Makromol. Chem. **179**, *2489–2506 (1978)*

Effect of Polymer Matrix on the *Cis-Trans* Isomerization of Azobenzene Residues in Bulk Polymers

Claus D. Eisenbach

Institut für Makromolekulare Chemie, Universität Freiburg,
Stefan-Meier-Straße 31, D-7800 Freiburg i. Br., BRD

(Date of receipt: January 24, 1977)

SUMMARY:

Several acrylates and methacrylates were copolymerized with two 4-aminoazobenzene methacrylic derivatives. The photochemical and thermal *cis-trans* isomerization about the azolink was investigated in the bulk polymers. All the copolymers show photochromic behaviour without fading; the photostationary states upon irradiation with UV-light of the appropriate wavelengths were similar in bulk and in solution. The thermal *cis-trans* isomerization follows simple first order kinetics in the rubbery specimens as in solution. Below the glass transition temperature T_g, the isomerization can only be described by two simultaneous first order reactions. Depending on the conditions of irradiation and on the reaction temperature, a portion of the azoaromatic compound reacts anomalously fast. The temperature dependence of the relaxation time of the isomerization reaction in all the polymer films investigated can be represented by a single WLF-type graph; the corresponding Arrhenius plot is curved above T_g. The findings are interpreted by considering the effects of the free volume and of the chain segmental mobility on the *cis-trans* isomerization. A rotational and a translational relaxation mechanism is discussed for the normal and the anomalously fast reaction below T_g.

Introduction

The investigation of the chemical and physical behaviour of photochromic moieties in polymer matrices and the influence of polymers on photochromism has been started only recently; a detailed review of the work in that field has been given by Williams and Daly[1].

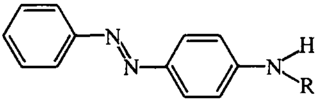
From literature studies it is obvious, that the nature and the morphology of the polymer has an essential influence on the photo- and thermochromism of a chromophore in a polymer matrix. A comparison of results of different authors is difficult, however, because the systems investigated and the experimental conditions employed are too different; i.e. besides some vague conclusions, no meaningful theories exist how photochromic processes are linked to polymer properties. Therefore it is interesting to study systematically the effects of structure and morphology of a family of polymers on the reactivity of a chromophore, including the influence of covalent bonding of the chromophore to the polymer and the spacer length.

In this work the *cis-trans* isomerization of aromatic azo compounds was investigated. These chromophores do not show any fading, thus excluding a decrease in the concentration of the isomerizable azo groups during the experiments; besides, one can easily manipulate the rate of isomerization by introducing various substituents at the aromatic nuclei[2].

Polymeric matrices were acrylate and methacrylate polymers; this class of polymers allows a broad variation of the physical properties of the polymer matrix in a suitable temperature range by varying the ester groups[3]. The monomers chosen were methyl (MMA), ethyl (EMA), butyl (nBMA) and isobutyl methacrylate (iBMA) as well as methyl (MA) and ethyl acrylate

(EA). The corresponding polymers differ in their glass transition temperature T_g by about 130°C, going from +105°C (PMMA) to −24°C (PEMA)[4].

The chromophoric comonomers were derivatives of 4-aminoazobenzene (**1**, R = H), i.e. 4-methacryloylaminoazobenzene (**1a**) and 4-[4-(methacryloyloxy)butyrylamino]azobenzene (**1c**), both comonomers giving comonomeric units with different spacer length. The corresponding isobutyramide **1b** and acetic acid ester **1d** were chosen as model compounds for the chromophoric comonomers.



1

	R
1a	$H_2C{=}C(CH_3)CO$
b	$(H_3C)_2CHCO$
c	$H_2C{=}C(CH_3)CO_2(CH_2)_3CO$
d	$H_3CCO_2(CH_2)_3CO$

Experimental Part

Monomers and model compounds

The various alkyl acrylate and methacrylate monomers employed were purified in the usual way and fractionated under Ar in vacuo.

4-Methacryloylaminoazobenzene (**1a**): 1,57 g (0,015 mol) methacryloyl chloride were slowly dropped into a solution of 1,97 g (0,01 mol) 4-aminoazobenzene (Eastman Kodak) in 20 ml pyridine at 30°C and the mixture was kept at 60°C for 1 h. The reaction mixture was poured into 50 ml of ice water and acidified with conc. aq. hydrochloric acid; the amide was collected on a Büchner-funnel, washed with 10% aq. sodium bicarbonate solution followed by water and recrystallized from ethanol. Yield: 1,9 g (72%); mp 148°C (150°C[5]).

4-Isobutyrylaminoazobenzene (**1b**) was synthesized with isobutyryl chloride in the same way as described for **1a**. Yield: 2,2 g (82%); mp 169°C.

$C_{16}H_{17}N_3O$ (267,3)	Calc.	C 71,89	H 6,41
	Found	C 71,53	H 6,54

UV (Ethyl acetate): $\lambda_{max} = 353$ nm ($\varepsilon = 25400$ l·mol^{-1}·cm^{-1}).

4-[4-(Methacryloyloxy)butyrylamino]azobenzene (**1c**) was synthesized in a three step procedure: 7,5 g (0,045 mol) 4-acetoxybutyryl chloride[6], dissolved in 10 ml acetonitrile, were dropped slowly at 30–40°C into a solution of 7,0 g (0,036 mol) 4-aminoazobenzene in 25 ml acetonitrile and 10 ml pyridine; the mixture was stirred for 40 min at room temperature and then the 4-(4-acetoxybutyrylamino)azobenzene (**1d**) was isolated and purified as described above. Yield: 8,9 g (76%); mp 136°C.

$C_{18}H_{19}N_3O_3$ (325,4)	Calc.	C 66,45	H 5,89
	Found	C 66,22	H 5,78

UV (Ethyl acetate): $\lambda_{max} = 353$ nm ($\varepsilon = 28300$ l·mol^{-1}·cm^{-1}).

For the aminolysis of the acetyl group 3,25 g (0,01 mol) of **1d** were dissolved in 1,3 ml 3-aminopropanol and 0,9 ml DMF and the solution was stirred at 85°C for 24 h. After cooling of the reaction mixture, water was added until the 4-hydroxybutyramide, i.e. 4-(4-hydroxybutyrylamino)azobenzene, had precipitated. The product was collected on a Büchner-funnel, washed with water, and recrystallized from aq. ethanol. Yield: 2,2 g (77%); mp 151°C.

$C_{16}H_{17}N_3O_2$ (283,3)	Calc.	C 67,83	H 6,14
	Found	C 67,63	H 6,09

The methacrylic acid ester **1c** was obtained by dropping 0,23 g (2,2 mmol) methacryloyl chloride, dissolved in 2,5 ml acetonitrile, into a solution of 0,5 g (1,77 mmol) of 4-(4-hydroxybutyrylamino)azobenzene (s. above) in 10 ml acetonitrile and 25 ml pyridine at 10°C. The mixture was then stirred at room temperature for 30 min; the product was purified in the usual way and recrystallized from aq. ethanol. Yield: 0,49 g (79%); mp 145°C.

$C_{20}H_{21}N_3O_3$ (351,4)	Calc.	C 68,36	H 6,02
	Found	C 67,92	H 6,16

Polymers

All polymerizations were carried out under Ar at 75°C in toluene as solvent with azoisobutyronitrile (AIBN) as initiator; in the copolymer synthesis the reaction mixture contained about 0,1 mole-% of the azoaromatic comonomer. The copolymers were reprecipitated twice from toluene/heptane and dried for 48 h at 40°C in vacuo. Molecular weights were determined by viscosity measurements (acetone, 25°C) and found to be in the range of $6-8\cdot10^4$ for all polymers, i.e. the copolymers contained about one azo chromophore per polymer chain.

In a typical run, a 100 ml long-necked flask was charged with 8,0 mg ($3{,}02\cdot10^{-5}$ mol) **1a**, 8,0 mg ($4{,}9\cdot10^{-6}$ mol) AIBN and then 50 ml dry toluene were distilled in under Ar. The flask was closed with a three-way stop cock fitted with a serum cap and an Ar-balloon and then 3,0 ml (28,3 mmol) MMA were injected by using a syringe. After 24 h polymerization, the reaction mixture was cooled and the copolymer CoP(MMA-**1a**)*) precipitated into heptane. Yield after twofold precipitation: 2,25 g (79%); M_n (osm) = 61000; intrinsic viscosity $[\eta] = 21{,}3$ ml/g (acetone, 25°C), $M_v = 86000$[7]. Films of about 0,03 mm thickness were prepared by casting 3% acetone solutions on glass plates. After the solvent had evaporated, the films were first dried at 40°C and 0,01 Torr for 48 h, then peeled off under water (except CoP(MA-**1a**) and CoP(EA-**1a**)) and dried again for 48 h.

Kinetic studies

Solutions of the model compounds and the copolymers in ethyl acetate and the copolymer films were placed in 1 cm quartz-cells which could be thermostatted at ±0,5°C.

Photoisomerizations were carried out by irradiation with a 150 W High Pressure Xenon Lamp (Osram HBX 150). The appropriate wave lengths were selected with a Leitz monochromator, picking out a spectral window at 355 nm (half width 38 nm) and 450 nm (half width 27 nm). The light intensities, as measured with a radiometer (YS1-Model 65 A, Curtin Matheson Scientific, Inc.) were 8,9 and 6,7 W/m², respectively.

After irradiation, the UV-spectra were recorded with a Hitachi Perkin Elmer Model 200 Spectrophotometer. When investigating the solutions of the model compounds or the copolymers, the pure solvent or a solution of corresponding homopolymer of the same concentration, respectively, were placed in the reference beam; in the case of copolymer films, a homopolymer film of the same thickness was placed in the reference beam.

The rate of isomerization was followed by measuring the increase of the absorption at $\lambda = 353$ nm with the reaction time. Validity of Beer's law was assured, so that the absorbance A could be used directly for the evaluation of the data; it was assumed, that the absorption coefficients of the model compounds (**1b** and **1d**) and the corresponding comonomeric units in the polymer chain were identical.

Results

Photochemical isomerization

Aromatic azo compounds can easily be isomerized by irradiation with UV-light of the appropriate wave length[2,8]. Irradiation in the region of the main absorption band (Π—Π^*-transition) of the *trans*-form ($\lambda_{max} = 353$ nm for **1a** and **1d**) creates the *cis*-isomer in high yields,

---

*) In the following the same abbreviations are used for the other copolymers, too, i.e. CoP(EMA-**1a**) means copolymer of ethyl methacrylate and **1a**, etc.

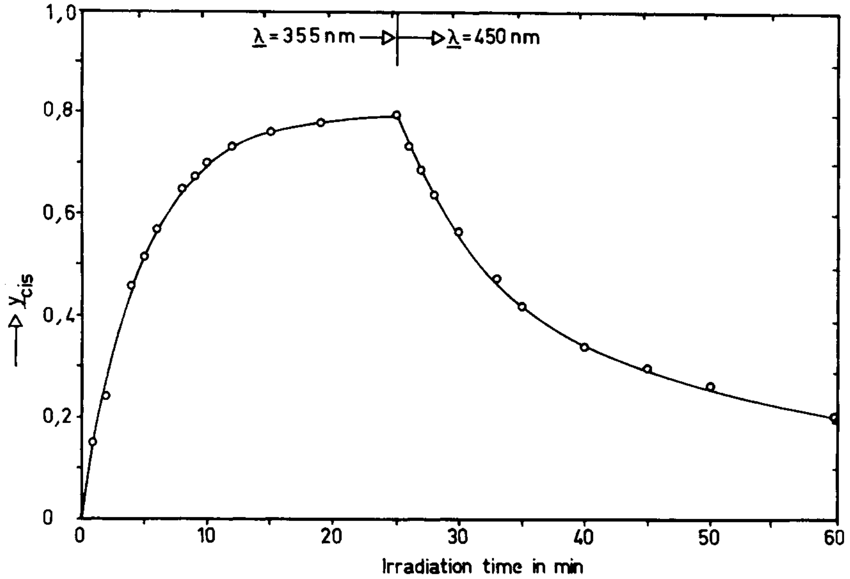


Fig. 1. Photochemical *trans-cis* and *cis-trans* isomerization cycle of the azo chromophore in bulk CoP(EMA-**1a**) at 25°C. Fraction y of *cis*-isomer as a function of irradiation time t; photostationary states: $y=0{,}84$ ($\lambda=353\,\text{nm}$) and $y=0{,}19$ ($\lambda=450\,\text{nm}$)

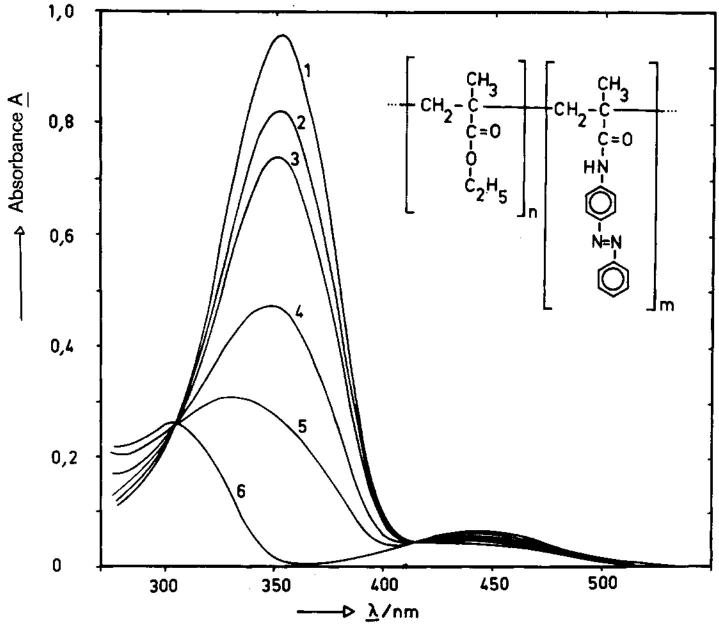


Fig. 2. Absorption spectra of bulk CoP(EMA-**1a**) after different periods of irradiation at $\lambda=355\,\text{nm}$. 1: before irradiation; 2: 1 min ($y=0{,}15$); 3: 2 min ($y=0{,}24$); 4: 5 min ($y=0{,}51$); 5: 12 min ($y=0{,}73$); 6: calculated curve for pure *cis*-isomer

whereas by irradiation in the $n-\Pi^*$-absorption band region around 440 nm, mainly the *trans*-isomer is formed (Fig. 1). This photoisomerization cycle can be repeated without fading both in solution and in bulk polymers. The absorption spectra of a CoP(EMA-**1a**) film with different fractions y of the *cis*-isomer are depicted in Fig. 2. The occurrence of isosbestic points ($\lambda=413$ and 303 nm) shows, that in a polymeric matrix, too, this monomolecular transformation is characterized by the presence of only two spectrophotometrically distinguishable species.

The whole absorption spectrum can be described by the overlapping of several Gaussian curves (Fig. 3). Both the $\Pi-\Pi^*$-absorption bands of the *trans*-form at 353 nm and of the *cis*-form at 309 nm (s. curves 2 and 3, Fig. 3) could be resolved, each by two in their shape unchangable Gaussian curves. This finding allows the $\Pi-\Pi^*$-absorption bands of the two isomers to be separated and the area below these bands is directly proportional to the concentration of the *trans*- and *cis*-isomer in the sample. The weak $n-\Pi^*$-absorption band at 440 nm, which increases with increasing *cis*-content (accompanied by a slight shift in the absorption maximum to shorter wave lengths) can be represented by a single Gaussian curve. On conversion to the *cis*-isomer, there is an additional increase in the absorption on the short-wave edge, which is due to a *cis*-absorption band near 250 nm (as could be shown with **1b** in cyclohexane solution); this peak can be matched with a single Gaussian curve, too.

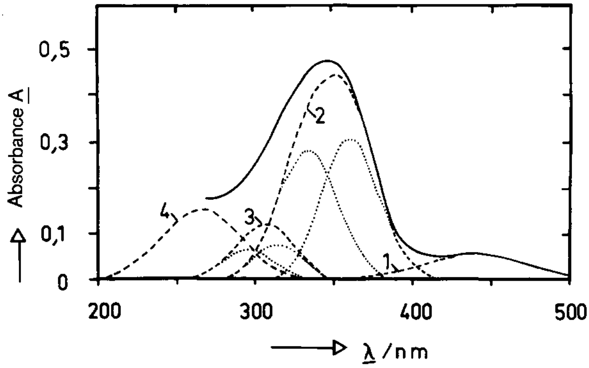


Fig. 3. Absorption spectra of bulk CoP(EMA-**1a**) with a fraction of *cis*-isomer $y=0{,}51$ (s. curve 4, Fig. 2). Resolution of the different absorption bands (dashed lines) by Gaussian curves (dotted lines). 1: $n-\Pi^*$-transition: 2: *trans*-$\Pi-\Pi^*$ transition; 3: *cis*-$\Pi-\Pi^*$ transition; 4: edge + *cis*-absorption

Calibration curves for the resolved absorption bands were set up and, knowing the shape of these Gaussian curves, one is able to construct the absorption curve for any *cis*/*trans*-ratio of the azobenzene derivatives in the UV and visible region (e.g. curve 6, Fig. 2). So it was proven, that the maximum of the $\Pi-\Pi^*$-absorption curve of the *trans*-form does not overlap with the corresponding *cis*-band (s. curves 2 and 3, Fig. 3), which had been postulated but was not yet proven[5,9,10].

No deviations from Beer's law were detected in solution or in the bulk polymer samples, i.e. the degree of isomerization can be calculated directly from the intensity of the maximum *trans*-absorption band.

At a given temperature and irradiation time, the concentration of the *cis*-isomer is lower in a glassy film than in a rubbery film (Tab. 1), due to the restrictions in segmental mobility below T_g; but the values achieved in rubbery samples approach those found for solutions of the copolymers or model compounds in ethyl acetate. After sufficiently long irradiation

Tab. 1. Fraction y of the azo chromophore **1** in the *cis*-form in different bulk polymer samples after 20 min irradiation ($\lambda = 355$ nm) at room temperature

Sample	T_g/°C[a]	y
1b		0,85[b]
1d		0,86[b]
CoP(MMA-**1a**)[c]	105	0,61
CoP(EMA-**1a**)	65	0,73
		0,78[d]
		0,83[e]
		0,88[b]
CoP(EMA-**1c**)	65	0,73
PEMA + **1b**[f]	65	0,80
CoP(iBMA-**1a**)	53	0,77
		0,82[g]
CoP(nBMA-**1a**)	20	0,78
CoP(MA-**1a**)	10	0,76
CoP(EA-**1a**)	−24	0,75

[a] Figures from ref.[3] for the corresponding polyacrylates and -methacrylates. T_g = glass transition temperature.

[b] In ethyl acetate solution.

[c] For the meaning of the abbreviations used s. footnote p. 2491.

[d] Irradiation at 80°C (average of No 7 and 12, Tab. 4).

[e] Irradiation time: 14 h (No 6, Tab. 4).

[f] Model compound **1b** in poly(ethyl methacrylate).

[g] Irradiation at 70°C (average of No 6 and 7, Tab. 5).

times similar photostationary equilibria as in solution were obtained in the glassy state. This shows, that even in a rigid polymer matrix the radiation induced *trans-cis* isomerization causes segmental motions for providing the space for the isomerization reaction, i.e. at least some redistribution of the free volume occurs.

Thermal cis-trans isomerization

In solution, the thermodynamically unstable *cis*-isomer[11] isomerizes thermally to the more stable *trans*-form by a first order reaction; the rate constants and the activation parameters usually depend only slightly on the solvent in polar aprotic media[12].

As was expected, simple first order kinetics were obtained for the thermal *cis-trans* isomerization of the polymer bound azoaromatic chromophore in solution, when plotting the change in the absorbance at $\lambda = 353$ nm (*trans*-isomer) vs. time (curve 1, Fig. 4); within the experimental error, there is only a very small polymer effect on the rate of isomerization, if any (Tab. 2).

In the solid state, straight first order plots up to high conversions were only obtained, if the copolymers were in the rubbery state (curve 3, Fig. 4). In the glassy state, the plots were curved (curve 2, Fig. 4). When extrapolating the linear portion of this curve to zero time, one obtaines from the difference between the experimental curve and the extrapolated line the time dependency of a second reaction[13]. In this way, the thermal *cis-trans* isomerization

Tab. 2. Kinetic parameters[a] of the thermal *cis-trans* isomerization of the model compounds **1b** and **1d** and of CoP(EMA-**1a**) in ethyl acetate solution; photochemical *trans-cis* isomerization by 20 min irradiation with $\lambda = 355$ nm at room temperature

Sample	$k_1 \cdot 10^3/\text{min}^{-1}$						E_A[b] kcal·mol^{-1}	$\Delta S^{\neq}$[b] cal·mol^{-1}·K^{-1}
	25°C	30°C	40°C	50°C	65°C	75°C		
1b	0,75	0,74	2,4	8,0	—	—	23,5	− 5,2
1d	0,64	—	2,9	7,7	49	110	22,1	− 9,8
CoP(EMA-**1a**)	—	0,78	2,3	6,4	—	—	20,1	−16,7

[a] k_1 = first order rate constant, E_A = apparent activation energy, $\Delta S^{\neq}$ = apparent activation entropy.
[b] SI-unit: 1 cal = 4,1868 J.

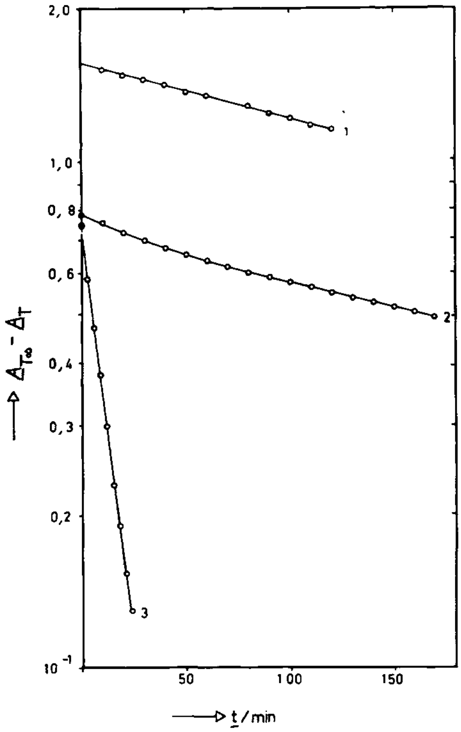


Fig. 4

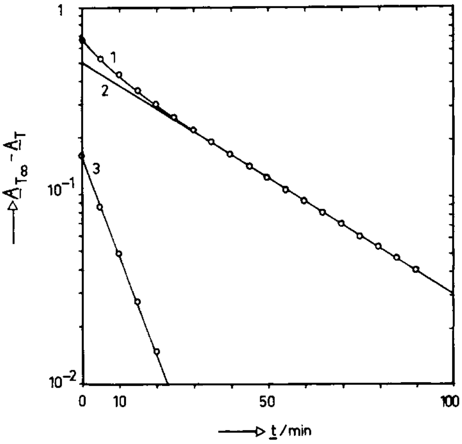


Fig. 5

Fig. 4. First order plots for the thermal *cis-trans* isomerization of the azo chromophore in CoP(EMA-**1a**) in ethyl acetate solution at 40°C (1) and in bulk at 40°C (2) and 80°C (3); $A_{T\infty}$, A_T: absorbance at $\lambda = 353$ nm (*trans*-isomer) at infinite time and at time *t*

Fig. 5. Resolution of the thermal *cis-trans* isomerization of the azo chromophore in CoP(EMA-**1a**) at 70°C using two first order reactions; $A_{T\infty}$, A_T: absorbance at $\lambda = 353$ nm (*trans*-isomer) at infinite time and at time *t*; exptl. curve (1): $\log[1{,}101 - A_T] = \log[0{,}521 \cdot \exp(-0{,}028t) + 0{,}168 \cdot \exp(-0{,}12t)]$; normal isomerization (curve 2: $\log A_{[A]} = \log[0{,}521 \cdot \exp(-0{,}028t)]$; anomalously fast reaction (curve 3): $\log A_{[B]} = \log[0{,}168 \cdot \exp(-0{,}12t)]$

in all the glassy polymer specimens could be resolved as the sum of two simultaneous first order reactions (Fig. 5). A portion of the azo-dye reacts anomalously fast, whereas the rest isomerizes nearly as fast as in solution. This suggests that the *cis*-isomers may exist in different environments in the polymer matrix; this will be discussed later.

The thermal *cis-trans* isomerization can now be described kinetically by the Eq. (1).

$$[T]_\infty - [T] = [A]_0 \cdot e^{-k_1 t} + [B]_0 \cdot e^{-k_2 t} \qquad (1)$$

with $[T]_\infty$ representing the total concentration of the *trans*-isomer at infinitive time and [T] its concentration at time t; $[A]_0$ and $[B]_0$ are the concentrations of "normally" and "anomalously fast" reacting *cis*-isomers at zero time (s. Fig. 5).

The rate constants thus obtained are summarized in Tab. 3. One sees, that the k_2/k_1-ratio decreases when approaching T_g and ideally, going through T_g, its value becomes 1; consequently Eq. (1) changes to a simple first order equation and this is in agreement with the experimental findings (s. above).

The individual Arrhenius plots for k_1 in CoP(iBMA-**1a**) and the different EMA polymer samples exhibit a break at the glass transition temperature (Fig. 6); the higher apparent activation energy above T_g is certainly associated with an additional activation energy for viscous flow, as was already assumed for spirobenzopyran photochrome containing polymers[14].

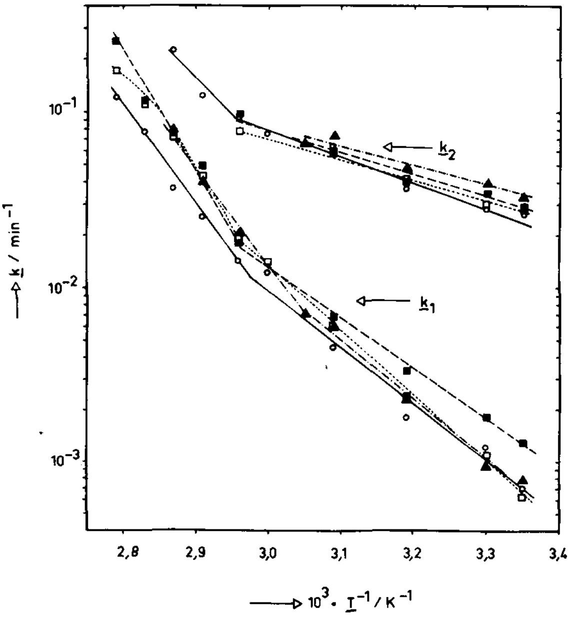


Fig. 6. Arrhenius plots of the rate constants k_1 (normal reaction) and k_2 (anomalously fast reaction) of the thermal *cis-trans* isomerization of the azo chromophore in different copolymers (figures from Tab. 3).
(——; ○): CoP(EMA-**1a**); (– – – –; ■): CoP(EMA-**1c**);
(······; □): PEMA + **1b**; (–·–·–; ▲): CoP(iBMA-**1a**)

With the exception of the polymer sample PEMA + **1b**, where the azo chromophore was not chemically bound, the two portions of these graphs as well as the Arrhenius plots for the other rate constants k_1 and k_2, in all the polymer samples investigated, showed no curvature,

Tab. 3. Kinetic parameters[a] of the thermal *cis-trans* isomerization of the azo chromophore in the different polymer samples in bulk; photochemical *trans-cis* isomerization by 20 min irradiation ($\lambda = 355$ nm) at room temperaure

T/°C	CoP(MMA-**1a**)		CoP(EMA-**1a**)		CoP(EMA-**1c**)		PEMA + **1b**		CoP(iBMA-**1a**)		CoP(nBMA-**1a**)	CoP(MA-**1a**)	CoP(EA-**1a**)
	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_2 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_2 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_2 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_2 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_2 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$	$\frac{k_1 \cdot 10^3}{\text{min}^{-1}}$
25	0,52	30	0,71	26	1,3	28	0,62	27	0,78	32	0,35	0,26	0,49
30	1,2	35	1,2	28	1,8	44	1,1	29	0,94	39	0,70	0,47	0,92
40	2,7	45	1,8	36	3,3	40	2,4	41	2,3	48	2,0	1,5	2,3
50	6,7	53	4,5	61	6,8	58	5,7	57	5,9	73	9,6	4,2	—
55	—	—	—	—	—	—	—	—	7,0	65	—	—	—
60	11	61	12	74	—	—	14	48	—	—	—	—	—
65	—	—	14	92	18	93	18	77	20	0	—	—	—
70	30	170	25	120	49	0	43	0	40	0	—	—	—
75	35	110	36	221	76	0	77	0	80	0	—	—	—
80	—	—	75	0	115	0	110	0	—	—	—	—	—
85	93	—	120	0	250	0	170	0	—	—	—	—	—
T_g/°C[b]	—		64	65	64		64		57		—		—
E_A[c]													
$T < T_g$	17,5	6,6	14,1	6,4	12,5	5,8	17,1	5,6	15,5	5,4	—	—	—
$T > T_g$	—		29,5	22,6	30,9		—		28,8		25,4	21,9	20,5
$\Delta S^{\ddagger}$[d]													
$T < T_g$	−25	−54	−36	−56	−40	−48	−27	−57	−31	−58	—	—	—
$T > T_g$			+10	− 7	+15		—		+ 9		+1	−12	−15

[a] k_1, k_2: first order rate constants of "normal" and "anomalously fast" isomerization, resp., T_g: glass transition temperature, E_A: apparent activation energy, $\Delta S^{\ddagger}$: apparent activation entropy.

[b] Calculated from the break in the Arrhenius plots (cf. Fig. 6).

[c] in kcal·mol^{-1}

[d] in cal·mol^{-1}·K^{-1}

i.e. from these graphs one might conclude that the overall activation energy E_A is temperature independent.

Using the Eyring equation, the apparent entropies of activation, ΔS^{+}, were calculated by plotting $\ln(k/T)$ vs. $1/T$ according Eq. (2)

$$\ln\frac{k}{T} = \ln\frac{k^{+}}{h} + \frac{\Delta S^{+}}{R} - \frac{\Delta H^{+}}{R}\cdot\frac{1}{T} \tag{2}$$

(k^{+} = Boltzmann constant, h = Planck constant)

Comparing the isomerization rate constants k_1 or k_2 in the different copolymers against one another at a given temperature, it is obvious, that the small differences in the chemical structure of the polymer matrices do not influence the reaction rate as e.g. compared to polystyrene as matrix[15]. It is also not important for k, how close the chromophore is bound to the polymer backbone (e.g. CoP(EMA-**1a**) and CoP(EMA-**1c**)) or if the chromophore is chemically bound to the polymer or not (PEMA + **1b**). But the curvature in the individual Arrhenius plot for k_1 only found with PEMA + **1b** and the occurrence of the anomalously fast reaction still above T_g only with CoP(EMA-**1a**) shows that the isomerization process itself can be influenced by the way in which the azo chromophore is incorporated into the polymer.

The comparison with the data for solution isomerization (s. Tab. 2) shows only some deviations for the rubbery samples in the glass transition temperature area: the rate constants are smaller

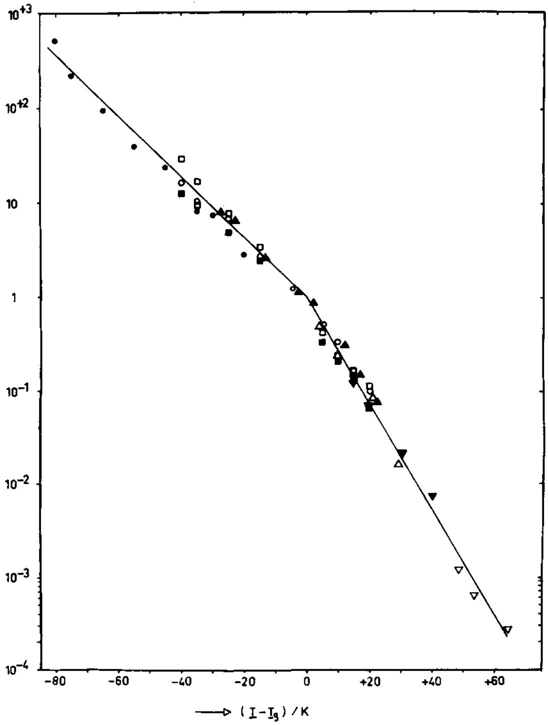


Fig. 7. Plot of log a_T (a_T is the ratio of the thermal *cis-trans* isomerization relaxation time ($1/k_1$) of the azo chromophore at temperature T to its value at T_g) vs. $T - T_g$ for the acrylate and methacrylate copolymers (cf. Tab. 3). The relaxation times at T_g were taken from the corresponding Arrhenius plots either directly (cf. Fig. 6) or by extrapolation to T_g where T_g was not in the range of measurement.
(●): CoP(MMA-**1a**); (○): CoP(EMA-**1a**);
(■): CoP(EMA-**1c**); (□): PEMA + **1b**;
(▲): CoP(iBMA-**1a**); (△): CoP(nBMA-**1a**);
(▼): CoP(MA-**1a**); (▽): CoP(EA-**1a**)

and at the same time the activation energies are higher. This is due to the high inner viscosity of the rubbery samples near T_g and with increasing temperature relative to T_g the rate constants as well as the activation parameters approach the figures of the isomerization in solution.

Following the treatment of the temperature dependence of mechanical and dielectric relaxation times in polymers[16], all the rate data obtained on the different polymer samples can be summarized in a WLF-type graph[17], when plotting semilogarithmically the ratio a_T of the *cis-trans* isomerization relaxation time (the reciprocal of the particular instantaneous first order rate constant, e.g. $1/k_1$) to its value at T_g vs. the reduced temperature, i.e. $T-T_g$ (Fig. 7). This means, that such isomerization processes are associated directly with relaxation phenomena of the polymer matrix itself. The assumption of a free volume dependency of the isomerization reaction is obvious and becomes evident when correlating the relaxation times found for the *cis-trans* isomerization in rubbery samples at different temperatures with the corresponding fraction f of the free volume at that temperature (Fig. 8).

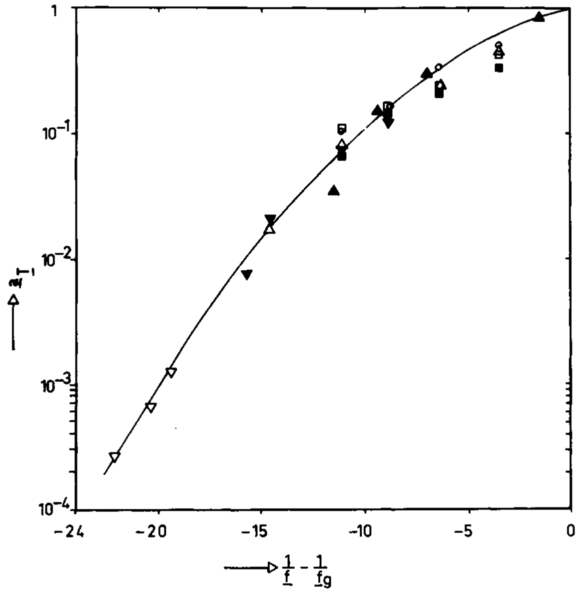


Fig. 8. Plot of log a_T vs. $(1/f-1/f_g)$ for the acrylate and methacrylate copolymers (cf. Tab. 3). The fractional free volume f was calculated by using the equation $f=f_g+\alpha_2\cdot(T-T_g)$ with $\alpha_2=4{,}8\cdot 10^{-4}\,K^{-1}$ and $f_g=0{,}025$[17]. (○): CoP(EMA-**1a**); (■): CoP(EMA-**1c**); (□): PEMA + **1b**; (▲): CoP(iBMA-**1a**); (△): CoP(nBMA-**1a**); (▼): CoP(MA-**1a**); (▽): CoP(EA-**1a**)

From the above findings, it is clear, that for the isomerization process in the rubbery state a non-temperature-dependent overall activation energy E_A, as was concluded from the apparent linear Arrhenius plots of the individual polymers (cf. Fig. 6), is not likely. In fact, in an Arrhenius-type plot which is normalized to T_g, again a_T for all the polymer samples can be represented in a single graph (Fig. 9) and for temperatures above T_g, not a straight line, but a curve with increasing slope towards T_g is obtained. This means that E_A continuously decreases as the temperature increases and at temperatures far above T_g its value is similar to the one found in solution. Assuming that this temperature dependency of the activation energy for the thermal *cis-trans* isomerization is connected to the inner viscosity of the polymer matrix, the differences between the activation energy in ethyl acetate solution and rubbery

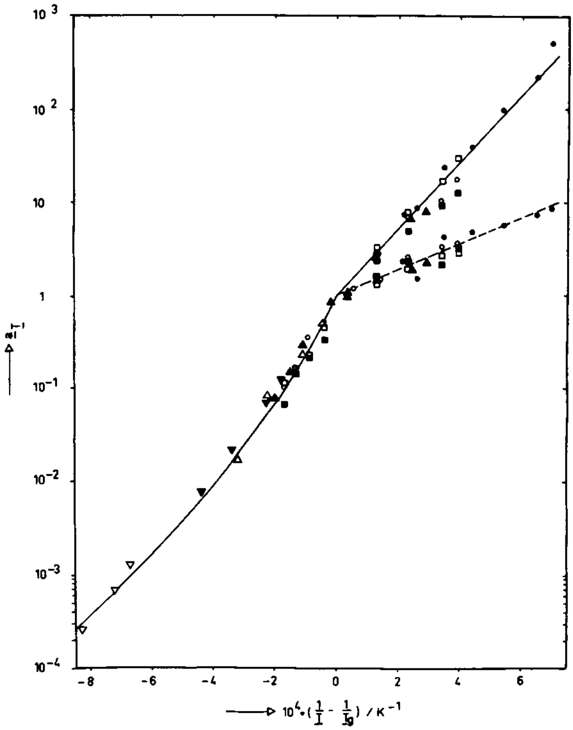


Fig. 9. Plot of log a_T vs. $(1/T - 1/T_g)$ for the acrylate and methacrylate copolymers (a_T is explained in Fig. 7).
(——): normal isomerization; (– – – –): anomalously fast isomerization
(●): CoP(MMA-**1a**); (○): CoP(EMA-**1a**);
(■): CoP(EMA-**1c**); (□): PEMA + **1b**;
(▲): CoP(iBMA-**1a**); (△): CoP(nBMA-**1a**);
(▼): CoP(MA-**1a**); (▽): CoP(EA-**1a**)

polymer matrix reflect the segmental friction on the *cis-trans* rearrangement. This view is supported by the linear correlation of the apparent energies and entropies of activation in the different rubbery samples (Fig. 10). Following Davies and Edwards[18] this linear relationship might be understood here if the activation energy is needed largely to displace adjacent chain segments: the larger the energy required, the larger the local disorder, i.e. the still relatively stiff and somewhat ordered polymer chains near T_g require a high energy to be moved which is associated with a relatively positive entropy change compared to higher temperatures, where this energy value and also the entropy change is smaller due to the increasing thermal motions of the polymer segments.

Below T_g, the overall apparent activation energy is temperature independent for the normally and anomalously fast reacting *cis*-isomers, as the linear portions in Fig. 9 show. In the glassy state, the apparent activation energies for both isomerization reactions are not affected by the nature of the polymer matrix and are in good agreement with the figures from the individual Arrhenius plots of the polymers (cf. Fig. 6). From the slopes of the straight portions in Fig. 9 for the normally isomerizing fraction an E_A of 16,4 kcal/mol and for the anomalously fast reacting portion an E_A of 6,4 kcal/mol is calculated.

The apparent activation entropies in the glassy state are strongly negative, which means that the transition state is rather unfavoured: on the one hand the activated complex cannot be solvated as good as in the rubbery state (where the polymer chains are freely movable);

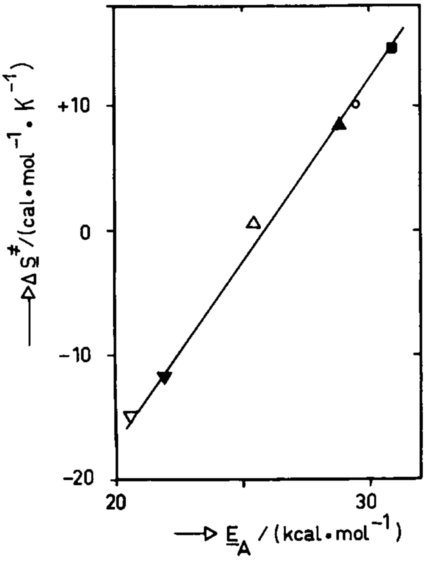


Fig. 10. Relation between the overall apparent entropy of activation $\Delta S^{\ddagger}$ and the overall apparent Arrhenius energy of activation E_A for the thermal *cis-trans* isomerization of the azo chromophore in the different copolymer samples above the glass transition temperature T_g.
(○): CoP(EMA+**1a**); (■): CoP(EMA-**1c**);
(▲): CoP(iBMA-**1a**); (△): CoP(nBMA-**1a**);
(▼): CoP(MA-**1a**); (▽): CoP(EA-**1a**)

on the other hand the chain segments in the neighbourhood of a chromophore have to be moved in a cooperative way, as will be discussed below.

The fast *cis-trans* isomerization reaction with the extremely small activation energy compared to the one for the normal isomerization reaction cannot be explained by two different *cis*-isomers, as e.g. for the spirobenzopyran photochromes, where the three existing isomers of the coloured form are discussed as being responsible for the three first order reactions found in the thermal decolouration[19,20]. Morawetz et al.[5] have attributed this fast isomerization to a rather unfavoured surrounding of a portion of the *cis*-isomers such as constraints by the matrix pushing the *cis*-isomer back to the *trans*-form.

These authors stated also, that about 14% of the *cis*-isomers isomerize faster than the remainder, this portion being independent of the reaction temperature (at which the thermal isomerization was investigated) as long as the photochemical *trans-cis* isomerization is carried out by irradiation below T_g[5,21]. Under these conditions it is found in the work presented here, however, that the anomalously fast isomerizing fraction x ($=[B]_0/([A]_0+[B]_0)$, s. Eq. (1)) of the total *cis*-isomer concentration increases when increasing the reaction temperature vs. T_g. The temperature dependence of this phenomenon can be represented for all the different polymer systems by a single graph, when relating this anomalous fraction x to the glass transition temperature of the given polymer (Fig. 11). One has to keep in mind, however, that this relation is only meaningful for temperatures up to the glass transition temperature of the given polymer.

For a given copolymer and a given temperature, the fraction x is only slightly affected by the irradiation time, but the thermal conditions, under which the *trans-cis* photoisomerization occurs, have a very distinctive influence on x. The *trans-cis* photoisomerization can be done at any temperature below T_g, and it doesn't matter if this temperature is higher or lower than the particular reaction temperature at which the thermal *cis-trans* isomerization is investi-

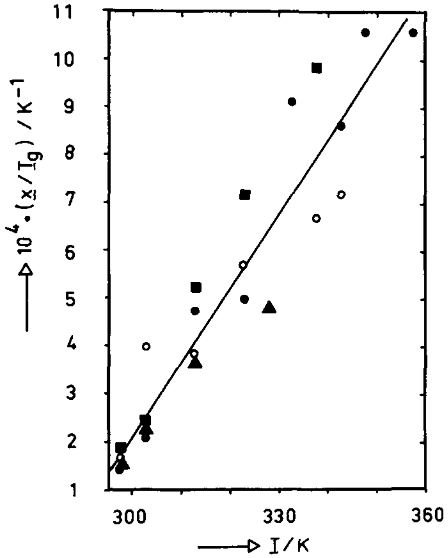


Fig. 11. Plot of the anomalously fast isomerizing fraction x of the total *cis*-isomer content reduced to T_g vs. the reaction temperature T for the different copolymer samples, obtained after 20 min irradiation ($\lambda = 355$ nm) at room temperature (experiments of Tab. 3); (●): CoP(MMA-**1a**); (○): CoP(EMA-**1a**); (■): CoP(EMA-**1c**); (▲): CoP(iBMA-**1a**)

gated, within the experimental error, always the same fraction x is obtained for that reaction temperature (Tabs. 4 and 5).

When photoisomerization is carried out above T_g and the irradiation is stopped before cooling the sample through T_g to the particular reaction temperature T_2, still about 50% of the *cis*-isomers created isomerized anomalously fast (s. No 4 and 5, Tab. 5). Only if the sample is irradiated above T_g, is then cooled through T_g while under irradiation, then the

Tab. 4. Thermal *cis-trans* isomerization of the azo chromophore in CoP(EMA-**1a**) at temperature T_2: dependence of the anomalously fast reacting fraction x of the total fraction y of the azo chromphore in the *cis*-form on the time t and the temperature T_1 of the photochemical *trans-cis* isomerization ($\lambda = 355$ nm)

No	t/h	T_1/°C	T_2/°C	$\frac{10^3 \cdot k_1}{\text{min}^{-1}}$	$\frac{10^3 \cdot k_2}{\text{min}^{-1}}$	y	x
1	0,33	25	40	2,1	36	0,79	0,08
2	0,33	40	40	3,0	42	0,81	0,10
3	0,33	60	40	2,3	36	0,78	0,10
4	0,33	25	50	4,5	61	0,76	0,19
5	0,33	50	50	5,2	72	0,82	0,16
6	14	25	50	4,5	44	0,82	0,09
7[a]	0,33	80	50	4,9	69	0,75	0,05
8	0,33	25	60	12	74	0,76	0,18
9	0,33	60	60	10	61	0,77	0,19
10	0,33	25	65	14	92	0,69	0,26
11	3	25	65	20	116	0,78	0,18
12[a]	0,33	80	65	22	113	0,81	0,03

[a] Cooling through T_g under irradiation.

Tab. 5. Thermal *cis-trans* isomerization of the azo chromophore in CoP(iBMA-**1a**) at 50 °C: dependence of the anomalously fast reacting fraction x of the total fraction y of the azo chromophore in the *cis*-form on the temperature T of the photochemical *trans-cis* isomerization ($\lambda = 355$ nm; $t = 20$ min)

No	$T/°C$	$\frac{10^3 \cdot k_1}{\mathrm{min}^{-1}}$	$\frac{10^3 \cdot k_2}{\mathrm{min}^{-1}}$	y	x
1	25	5,9	73	0,78	0,16
2[a]	25	5,3	71	0,82	0,11
3	50	5,6	58	0,80	0,18
4	70	5,6	39	0,78	0,06
5	70	5,3	53	0,82	0,07
6[b]	70	6,0	—	0,81	0
7[b]	70	5,5	—	0,83	0

[a] This experiment was done immediately after No. 6.

[b] Cooling through T_g under irradiation.

anomalous portion either completely (e.g. CoP(iBMA-**1a**), s. No 6 and 7, Tab. 5) or at least for the most part (CoP(EMA-**1a**), No 7 and 12, Tab. 4) disappears.

These phenomena can only be understood with the assumption of a temperature dependent distribution of relaxation times for both types of isomerization reactions in the static state below T_g, the origin of which will be discussed below. At a given temperature one picks out the corresponding "distribution" more or less independent of the thermal history, except in the case when the dynamic state above T_g is frozen in by continuing the irradiation when cooling through T_g.

Discussion

From the above findings it is quite evident, that photochemical and thermal *cis-trans* isomerization processes are very sensitive to the reaction media; distinctive differences between the reaction in solution and in a polymer matrix are exhibited. This is due to the requirement of segmental movements of the polymer chains and rearrangements in the conformation of polymer chains neighbouring the chromophore, which are both necessary for the succeeding of the isomerization reaction.

Above T_g, i.e. in the rubbery state, the thermal *cis-trans* isomerization of azoaromatic compounds incorporated in or chemically bound to a polymer matrix can only roughly be considered to be solution like, if at all. The temperature dependency of the relaxation time can only be described by a WLF-type graph (Figs. 7 and 8) due to the free volume effects in rubbery polymers. The curvature in the corresponding Arrhenius plot (Fig. 9) shows, that no single value of the overall apparent activation energy is sufficient to describe the temperature dependency of the thermal *cis-trans* isomerization. In addition to the activation energy needed for the isomerization about the azo group, an increasing amount of energy is required to overcome the inner viscosity of the matrix, i.e. the restricted chain mobility, as the temperature approaches T_g. Only at temperatures well above T_g can this influence be neglected and then the Arrhenius activation energy concept is valid and solution like behaviour is shown.

Below T_g where the free volume is considered to be constant and relatively little segmental motions are possible, the immediate neighbourhood of the chromophore and the thermal history of the sample (i.e. the conditions under which the photochemical isomerization took place) are the decisive factors.

From the present data it is assumed, that not, as stated by Paik and Morawetz$^{5)}$, steric strains are responsible for the anomalously fast reacting portion of the *cis*-isomers, but the occurrence of two different relaxation mechanisms. The isomerization process of the azo dyestuff is considered to be linked directly to the local segmental mobility around the chromophore—which is associated with the distribution of the free volume$^{22)}$—and these segments may relax in a rotational or "crankshaft"-like motion and in a translational motion. The anomalously fast isomerization, for which the small activation energy of 6,4 kcal/mol was found, is attributed to a translational relaxation mechanism, whereas the "normal" isomerization is associated with a rotational relaxation, a process which generally requires the higher activation energy.

The rotational crankshaft-like motion is only possible, if sufficient free volume is in the direct neighbourhood of the chromophore. This can completely be achieved, if the polymer film is irradiated above T_g and irradiation is continued during cooling through T_g. In this case, the free volume is built up in the dynamic state above T_g around the chromophore; due to the photoreversible process it is kept there when cooling through T_g. Therefore, only one, the normal reaction is observed. The *cis*-isomers can retain their equilibrium arrangement with the neighbouring chain molecules and we have a coinciding equilibrium distribution of the chromophores and the free volume in the polymer matrix. When the irradiation is stopped before cooling through T_g, then this distribution is no longer possible and to a certain extent the same behaviour is found as for the experiments carried out with photoisomerization only below T_g.

When irradiated below T_g, i.e. in a nondynamic state with regard to the free volume, the overall distribution of the free volume relative to the position of the chromophores in the matrix is not as greatly affected by the photochemical *trans-cis* isomerization. This means, that the rotational relaxation mechanism is only possible to a certain extent, and the isomerization of a portion of the *cis*-isomers is associated with a translational movement of chain segments; this kind of isomerization mechanism takes place simultaneously with a cooperative translational movement of chain segments, thus providing the space for the isomerization. With increasing temperature, larger segments can be moved in a cooperative process, and this explains the increasing portion of the anomalously fast reacting *cis*-isomers with temperature.

The lower apparent energies of activation for both the rotational ($E_A = 16{,}4$ kcal/mol) and the translational ($E_A = 6{,}4$ kcal/mol) relaxation process in the glassy polymers compared to the isomerization in solution (E_A over 20 kcal/mol) suggests some "catalytic" effect of the glassy polymer matrix on the thermal *cis-trans* isomerization. In this regard it is striking, that the values and differences of these two activation energies are in the same range as both the total activation energies for the crankshaft-like motion (≈ 13–15 kcal/mol) and the portion of the energy required to overcome van der Waals hindrance (≈ 6 kcal/mol) in polyethylene$^{23)}$; with this coincidence, one might be tempted to ask, how much, if any, activation energy is needed for the *cis-trans* isomerization itself or rather for the segmental movements in the glassy state, especially when considering the extremely low activation energies also found for the thermal decoloration of spirobenzopyrans in glassy polymer matrices, which are in the same energy range$^{14,19)}$.

Above T_g all the polymer chains and the azo chromophores are freely movable and particularly distinguishable relaxation processes are not present; we have then solution-like behaviour with the restrictions stated above when approaching T_g. The only deviation from this statement was found for the EMA-copolymer, where up to 10 K above T_g the anomalously fast reaction was still present. This implies a possible influence of the polymer structure and the kind of attachment of the chromophore to the polymer on the isomerization mechanism in the glass transition temperature area.

Conclusion

In the present work the effect of a polymeric matrix on the *cis-trans* isomerization of aromatic azo compounds has been investigated. The data have clarified that, in bulk polymers, the *cis-trans* isomerization process about the azo-link is fixed by the nature of the polymer matrix, i.e. whether the matrix is in the glassy or in the rubbery state. The isomerization is mainly affected by the free volume and by relaxation phenomena of the polymer backbone; the temperature dependence of the *cis-trans* isomerization relaxation time could be represented by a WLF-type graph. The occurrence of two simultaneous first order processes at temperatures below the glass transition temperature was interpreted on the basis of rotational and translational relaxation processes of chain segments.

These findings might be valid in general for isomerization reactions in bulk polymers. It seems to be interesting to investigate the isomerization of azo compounds when built into the backbone of the polymer chain or in a crosslinking agent. In this case the isomerizable group is fixed on both ends and the isomerization is only possible with a simultaneous movement of at least one of the two adjacent chain segments; i.e. the change in the geometry of the chromophore forces the polymer chains to be moved along each other or it induces a change in the network structure. This will be studied in future work.

Financial support by the *Deutsche Forschungsgemeinschaft* and a contribution from the *Kuratorium der Wissenschaftlichen Gesellschaft in Freiburg* is gratefully acknowledged. The author is also indebted to the *Fonds der Chemischen Industrie* for providing a Liebig Fellowship and he wishes to thank *Prof. Wegner* for his fruitful discussions.

[1] J. L. R. Williams, R. C. Daly, Prog. Polym. Sci. **5,** 61 (1977)

[2] D. L. Ross, J. Blanc, Photochromism by *cis-trans* Isomerism, in "Techniques of Chemistry", edited by G. H. Brown, Wiley-Interscience, New York 1971, Vol. III, pp. 471

[3] L. S. Luskin, R. J. Myers, Acrylic Ester Polymers, in "Encyclopedia of Polymer Science and Technology", edited by H. F. Mark, N. G. Gaylord, N. M. Bikales, Interscience Publishers, New York 1964, Vol. I, pp. 246

[4] W. A. Lee, R. A. Rutherford, Glass Transition Temperatures of Polymers, in "Polymer Handbook", edited by J. Brandrup, H. Immergut, John Wiley a. Sons, Inc., New York 1975, pp. III-139

[5] C. S. Paik, H. Morawetz, Macromolecules **5,** 171 (1972)

[6] H. R. Kricheldorf, J. Kaschig, Justus Liebigs Ann. Chem. **1976,** 882

[7] H.-J. Cantow, G. V. Schulz, Z. Phys. Chem. (Frankfurt am Main) **2,** 117 (1954)

[8] W. R. Brode, J. H. Gould, G. M. Wyman, J. Am. Chem. Soc. **74,** 4641 (1952)

[9] G. Zimmermann, L. Chow, U. Paik, J. Am. Chem. Soc. **80,** 3528 (1958)

[10] M. Frenkel, R. Wolowsky, E. Fischer, J. Chem. Soc. **1955,** 3441

[11] G. S. Hartley, J. Chem. Soc. **1938,** 633

[12] J. Halpern, G. U. Brady, C. A. Winkler, Can. J. Res., Sect. B: **28,** 140 (1950)

[13] A. A. Frost, R. G. Pearson, Kinetik und Mechanismus homogener chemischer Reaktionen, Verlag Chemie, Weinheim/Bergstr. 1964, p. 150

[14] G. Smets, Pure Appl. Chem. **30,** 1 (1971)

[15] H. Kamogawa, M. Kato, H. Sugiyama, J. Polym. Sci., Part A-1, **6,** 2967 (1968)

[16] N. G. McCrum, B. E. Read, G. Williams, Anelastic and Dielectric Effects in Polymeric Solids, John Wiley a. Sons, London 1967, pp. 102 and pp. 141

[17] M. L. Williams, R. F. Landel, J. D. Ferry, J. Am. Chem. Soc. **77,** 3701 (1955)

[18] M. Davies, A. Edwards, Trans. Farad. Soc. **63,** 2163 (1967)

[19] J. Verborgt, G. Smets, J. Polym. Sci., Pol. Chem. Ed. **12,** 2511 (1974)

[20] Z. G. Gardlund, J. J. Laverty, J. Polym. Sci., Part B, **7,** 719 (1969)

[21] D. Tabek, H. Morawetz, Macromolecules **3,** 403 (1970)

[22] F. Bueche, J. Chem. Phys. **21,** 1850 (1953)

[23] T. Schatzki, J. Polym. Sci. **57,** 496 (1962); T. Schatzki, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem. **6,** 646 (1965)