with tolylene-2,4-diisocyanate (molar ratio NCO/OH = 1,7) and subsequent addition of carbohydrazide to the DMF solution ^{10, 11)}. The polymers were purified by two reprecipitations from CH₂Cl₂/methanol and dried for 48 hrs. at 40 °C in vacuo.

The polymers were characterized by GPC and osmotic measurements. The melting and annealing behaviour of the poly(ester urethanes) was investigated with a Perkin-Elmer DSC-2 and the relaxation behaviour was measured using a Lonza Torsions Automat.

Polymer films were prepared by casting 0,5% CH₂Cl₂-solutions on glass plates. After the solvent had evaporated the films were peeled off under water, dried for 48 hrs. at 100 °C in vacuo and then quenched by dipping a test tube with the film in ice water. For annealing the films were kept for 24 hrs at 43 °C.

The experimental conditions for the photoisomerization and the kinetic studies were the same as described earlier ¹⁾.

Results and discussion

The melting and annealing behaviour of the polymers was first investigated in order to check the influence of the thermal history on the morphology of the poly(ester urethane). The polymers precipitated from solution exhibited in the DSC-measurements a melt endotherm at $T_m = 45$ °C which was also found in the starting polyester and which is ascribed to the melting of crystalline aggregates of soft segments. This endotherm peak disappears after the sample was heated up to 100 °C and then quenched from the melt, but when the sample was annealed some degrees below the temperature of the peak maximum again a melt endotherm could be detected. This shows that the morphology of the sample under investigation can be changed by different thermal treatment of the polymer film and it allows to study the influence of crystalline aggregates of soft segments on the isomerization behaviour of the

azo chromophores in the soft phase. The glass transition temperature T_g of the polyester in the poly(ester urethanes) is around $-40\text{ }^\circ\text{C}$. The same figures for T_g and T_m were also obtained from mechanical dynamical experiments. Little evidence for crystalline domains of the hard segments was obtained from the DSC-data; this explains why these poly(ester urethanes) were poor elastomers and thus started to flow already at around $70\text{ }^\circ\text{C}$ in the torsion pendulum experiment.

The photochemical trans-cis isomerization of the aromatic azo compound was achieved by irradiation at the maximum absorption band of the trans-isomer at $\lambda = 378\text{ nm}$ (Fig. 1). The rate of isomerization and the fraction y of cis-isomers in the photostationary state is lower in the bulk polymer than in solution (Fig. 2)

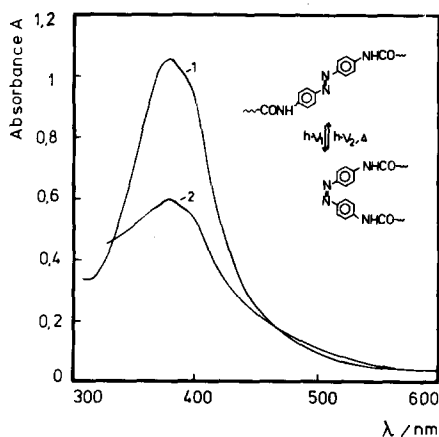


Fig. 1

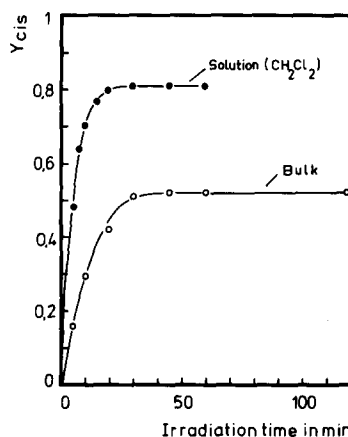


Fig. 2

Fig. 1: UV-Absorption spectra of PEUC-2-film before (curve 1) and after 20 min irradiation at $\lambda = 378\text{ nm}$ (curve 2).

Fig. 2: Photoisomerization ($\lambda = 378\text{ nm}$) of the azo chromophore in PEUC-1-film.

The photoisomerization proceeds only little faster in the sample quenched from the melt but the fraction y of cis-isomers in the photostationary state ($y = 0,53$) remained unchanged and could not be increased by prolonged irradiation. Obviously the mobility of the chromophore is decreased by placing the chromophore in the backbone of a polymer. In order to achieve the trans-cis isomerization a pendent chain segment has to slip through the polymer matrix and this process certainly is restricted in the bulk polymer. The process involves a decrease in the distance between the para carbons in the azobenzene derivative from $9,0$ to $5,5\text{ \AA}$ (12) and the local contraction is even larger because of the rigidly attached amide groups (cf. ⁷). This contraction might induce some tension in the matrix which favours the cis-trans back reaction and therefore a lower fraction y of cis-isomers is obtained.

The thermal cis-trans isomerization was followed by measuring

the change in the absorption at $\lambda = 378$ nm. Simple first order kinetics were obtained for the chromophoric polyester in ethyl acetate solution with slightly lower rate constants and activation parameters as for the corresponding low molecular weight azo chromophore 4,4'-(isobutyrylamino)azobenzene ($E_a = 80,0$ kJ/mol).

In polymer films straight first order plots were obtained at temperatures above T_m but below T_m only for the samples quenched from the melt (curve 4, Fig. 3); the rate constants k_3 were similar to those in solution. For the annealed samples the plots were curved (curve 1, Fig. 3) but could be resolved by two simultaneous first order reactions, i.e. the total rate equation is given by

$$[T]_{\infty} - [T] = [A]_0 \cdot \exp(-k_1 t) + [B]_0 \cdot \exp(-k_2 t)$$

with $[T]_{\infty}$ representing the total concentration of trans-isomers at infinite time, $[T]$ its concentration at time t and $[A]_0$ and $[B]_0$ are the concentrations of the two differently fast isomerizing cis-isomers. The rate constants of the thermal cis-trans isomerization of the azo chromophores in thermal differently treated polymer film at various temperatures are represented in the Arrhenius-plot (Fig. 4).

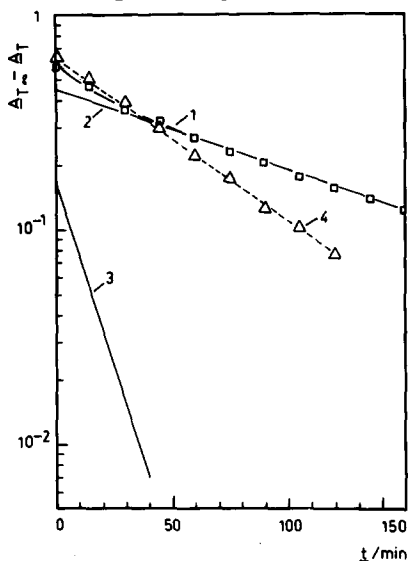


Fig. 3

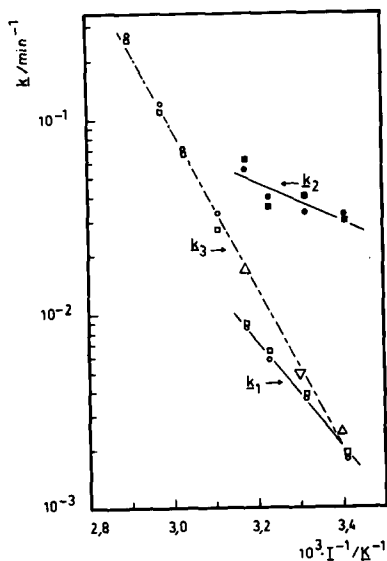


Fig. 4

Fig. 3: First order plots for the thermal cis-trans isomerization of the azo chromophore at 40°C in bulk PEUC-2. Experimental curve (\square , 1) for the annealed polymer, its resolution by two first order reactions (2, 3) and for the polymer quenched from the melt (Δ , 4).

Fig. 4: Arrhenius plot for the different rate constants k of the thermal cis-trans isomerization of the azo chromophore in bulk PEUC-1 (∇ ; \circ ; \bullet) and PEUC-2 (Δ ; \square ; \blacksquare); (—): annealed polymer; (---): polymer with amorphous soft phase.

The temperature dependence of the rate of isomerization in the completely amorphous samples (k_3) is characterized by a single apparent energy of activation $E_a = 79,7$ kJ/mol, a similar figure as found in solution (s. above). This result is in agreement with the data obtained for dissolved or pendent azo chromophores in rubbery polymers ¹⁾. It shows that the thermal back reaction proceeds in rubbery matrices far above T_g as in solution and that in this case it is independent from the kind of attachment of the chromophore to the polymer.

In the annealed samples, in contrast to this, the thermal relaxation from the cis- to the trans-isomer is characterized by two simultaneous processes with lower apparent energies of activation than in solution. This behaviour and the figures are comparable to those found for the isomerization of pendent or dissolved azo chromophores in glassy acrylic or methacrylic polymers ¹⁾. The two processes are characterized by an activation energy of $E_a = 59,1$ kJ/mol (k_1 , Fig. 4) and $E_a = 19,1$ kJ/mol (k_2 , Fig. 4) and these figures again are in agreement with the energies required for a crankshaft motion ¹³⁾ and a translational motion ^{1, 13)}. This suggests that in the annealed samples rotational and translational motions of chain segments are the controlling parameters for the thermal cis-trans relaxation, too. The effect of annealing the sample is considered to create more physical crosslinks between polyester segments which reduces the overall chain segmental mobility; this leads to similar controlling parameters for the thermal back reactions as in a glassy amorphous phase. From the presently available data it can not yet be decided if or to which extent the apparent energies of activation observed for the thermal cis-trans reaction reflect motions of the polymer chain fixed to the chromophore or of neighbouring chain segments.

In conclusion it can be summarized that the kinetics of the cis-trans isomerization of aromatic azo compounds built into the backbone of flexible chains are strongly affected by the thermal history of the sample. Changes in the morphology lead to different chain segmental mobilities which are reflected by the apparent energies of activation for the thermal back reaction. These relations clearly show that photochromic processes can be employed for studying structure and morphology of polymers and chain segmental mobilities. This will be studied in more detail in future work on partially crystalline polymers and polymer networks.

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