

Isomerization of aromatic azo chromophores in poly(ethyl acrylate) networks and photomechanical effect

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The photochemical and thermal *cis-trans* isomerization of azo chromophores which were either dissolved, a pendant group or part of a crosslink in rubbery poly(ethyl acrylate) networks has been investigated. The thermal relaxation behaviour of the azo compound in the networks depends on the crosslinking density and can be described by a WLF-equation with the same parameters as found for non-crosslinked polymers. For stretched polymer films with azo-aromatic crosslinks, a photomechanical effect, i.e., a reversible contraction and expansion was observed, which is mainly ascribed to conformational change of the azo chromophore.

INTRODUCTION

The photochemical and thermal *cis-trans* isomerization of aromatic azo chromophores, which were dissolved in a polymer matrix, a pendant group or part of the polymer backbone has been described in previous publications¹⁻³. The main conclusion of this work was that photochromic processes in bulk polymers are linked to particular motions of chain segments^{4,5} and that the relaxation behaviour of the photochrome depends on the free volume as described by a form of the WLF-equation⁵. These relations were found not only to be valid for aromatic azo compounds but also for spiropyrans⁴⁻⁶, and since these two systems greatly differ in their reaction mechanism, it was concluded that these relations generally are valid for photochromic systems.

The investigations of the *cis-trans* isomerization of aromatic azo compounds mentioned above were all carried out on linear polyacrylates, polymethacrylates and segmented poly(ester urethanes). The remaining question was how the photochromism of azo-aromatic chromophores would be influenced by a chemically crosslinked polymer matrix, and to which extent analogies with spiropyran containing networks could be drawn. In order to study this effect a series of poly(ethyl acrylate) networks with azo-aromatic crosslinks and also with the photochrome being dissolved or a pendant group in the network was prepared. The investigation of the photochemical and thermal *cis-trans* isomerization of these azo-aromatic compounds is described in this paper.

EXPERIMENTAL

The model compound 4,4'-di(isobutyrylaminoazobenzene) (DBAAB) and the difunctional azo-aromatic crosslinking agent 4,4'-di(methacryloylaminoazobenzene) (DMAAB) were prepared in the same way as described for the mono-substituted analogue¹. DBAAB: m.p. 295°C;

u.v. (ethyl acetate): $\lambda_{max} = 372$ nm ($\epsilon = 40\,300$ l mol⁻¹ cm⁻¹). C₂₀H₂₄N₄O₂ (352.4). Calculated: C, 68.17; H, 6.85; found: C, 68.06; H, 7.08%. DMAAB: m.p. 275°C; C₂₀H₂₀N₄O₂ (348.4). Calculated: C, 68.96; H, 5.78; found: C, 68.87; H, 5.94%.

Clear, transparent crosslinked films were prepared by polymerizing ethyl acrylate (EA) in the presence of DMAAB and/or ethylene glycol dimethacrylate (EGDMA) with AIBN as initiator. The polymerizations were carried out between two glass plates separated by a Teflon spacer ring of 0.15–0.5 mm thickness. The system was slowly heated up to 75 °C for 4 h and then kept at this temperature for two days to achieve complete monomer conversion. The film was then separated from the glass plates and dried *in vacuo* for 48 h at 50 °C. The composition of the reaction mixtures for the different polymer samples is given in Table 1. For the preparation of films with higher content of azo-aromatic crosslinks

Table 1 Comonomer composition (mol %) in the synthesis of chromophoric poly(ethyl acrylate) networks

Copolymer	EA ^a	MAAB ^b	DMAAB ^c	EGDMA ^d
CoP (EA/MAAB) ^{e,1}	99.89	0.11	0	0
CoP(EA/MAAB/ EGDMA)	97.39	0.02	0	2.59
CoP (EA/EGDMA) + DBAAB ^f	98.91	0	(0.02 ^g)	1.07
CoP (EA/DMAAB)	99.98	0	0.02	0
CoP (EA/DMAAB/ EGDMA)	97.39	0	0.02	2.59

^a EA = ethyl acrylate

^b MAAB = 4-methacryloylaminoazobenzene

^c DMAAB = 4,4'-di(methacryloylamino)azobenzene

^d EGDMA = ethylene glycol dimethacrylate

^e CoP (EA/MAAB) = copolymer of EA and MAAB; the same

abbreviations are used for the other copolymers

^f DBAAB = 4,4'-di(isobutyrylamino)azobenzene

^g mol % of DBAAB in CoP (EA/EGDMA)

(≈ 0.5 – 2 mol%) used in the photomechanical experiments, DMF (about 20 vol. %) was added in order to dissolve DMAAB which in these concentrations is no longer soluble in the monomer EA alone. In this case the swollen polymer film was first placed into toluene and then deswollen by dipping into heptane.

The glass transition temperatures of the polymers were determined by d.s.c. measurements using a Perkin-Elmer DSC-2; heating rate was 20 °C/min. The temperatures T_g refer to mercury as standard measured at the same conditions.

The experimental conditions for the photoisomerization and the kinetic studies were the same as described earlier¹. For the photomechanical experiments a 200 W Super Pressure Mercury Lamp was used and the appropriate wavelengths were filtered off by using a 365.0 nm and a 435.8 nm Oriol interference filter (halfwidth 10 nm). The change in length of the sample as a function of irradiation time was followed in a set up similar to the one described by Ikeda and Gay⁷.

RESULTS AND DISCUSSION

By copolymerizing EA with difunctional azo-aromatic crosslinking agent DMAAB or EGDMA, alone or both together, clear and transparent elastomeric films were obtained. The comonomer compositions of the various elastomers are given in Table 1 and a representative portion of the three-dimensional network structure of the photochromic polymer is shown in Figure 1.

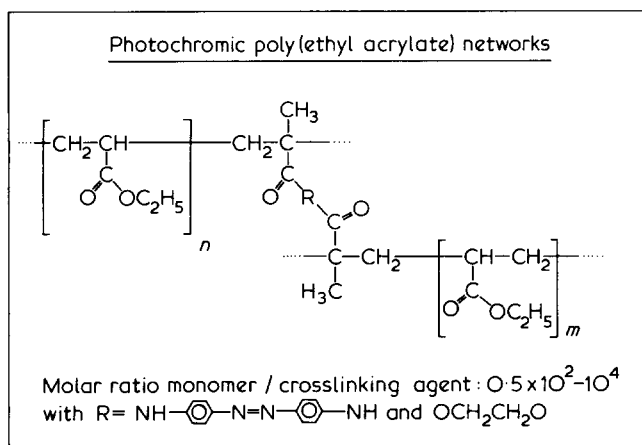


Figure 1 Portion of the structure of photochromic poly(ethyl acrylate) network with azo-aromatic crosslinks

As found for linear photochromic poly(ethyl acrylate)¹ (CoP(EA/MAAB), Table 1), the photochemical *cis*–*trans* isomerization of the azobenzene derivatives in the cross-linked copolymers (Table 1) can be achieved by irradiation in the region of the main absorption band of the *trans* form ($\lambda_{max} = 372$ nm, see Figure 2). The photoisomerization proceeds with no appreciable deviations from solution and the same small deviations in the fraction γ of *cis* isomers in the photostationary state ($\gamma = 0.75$ vs. 0.85 in solution) were observed in the bulk polymers for the azo-aromatic crosslinks as for the pendant or dissolved chromophores¹. Upon irradiation in the n – π^* absorption band region at 436 nm the *cis* isomer content decreases and the *trans* isomers are predominant. A typical absorption spectrum of a photochromic PEA network is shown in Figure 2 for CoP(EA/DMAAB/EGDMA) before irradiation and after reaching the photostationary state.

The thermal *cis*–*trans* isomerization was followed by measuring the change in the absorption of the maximum *trans* absorption band at 372 nm. Single first order kinetics were found in all types of photochromic networks, as was the case for pendant azo chromophores in linear polymers above T_g ¹ and for azo chromophores in the chain backbone of the polyester segments of poly(ester urethanes) with amorphous soft phase². However, as it is evident from the comparison of the first order rate constants given in Table 2, the rate of the isomerization

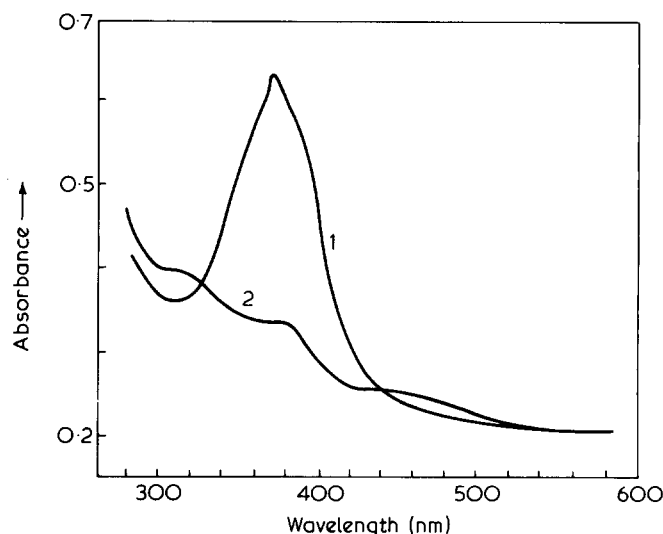


Figure 2 U.v. absorption spectra of CoP(EA/DMAAB/EGDMA) film before (curve 1) and after irradiation at $\lambda = 372$ nm (curve 2)

Table 2 First order rate constants k ($\times 10^3 \text{ min}^{-1}$) of the thermal *cis*–*trans* isomerization of the azo chromophore in different copolymer films; photochemical *trans*–*cis* isomerization by 20 min irradiation ($\lambda = 372$ nm) at room temperature; see Table 1 for abbreviations

T/K	BAAB ^a	CoP(EA/MAAB)	CoP(EA/MAAB/EGDMA)	DBAAB ^a	CoP(EA/EGDMA) + DMAAB	Cop(EA/DMAAB)	CoP(EA/DMAAB/EGDMA)
263.2	–	–	–	–	0.0093	–	0.0075
293.2	–	–	0.19	–	0.77	1.44	0.91
298.2	0.75	0.49	–	2.4	–	–	–
303.2	0.74	0.92	0.55	–	3.2	3.8	2.8
313.2	2.4	2.3	1.63	14.0	9.0	10.8	8.5
323.2	8.0	–	4.90	39.0	27.0	26.8	24.0
333.2	–	–	–	–	–	62.0	69.0
T_g/K^b	–	253	257	–	254	252	258

^a In ethyl acetate solution

^b Determined by d.s.c. analysis

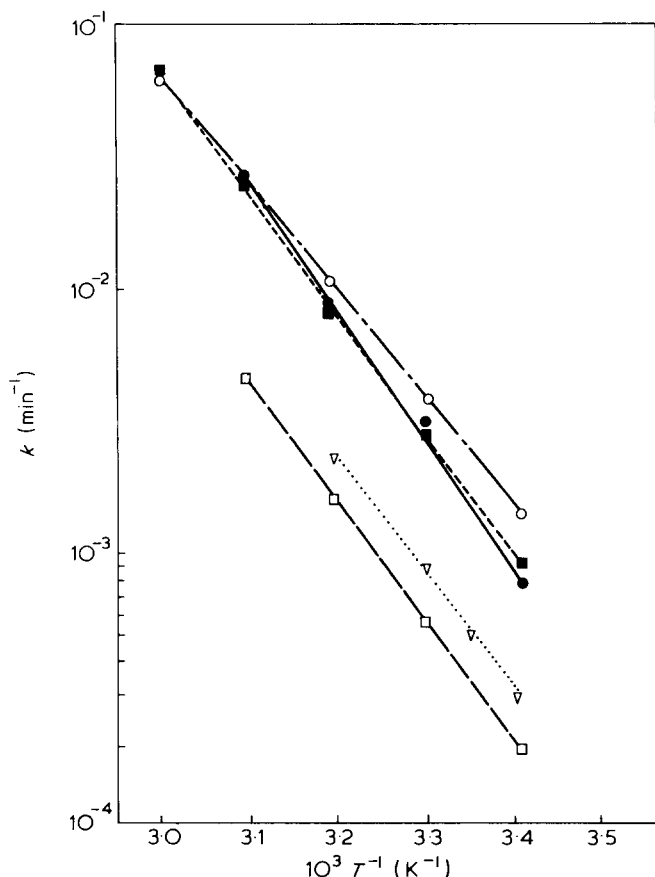


Figure 3 Arrhenius plot of the first order rate constants k of the thermal *cis-trans* isomerization of the azo chromophores in different polymer networks (figures from Table 2); (\cdots , ∇): CoP (EA/MAAB); ($-\cdots$, \square): CoP (EA/MAAB/EGDMA); ($---$, \bullet): CoP (EA/EGDMA) + DBAAB; ($-\cdot-$, \circ): CoP (EA/DMAAB); ($-\cdots$, \blacksquare): CoP (EA/DMAAB/EGDMA)

process is affected by the polymer matrix and also by the way the chromophore is fixed. Whereas for the model compound BAAB in solution and for the pendant azo chromophore in solid, linear CoP(EA/MAAB) no deviations occurred, however, crosslinking of the matrix alone (CoP(EA/MAAB/EGDMA)) decreased the rate of isomerization. The predominant effect of crosslinking is also seen from the comparison of the isomerization rate of the model compound for azo-aromatic crosslinks, DBAAB, in solution and in the bulk crosslinked polymer (CoP(EA/EGDMA)+DBAAB) with the isomerization rate of the crosslinks: incorporation of DBAAB in the crosslinked matrix considerably decreases the rate of isomerization compared to solution, but only little changes are observed between the isomerization rate of the model compound DBAAB dissolved in the network and of the azoaromatic crosslinks in CoP(EA/DMAAB) and CoP(EA/DMAAB/EGDMA) (Table 2). Obviously crosslinking itself and also the degree of crosslinking retards the thermal isomerization process. This phenomenon is graphically shown in Figure 3, where a shift in the Arrhenius graphs is observed together with a slight increase in the apparent energy of activation, E_A (increase of the slope) upon crosslinking (CoP(EA/MAAB) vs. CoP(EA/MAAB/EGDMA)) or change in the crosslinking density (CoP(EA/DMAAB) vs. CoP(EA/DMAAB/EGDMA)). In comparison to this, for the spiropyrans, the fixation of the chromophore at both ends causes a much more pronounced decrease in the rate

constants because of the severe steric requirements for this reaction as compared to the azo compounds^{4,8}.

The effect of crosslinking is a decrease in the overall segmental mobility of the polymer system and goes along with an increase of the glass transition temperature T_g (Table 2). The correlation of the deviations in the kinetic constants upon crosslinking with the glass transition temperature is best seen in the reduced Arrhenius-plot (Figure 4) and in the WLF-plot (Figure 5).

In Figure 4, the ratio of the thermal *cis-trans* relaxation time of the azo chromophore at temperature T to its value at T_g is plotted vs. the reduced temperature. As was also found for pendant azo chromophores in polymers of different T_g ¹, here the kinetic data (Table 2) can also be represented by a single line. The apparent energy of activation as calculated from the slope of this graph is 75.5 kJ/mol, a value lower than the E_A of 80–100 kJ/mol found in solution. The energy of activation required for a rotational, crankshaft-like motion in polymers is about 55–60 kJ/mol⁹, and the comparison with the E_A found for the photochromic relaxation^{1,2,4} suggests that rotational chain segmental motions affect the *cis-trans* isomerization in rubbery polymer networks.

The effect of the free volume is revealed from the plot of a_T vs. $T-T_g$ (Figure 5) which further confirms the validity of a form of the WLF-equation:

$$\log a_T = -\frac{C_1 \cdot (T-T_g)}{C_2 + T-T_g} \quad (1)$$

for the description of the relaxation behaviour of azo chromophores in polymer networks. The curve in Figure 5 has been calculated after equation (1) with $C_1 = 13.3$ and $C_2 = 210$ K, which are the same parameters as deter-

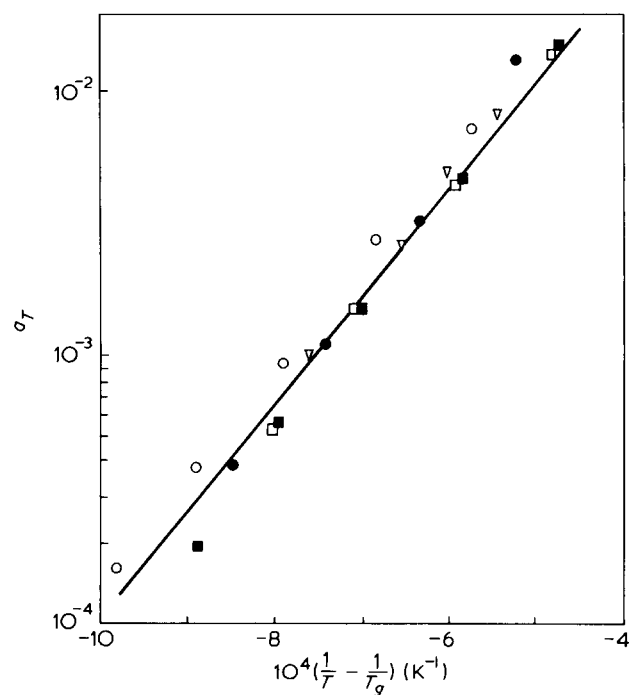


Figure 4 Reduced Arrhenius-plot of a_T (ratio of the thermal *cis-trans* isomerization relaxation time ($1/k$) of the azo chromophore at temperature T to its value at T_g) in the chromophoric poly(ethyl acrylate) networks; relaxation time at T_g obtained from the corresponding Arrhenius plot by extrapolation to T_g ; symbols see Figure 3

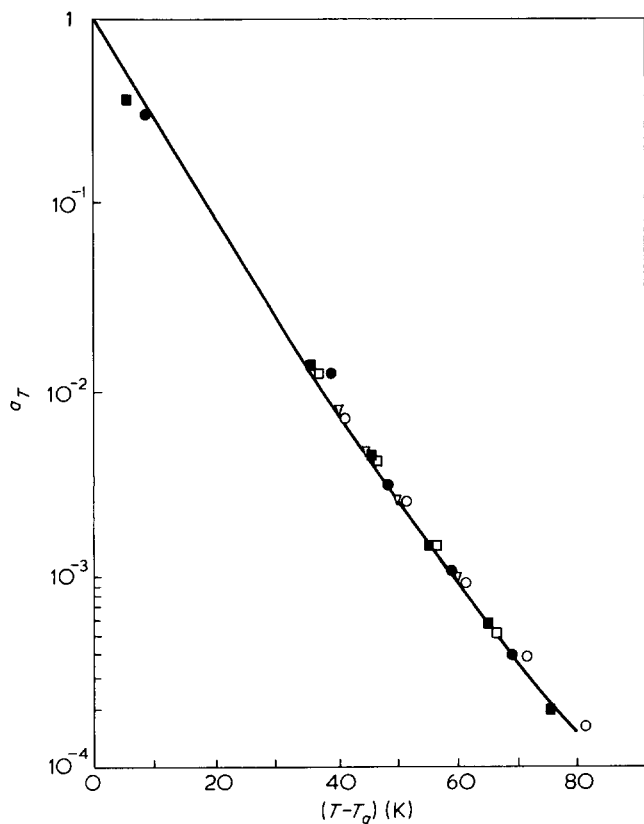


Figure 5 WLF plot of a_T for the thermal *cis*-*trans* relaxation of azo-aromatic chromophores in poly(ethyl acrylate) networks (cf. Table 2)); curve calculated after equation (1) with $C_1 = 13.3$ and $C_2 = 210$ K; symbols see Figure 3

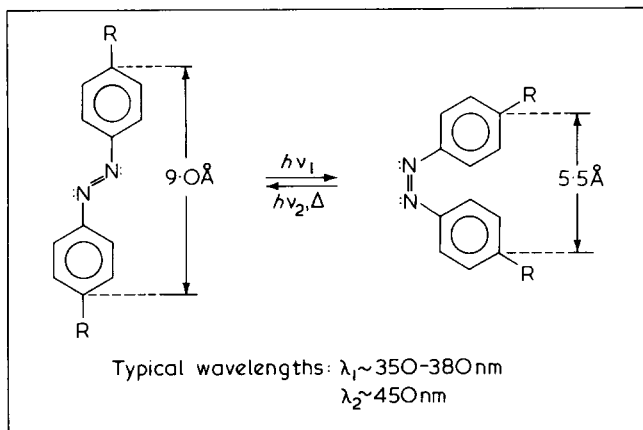


Figure 6 Change in dimensions of the aromatic azo chromophore upon irradiation

mined for pendant azo chromophores in linear polyacrylates and -methacrylates⁵. The validity of this equation with the same parameters for both linear and crosslinked azo-aromatic polymers clearly shows the universal applicability of a single WLF equation to describe the photochromic relaxation behaviour of aromatic azo compounds in solid polymers, and again proves the general validity of the free volume theory for photochromic relaxation processes in polymer matrices⁵.

A particular and interesting property of such PEA networks with azo-aromatic crosslinks is the appearance of a photomechanical effect¹⁰, i.e., a reversible contraction and expansion of such an oriented rubbery film upon

irradiation based on the change of the dimensions of the *cis*- and *trans*-form of the azo chromophore. Such an effect has first been described for azo-aromatic chromophores in the backbone of partly crystalline polyimide by Agolini and Gay¹¹ and was also found for polymers¹² and membranes¹³ with pendant azobenzene derivatives.

As can be seen from Figure 6, the isomerization process from the *trans*- to the *cis*-form involves a decrease in the distance between the *para* carbon atoms in the azobenzene derivative from about 9.0 to 5.5 Å¹⁴, and the local contraction is even larger because of the rigidly attached amide groups. If the chromophore is part of a polymer network and the network is stretched, the chromophores are preferentially oriented parallel to the stretching axis as schematically shown in Figure 7. Upon irradiation of such an oriented sample in the maximum *trans*-absorption range ($\lambda = 365$ nm), the change in the conformation of the azo chromophore causes a change in the conformation of an adjacent chain segment, which is considered to be the main effect responsible for the contraction.

The photomechanical behaviour of PEA networks with azo-aromatic crosslinks was investigated under constant load on the elastomeric film at room temperature. A typical response of a photochromic network is shown in Figure 8. Irradiation in the maximum *trans*-absorption range ($\lambda = 365$ nm) induces a *trans*-*cis* isomerization and contraction occurs. By changing the wavelength of ra-

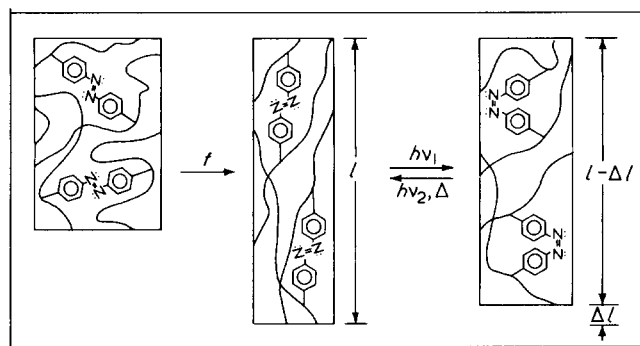


Figure 7 Schematic representation of the photomechanical effect induced in chromophoric poly(ethyl acrylate) networks with azo-aromatic crosslinks upon irradiation

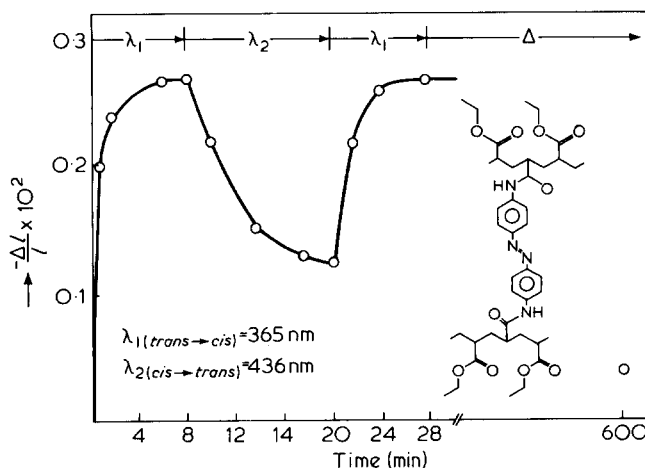


Figure 8 Photomechanical behaviour of poly(ethylacrylate) network with azo-aromatic crosslinks upon irradiation; molar ratio monomer/crosslinking agent: 100; elongation about 150%

diation ($\lambda = 436$ nm) the fraction of *cis*-isomers is decreased and partial length recovery takes place. Complete length recovery only occurs when the light source is cut off. This contraction–expansion cycle can be repeated many times and the average photomechanical effect is about 0.15 to 0.25 %. This effect is small, but real and it proves that the conversion of electromagnetic radiation into mechanical energy is possible by using photochromic azochromophores containing elastomers. Poly(ester urethane) elastomers previously described² with azo-aromatic groups in the backbone of the polyester soft segment also show a small photomechanical effect and efforts are being made to further improve this effect.

The question to which extent the photomechanical effect is caused by the conformational change of the chromophore or by local heat effects¹² due to the conversion of the energy stored by the photochrome cannot yet be answered definitively. However, recently Smets *et al.*¹⁵ have shown that the photomechanical effect in spiropyran containing PEA networks is mainly due to *cis*–*trans* isomerizations of the merocyanine isomers and not to the ring opening of the spiropyran¹⁶. They concluded that the fraction of thermal contraction was only one-third of the total effect. Therefore it is most likely that for azo-aromatic polymer networks also the conformational effect of the *trans*–*cis* isomerization is predominant. This is confirmed by the expansion of the contracted sample occurring when the film is exposed to light (436 nm, see Figure 8) by which the *trans* isomer content is enriched.

CONCLUSION

From the photochromic behaviour of the azo-aromatic chromophores in poly(ethyl acrylate) networks it is concluded that the same parameters of chain segmental mobility and of free volume as found for pendant groups in e.g. linear poly-acrylates or -methacrylates are valid.

The thermal relaxation behaviour of both crosslinked and non-crosslinked rubbery systems can be described by a single WLF equation.

The rubbery networks show a photomechanical effect which is believed mainly to be caused by the conformational change in the *trans*–*cis* isomerization of the fixed azo chromophore. This photomechanical effect is interesting since it allows the direct conversion of light energy into mechanical energy. On the other hand, such systems showing photocontractions are of some interest, too, with respect to life sciences, e.g., in connection with the vision process¹⁷ and phototropism or photonasty in plant life¹⁸. These aspects and the improvement of the photomechanical effect will be investigated in future work.

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