Azo-dye junctions in elastomeric networks: 1. Influence of network density on *cis–trans* isomerization in swollen gels

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Starting from 4,4'-diaminoazobenzene, 4,4'-(4,4'-bis-1,2,4-triazoline-3,5-dione)azobenzene has been synthesized. This compound acts as efficient crosslinking agent similar to the corresponding diphenylmethylene derivative. Using this agent swollen gels of polyisobutylene of different crosslink density were prepared. In these systems the azo labels are located at crosslink junctions. The thermodynamically stable *trans* azo compound is isomerized by irradiation. The thermal isomerization from *cis* to *trans* follows simple first order kinetics. The reaction rate constant depends on the crosslink density. From measurements at various temperatures it is deduced that the activation enthalpy remains unaltered. The observed dependence of the reaction rate constant is caused by the dependence of the activation entropy on crosslink density. This influence is described in terms of the theory of rubber elasticity. It appears that local conformational constraints enhance the rate of back isomerization.

(Keywords: networks; rubber elasticity; conformational constraints; azo labels; isomerization)

INTRODUCTION

The local orientation behaviour of rubber-like materials is of considerable interest for the understanding of the overall mechanical behaviour of these materials. In previous studies it has been shown that ^{2}H n.m.r. studies as well as birefringence measurements[1-3] provide information on local orientation processes. While in the case of ^{2}H n.m.r. the molecular probe was introduced by specific deuteration[4], in the birefringence measurements the orientation of rodlike junctions was probed.

The experimental results so far were interpreted by a greater degree of orientation of the chain segments near crosslink junctions. This concept can be rationalized taking into account that near a crosslink junction the restrictions acting on a chain segment mainly arise from four chain branches while only two chain branches act on segments in a chain (*Figure 1*). These conformational restrictions, as a consequence, should be a function of the crosslink density. A final test of this concept involves direct measurement of the restrictions. One possibility of doing this is to introduce conformational changes by a chemical reaction and to detect the response of the elastomeric network to this disturbance.

A chemical reaction to change the conformational balance in polymer backbones is the *cis–trans* isomerization of aromatic azo derivatives[5-7]. The synthesis of networks that bear an azo-dye at the crosslink junction has been reported for acrylate polymers[8]. In the present paper we describe the synthesis of elastomeric networks with a derivative of azobenzene as crosslinker and initial results concerning isomerization kinetics in swollen gels.

EXPERIMENTAL

Synthesis of the azo-crosslinker

In our study on the orientation behaviour the rodlike crosslink junctions were introduced by the reaction of 4,4'-(4,4'-diphenylmethylene)-1,2,4-triazoline-3,5-dione with polymers bearing allylic hydrogen atoms. The basic reaction scheme is given by
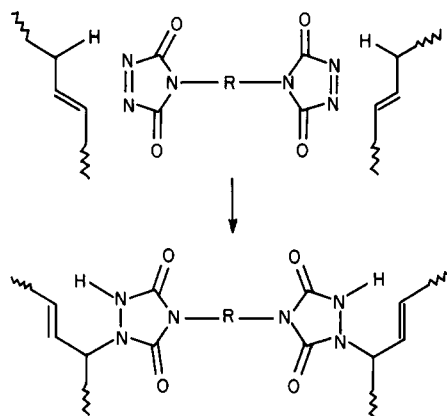
This allows a quantitative introduction of network junctions by a well established reaction and was reported first by Butler *et al.*[9] The main disadvantage is the high reactivity of the 1,2,4-triazoline-3,5-dione group, which prohibits the use of this reaction in bulk. A detailed kinetic study of the crosslink reaction is given elsewhere[10,11]. To introduce the azo chromophore in an analogous way
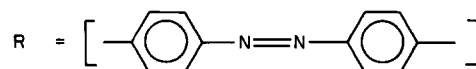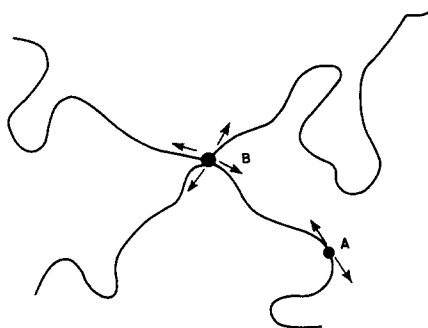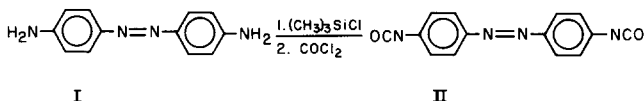

we started from 4,4'-diaminoazobenzene, **I**.

Figure 1 Schematic representation of the restrictions (→) acting on a polymer segment in a chain (A) and near crosslink junctions (B)

After silylation using $(CH_3)_3SiCl$ and phosgenation[12] the corresponding diisocyanate, **II**, was obtained. According to literature descriptions of the synthesis of 1,2,4-triazoline-3,5-diones[13] **II** was reacted with ethyl carbazate to the semicarbazide, **III**.
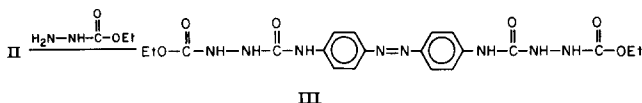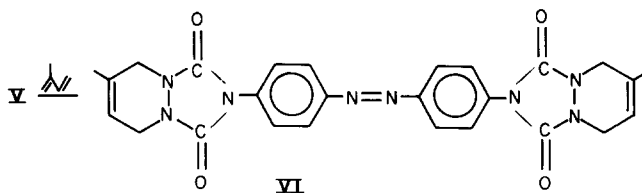

The ring closure to 4,4'-(4,4'-bis-1,2,4-triazolidine-3,5-dione)azobenzene, **IV**, was performed using aqueous potassium hydroxide.
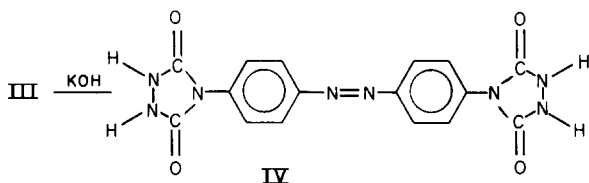
From **IV** the reactive crosslinker 4,4'-(4,4'-bis-1,2,4-triazoline-3,5-dione)azobenzene is obtained by oxidation with NO_2:
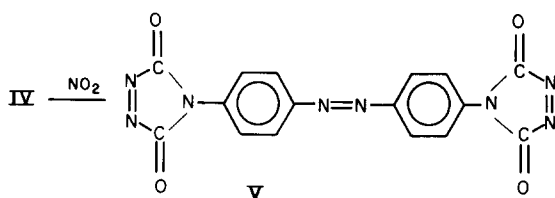
As low molecular weight model for the isomerization kinetics **V** was reacted with isoprene to the Diels–Alder addition product, **VI**

Silylation of 4,4'-diaminoazobenzene **VI**. 10 g (0.047 mol) of the diamino compound was dissolved in 100 ml dried THF. 18.5 ml (0.14 mol) triethylamine was added. The mixture was heated under reflux, then 17.9 ml

(0.14 mol) trimethylchlorosilane was added slowly. The reaction mixture was kept under reflux for 2 h. The solvent was distilled off under nitrogen and the residual dark brown oil was reacted with phosgene without further purification.

Characterization: I.r. (cm^{-1}): 3360 (m, NH), 2950 (m, CH_3), 1590 (vs), 1500 (s), 1450 (m), 1380 (m), 1310 (vs), 1250 (s), 1230 (w), 1145 (s), 900 (vs), 840 (vs).

Synthesis of 4,4'-azobenzene diisocyanate. The crude silylated amine was dissolved in chlorobenzene and added slowly at 0°C to a solution of phosgene in chlorobenzene. After addition the reaction mixture was kept at room temperature over night. The reaction mixture was heated to 80°C in a stream of phosgene. After the product dissolved the phosgene stream was turned off and the reaction mixture was heated under reflux for 3 h. The chlorobenzene was distilled off under vacuum. The crude product was used for the next reaction without further purification.

I.r. (cm^{-1}): 730 (w), 820 (w), 850 (vs), 1000 (w), 1100 (vs), 1140 (vs), 1510 (s), 1590 (vs), 2300 (vs).

Synthesis of the semicarbazide, **III**. The diisocyanate, **II**, was dissolved in benzene and cooled under nitrogen in an ice bath. A solution of 9.7 g ethyl carbazate in dried benzene was added. The reaction mixture was then heated to reflux. The precipitated product was recrystallized in methanol. Yield: 45% with respect to diamino-azobenzene. Elemental analysis: $C_{20}H_{24}N_8O_6$ C: 49.9 (calc. 50.8); H: 5.43 (5.1); N: 23.94 (23.7). I.r. (cm^{-1}): 780 (w), 830 (w), 850 (w), 885 (vs), 975 (m), 1050 (s), 1250 (vs), 1350 (s), 1430 (m), 1590 (vs), 1620 (vs), 1700 (vs), 1750 (vs), 3250–3450 (s). N.m.r. $-CH_3$, 1.24 ppm, triplet; $-CH_2-$, 4.15 ppm, quartet; aromatic ABA'B' 7.8 ppm; $-NH-$, 8.24, 8.95, 9.18 ppm, three singlets (broadened).

Synthesis of 4,4'-(4,4'-bis-1,2,4-triazolidine-3,5-dione) azobenzene. 3 g of the semicarbazide, **III**, were dispersed at 0°C in 6 ml aqueous potassium hydroxyde (4 molar). 20 ml distilled water were added and the mixture was heated under reflux for 20 min. The mixture was filtered at high temperature. After cooling the solution to room temperature, aqueous HCl ($\sim$2 molar) was added to pH 1. The precipitated product was filtered, washed with water and dried at 40°C under vacuum.

Yield: 2.1 g (87% of theory). Elemental analysis: $C_{16}H_{12}N_8O_4$ C: 49.2 (calc. 50.54), H: 3.24 (3.15), N: 28.3 (29.47). I.r. (cm^{-1}) 720 (w), 760 (w), 790 (s), 845 (s), 1430 (s), 1500 (s), 1600 (w), 1705 (vs), 1770 (w), 3200–3300. N.m.r. aromatic (8) ABA'B' 7.9 ppm; $-NH-$ (4), 10.6 ppm, (broad).

Synthesis of 4,4'-(4,4'-bis-1,2,4-triazoline-3,5-dione) azobenzene, **V**. 1 g **IV** was dispersed in 200 ml dried methylene chloride. 20 g of freshly dried Na_2SO_4 was added. The mixture was cooled in an ice bath under a stream of nitrogen. Gaseous NO_2 dried by passing through an anhydrous $CaCl_2$ column was bubbled through the reaction mixture. The insoluble triazolidine, **IV**, dissolved to a deep red solution of **V**. After 2 h, the stream of NO_2 was turned off. The excess of NO_2 was removed by a nitrogen stream. Unreacted **IV** and sodium sulphate were filtered off and the solvent was removed at 0°C under vacuum. The product was stored at -16°C until used for the crosslinking reaction.

Elemental analysis: $C_{16}H_8N_8O_4$ C: 50.3% (calc. 51.06); H: 2.35 (2.12); N: 28.9 (29.7). I.r. (cm^{-1}): 690 (s), 720 (w), 760 (s), 800 (w), 850 (vs), 900 (s), 1200 (s), 1290 (s), 1530 (s), 1620 (s), 1730 (vs, double), 1790 (vs), 2350 (w), 3040 (w). N.m.r.: aromatic ABA'B', 7.9 ppm.

Synthesis of the model compound, VI. A twenty-fold excess of freshly distilled 2-methylbutadiene (isoprene) was dissolved in methylene chloride and a solution of V was added slowly. Immediate reaction occurred and the product, VI, precipitated from the solution.

Elemental analysis: $C_{26}H_{24}N_8O_4$ C: 61.2 (calc. 60.94), H: 4.69 (4.57), N: 22.05 (21.87). I.r. (cm^{-1}): 745 (vs), 810 (vs), 855 (s), 1300 (b), 1420 (s), 1500 (w), 1595 (w), 1720 (vs), 1750 (w), 2950 (w). N.m.r.: –CH$_3$, 1.2 ppm, singlet; 2xCH$_2$, 4.1 ppm, singlet and doublet; –CH=, 5, 5.25, 5.6 ppm; aromatic ABA'B' 7.9 ppm.

Preparation of swollen gels

To avoid the formation of a large fraction of elastically ineffective loops by the crosslink reaction in solution[3], poly(isobutylene) containing few isoprene units (Butyl N 27) butyl rubber was used as elastomer. A benzene solution (5 wt%) of the polymer (2.4 ml) was mixed with 0.6 ml of a THF solution of crosslinker in a u.v.-cuvette. Owing to the high extinction coefficient, the azo-crosslinker was mixed with 4,4'-(4,4'-diphenyl-methylene)bis-1,2,4-triazoline-3,5-dione in the ratio 1:9 to obtain samples appropriate for u.v. measurements.

After about 1 min the gel had formed. Kinetic studies of the gelation process showed quantitative reaction after about 30 min in the case of butyl rubber[14]. The reaction rates depend strongly on the solvent and the olefin component in the polymer.

The cuvettes were closed and kept in the dark prior to the u.v. measurements. No solvent evaporation was observed. The crosslinking conditions for the different gels are listed in *Table 1.*

As reference for the isomerization kinetics 0.6 ml of a THF solution of VI was added to a butyl rubber solution of the same concentration as the polymer. The final concentration of azo compound was 4×10^{-5} molar.

Isomerization experiments

Azo-compounds are isomerized from the *trans* to the *cis*-form by irradiating at 350–370 nm, the absorption maximum of the *trans* isomer. A high pressure mercury lamp (40 W, Leitz) and a 365 nm filter (Balzers, half width 10 nm) was used. The irradiation was carried out directly in a modified sample holder of a Hitachi Perkin–Elmer model 200 spectrophotometer. The experimental set-up is given elsewhere[15].

In *Figure 2* the u.v. spectrum of BK-A-2 is given in the *trans* form as well as after different times (0–120 min) of irradiation. The irradiation was continued until changes

Table 1 Crosslinking conditions of the poly(isobutylene) gels

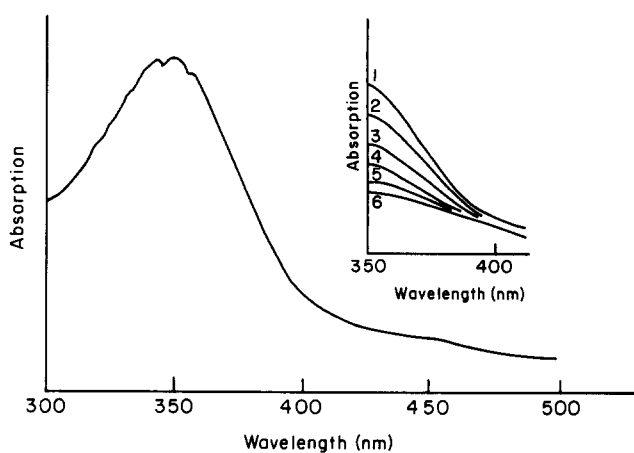|		Crosslinker concentration		
Sample	Concentration of polymer in gel (g l^{-1})	total (mol l^{-1}) × 10^3	azo-type (mol l^{-1}) × 10^3	Crosslink density (mol cm^{-3}) × 10^5
BK-A-1	27	0.733	0.0662	2.59
BK-A-2	27	1.173	0.1059	4.14
BK-A-3	27	1.466	0.132	5.17
BK-A-4	27	1.76	0.159	6.21

Figure 2 U.v. spectrum of crosslinked gel (crosslinker in the *trans* state) and after different times of irradiation: (1) 0; (2) 20; (3) 40; (4) 60; (5) 80; (6) 120 min
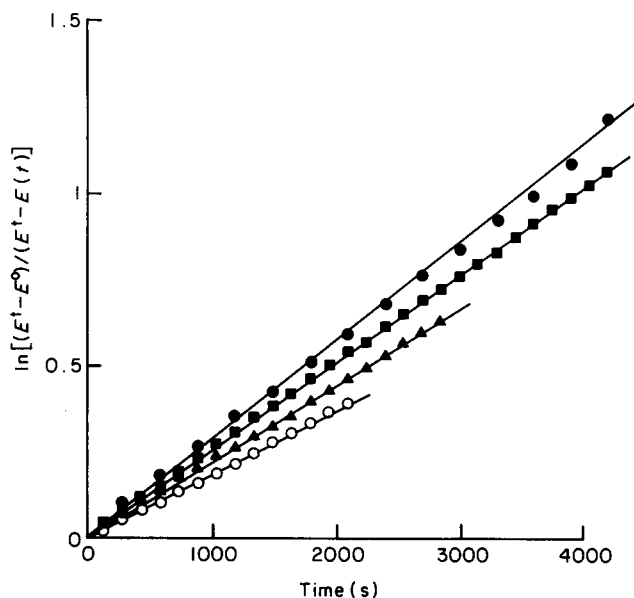

Figure 3 First order plot of the thermal *cis–trans* isomerization at 50°C for different swollen gels: ○, BK-A-1; ▲, BK-A-2; ■, BK-A-3; ●, BK-A-4

in the absorbance were negligible. Generally this was achieved after ~1 h. The thermal *cis–trans* isomerization was monitored by detecting the absorbance at 370 nm. The temperature range was 30°C–60°C.

RESULTS AND DISCUSSION

Kinetics of the cis–trans *isomerization*

The kinetics of the thermal *cis–trans* isomerization of azo-dyes in polymer backbones is known to be the same as for low molecular weight model compounds[5,6]. This holds as long as the measurement is carried out in solution. In all these cases typical first order behaviour is found. As a conclusion, the polymeric surrounding does not influence the isomerization process. Deviations from the simple first order scheme are observed in the solid state[15]. The butyl rubber gels are highly swollen and thus the isomerization behaviour should be similar to that of dissolved polymers and low molecular weight models, as far as there is no specific effect of the location of the azo dye at the crosslink junction.

In *Figure 3* the results for the *cis–trans* isomerization kinetics at 50°C are shown in a typical first order plot. E^t is

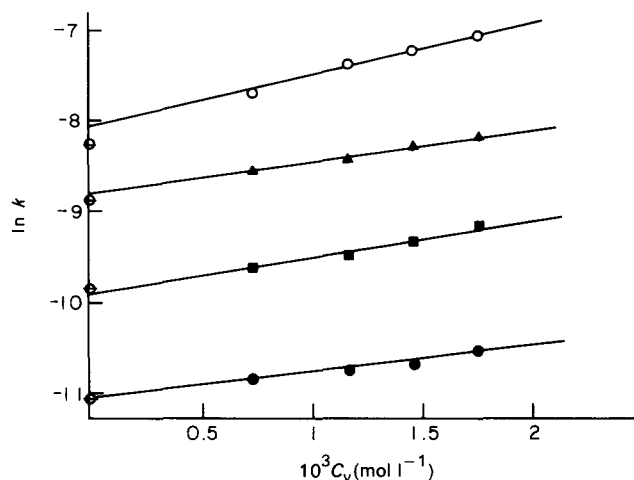**Table 2** Rate constants ($\ln k$) of the thermal *cis–trans* isomerization

T [K]	BK-A-1	BK-A-2	BK-A-3	BK-A-4	Extrapolated to zero cross-linking	Model VI
293	−12.07	—	—	—	—	—
303	−10.82	−10.73	−10.67	−10.51	−11.05	−11.02
313	−9.6	−9.48	−9.33	−9.15	−9.96	−9.91
323	−8.57	−8.42	−8.29	−8.2	−8.85	−8.86
333	−7.69	−7.38	−7.23	−7.06	−8.13	−8.26
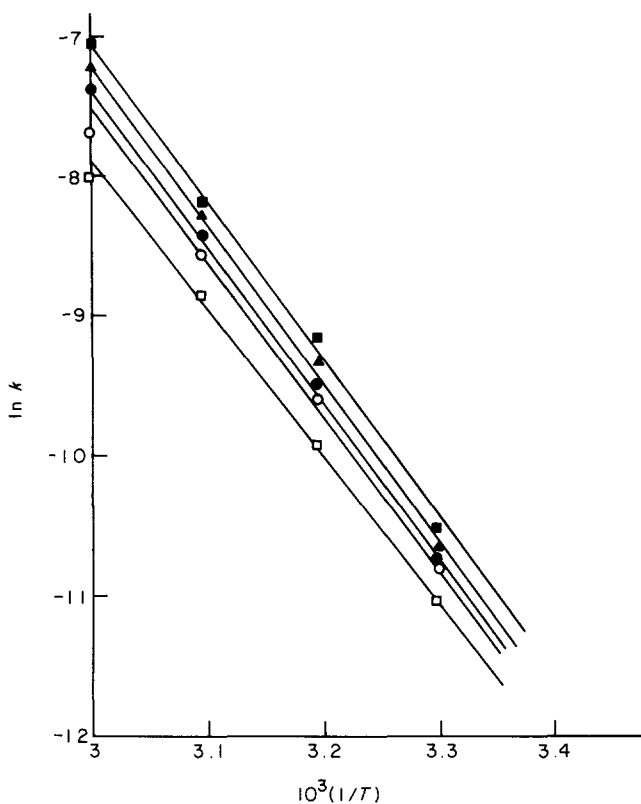
Figure 4 Arrhenius plot of the isomerization rate constants for the different gels (○, BK-A-1; ●, BK-A-2; △, BK-A-3; ■, BK-A-4) and the low molecular weight model (□)

Figure 5 Plot of the isomerization rate constant k as a function of the crosslinker concentration c_V for different temperatures (K): ●, 303; ■, 313; ▲, 323; ○, 333

the extinction of the *trans* component in the thermal equilibrium, E^0 the extinction after irradiation at time 0 and $E(t)$ the extinction at time t. The straight lines indicate that the isomerization obeys the expected first order kinetics. Surprisingly, the isomerization rate depends on the concentration or the crosslinker, i.e. on the crosslink density. The higher the crosslink density, the higher the rate of the back isomerization to the initial state.

Table 2 gives the observed rate constants. In *Figure 4* the Arrhenius plot of the reaction rate constants is shown for the different networks as well as for the model reaction. Approximately the same slopes are detected for all systems, i.e. the activation enthalpy for the isomerization process is independent of network density. The average activation enthalpy calculated from the slopes is 94 kJ mol^{-1}, which is in good accordance with other systems reported[8,16].

Because of the constant activation enthalpy the differences in the isomerization rate constants arise from differences in the activation entropy of the isomerization process. In *Figure 5* the isomerization rate constants are plotted *versus* the concentration of crosslinker, which for the present system is directly correlated to the degree of crosslinking. For all samples a linear dependence is found

in the concentration range that has been investigated. The extrapolated values for $\ln k$ to zero crosslinking correspond very well to the rate constants for the isomerization of the model reaction VI. The data in column 6 of *Table 2* correspond to these extrapolated values. The dependence of the logarithmic reaction rate constants on crosslink density implies a close relation between the activation entropy for the isomerization process and irradiation-induced entropy changes in the swollen gels. To consider the entropy of the isomerization reaction it is first assumed that the ground state S_t is the same for all gels. This is valid if the chains were in their equilibrium state in the crosslink process and the crosslinker was in the *trans* form during network formation. The second assumption, for the moment, is that the activation entropy $\Delta S^+_{t\rightarrow c}$ for the photochemical *trans–cis* isomerization is the same for all networks. Thus the differences in the activation entropy for the thermal back isomerization $\Delta S^+_{c\rightarrow t}$ must arise from differences in the entropy of the *cis*-form S_c. Consequently the photostationary equilibrium state, being proportional to the difference $S_c - S_t$, should be dependent on the crosslink density. These entropy changes are illustrated in *Figure 6* as a function of the reaction coordinate.

In *Figure 7* the estimated equilibrium constants in the photostationary state are given. The absolute values must be viewed with considerable care, because they depend strongly on the assumption that at 350 nm, i.e. at the absorption maximum of the *trans*-form there is no additional absorption of other species in the system. With this assumption the equilibrium constant is obtained from

$$K_{ph} = c_{cis}/c_{trans} = E^t - E^0/E^0 \qquad (1)$$

Isomerization progress
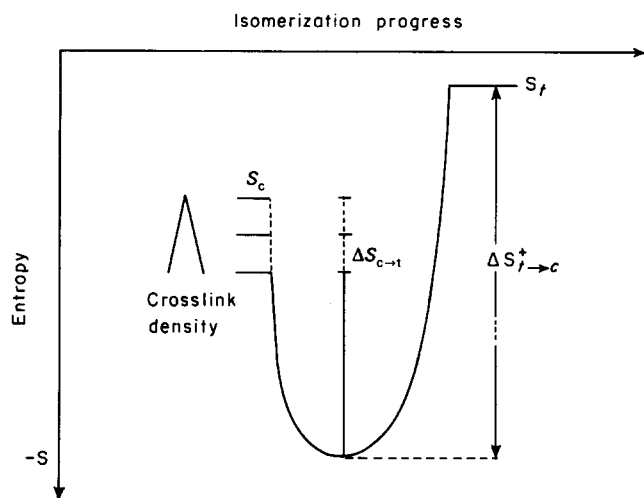

Figure 6 Schematic representation of the entropy changes for the isomerization process in the networks
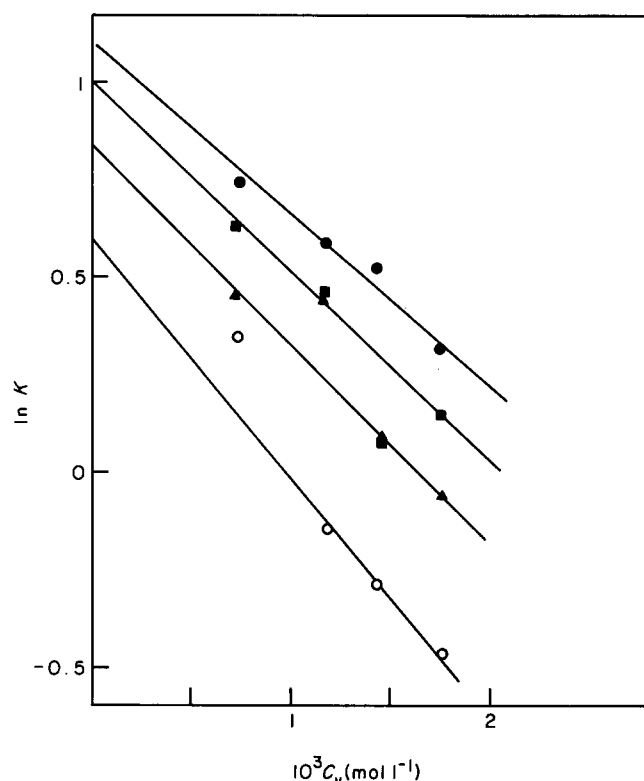

$10^3 c_v (\text{mol } l^{-1})$

Figure 7 Dependence of the equilibrium constant in the photostationary state on crosslink density and temperature (K): ●, 303; ■, 313; ▲, 323; ○, 333

The results are summarized in *Table 3*. The *cis* fraction obtainable in the photoequilibrium state decreases with increasing crosslink density. Again the temperature dependence of the equilibrium constants indicate that the effect is mainly due to entropy effects. The equilibrium constants for the photoequilibrium state reflect the results that have been obtained from the kinetic measurements.

The dependence of the isomerization rate constant on the concentration of crosslinking agent, c_v, is correlated with changes in the activation entropy by

$$dAS_{c \to t}^{0+}/dc_v = R(d \ln k/dc_v) \qquad (2)$$

A similar equation may be derived for the equilibrium constants in the photoequilibrium state assuming that

AH^0 is independent of the crosslink density.

$$dAS_{t \to c}^{0}/dc_v = R(d \ln K_{ph}/dc_v) \qquad (3)$$

While equation (2) has been derived for the thermal *cis–trans* form becomes more dominant in the photoequilibrium state and $dAS_{t \to c}^{0}/d \ c_v$ has a negative Increasing the crosslink density decreases the negative activation entropy (higher isomerization rate) so that $dAS_{c \to t}^{0+}/dc_v$ has a positive sign.

Correspondingly by increasing the crosslink density the *trans* form becomes more dominant in the photoequilibrium state and $dAS_{t \to c}^{0}/d \ c_v$ has a negative sign. The data for the slopes obtained from the different temperatures are listed in *Table 4*. The values from photoequilibrium and kinetic measurements are very similar, thus supporting the scheme discussed for the entropy changes in the isomerization reaction.

As mentioned above, the dependence of $\ln k$ and the activation entropy on the network density indicates the influence of conformational changes in the network during photoisomerization. These conformational changes of the polymer chains attached to the azo crosslinker will decrease the chain entropy and generate a local stress field, which could be responsible for the increasing rate of isomerization.

Eisenbach described the occurrence of a change in the length in a stretched crosslinked poly(butyl acrylate) after isomerization[8]. This 'photomechanical effect' was attributed to the reduction of the length of the azo label upon isomerization. A similar effect in the swollen gels would explain the dependence of the isomerization rate on the crosslink density.

The activation entropy $AS_{c \to t}^{0+}$ in this case can be written as a sum of the activation entropy for the process without a network influence only based on the chemistry AS_{ch}^{0+} and a contribution of the network $AS_{el}^{0}(c \to t)$

$$AS_{c \to t}^{0+} = AS_{ch}^{0+} + AS_{el}^{0}(c \to t) \qquad (4)$$

Table 3 Estimated equilibrium constants and fraction of *cis*-isomer in the photostationary state at various temperatures

	303 K		313 K		323 K		333 K	
	ln K	% cis	ln K	% cis	ln K	% cis	ln K	% cis
BK-A-1	0.74	68	0.63	65	0.46	61	0.35	58
BK-A-2	0.59	64	0.46	61	0.43	60	-0.15	46
BK-A-3	0.52	62	0.09	52	0.1	52	-0.28	43
BK-A-4	0.31	57	0.15	53	-0.06	48	-0.48	38

Table 4 Dependence of the activation entropy for the *cis–trans* isomerization $AS_{c \to t}^{0+}$ and the entropy of formation of the *cis*-isomer $AS_{c \to t}^{0}$ from the crosslinker concentration at various temperatures

	Temperature (K)			
Entropy form	303	313	323	333
$\dfrac{dAS_{c \to t}^{0+}}{dc_v}$ [kJ l mol^{-2} K^{-1}][a]	2.4	3.7	3.1	4.7
$\dfrac{dAS_{t \to c}^{0}}{dc_c}$ [kJ l mol^{-2} K^{-1}][b]	-3.6	-4.0	-4.1	-5.0

[a] from d ln k/dc_v;
[b] from d ln K/dc_v

$\Delta S_{el}^0(c \rightarrow t)$ is the entropy difference of a network with azo crosslinks, where the crosslinker is in the *cis* and the *trans* state, with respect to one mole of azo crosslinker.

To a first approximation the changes in the network entropy on isomerization can be described in terms of the classical theory of rubber elasticity.

Good progress towards a closer insight to the deformation behaviour of elastomeric networks has been made recently by the theory of Flory[17]. In this theory the 'phantom' case as developed in the theory of James and Guth[18] is considered as the lower limit in terms of entropy changes. Deviations of the 'phantom' network arise from local restrictions of the junction fluctuations. The upper limit is given by the affine theory developed by Kuhn and Grün[19], where the restrictions are assumed to be infinite, i.e. the crosslink junctions are kept fixed and the distances deform affinely with the macroscopic strain. For very small deformations the affine theory gives a somewhat more realistic description of the entropy changes. On the other hand the experiments discussed here were performed at a high degree of swelling which diminishes the restrictions arising from the local constraints[20]. In fact the experimental stress–strain dependence of swollen gels is in good agreement with the affine theory[21]. Thus in the case of swollen gels the simple classical theory appears to be a quite reasonable approach to estimate the entropy changes on isomerization.

Application of the theory of rubber elasticity

The entropy of a single chain is proportional to the square of its end-to-end distance according to Treloar[21]:

$$S = c - kb^2 r^2 \qquad (5)$$

The entropy change in a network on deformation is given by

$$\Delta S = -\tfrac{1}{2} N_c k (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \qquad (6)$$

where N_c is the number of network chains per unit volume, k the Boltzmann constant and λ_i the deformation ratios in x, y and z directions. This equation is valid for the assumption of an affine deformation. In the present case of an isotropic deformation where $\lambda_x = \lambda_y = \lambda_z$ equation (6) reduces to

$$\Delta S = -\tfrac{3}{2} N_c k (\lambda^2 - 1) \qquad (7)$$

The deformation ratio λ can be written as

$$\lambda = \langle r \rangle / \langle r \rangle_0 \qquad (8)$$

where $\langle r \rangle$ and $\langle r \rangle_0$ are the average radii of the network chains in the deformed and undeformed state.

Using the phantom theory instead of the affine one, N_c has to be substituted by the cycle rank ξ[17]. For a tetrafunctional network the entropy change in the phantom case is 0.5 of the entropy change given by equation (7).

For the specific case of the isomerization process the length of the crosslink molecule reduces from about 15 Å to 10.5 Å (*Figure 8*). Because the macroscopic dimensions are fixed the mean end-to-end distance of the network chains must increase by a certain value, Δr.
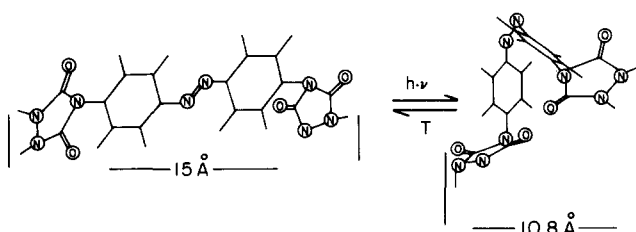

Figure 8 Steric structure of the *trans* and *cis* azo crosslinker; the length of the molecule changes from 15 to 10.8 Å upon isomerization

Using $\langle r \rangle - \langle r \rangle_0 + \Delta r$, the total entropy change can be written as

$$\Delta S = -\tfrac{3}{2} N_c k \left[\left(\frac{\Delta r}{\langle r \rangle_0} + 1 \right)^2 - 1 \right] \qquad (9)$$

For a tetrafunctional network the number of network chains is twice the number of crosslink junctions (for high primary molecular weight). Substituting N_c for $2c_v$ gives

$$\Delta S = -3c_v R \left[\left(\frac{\Delta r}{\langle r_0 \rangle} + 1 \right)^2 - 1 \right] \qquad (10)$$

This equation describes the entropy change per unit volume of a deformed rubber $[\text{J cm}^{-3} \text{K}^{-1}]$. To correlate with the reaction entropies obtained from the kinetic measurements, molar quantities $[\text{J mol}^{-1} \text{K}^{-1}]$ with respect to the azo crosslinker are required. Equation (10) is valid for the isomerization from the *trans* to the *cis* form of the azo label. For the thermal back isomerization the entropy increases, so that the sign changes.

Using $c_{azo} = 0.1 \, c_v$ the molar entropy change is given by

$$\Delta S_{el}^{0+}(c \rightarrow t) = -\frac{\Delta S}{c_A} = +30 R \left[\left(\frac{\Delta r}{\langle r \rangle_0} + 1 \right)^2 - 1 \right] \qquad (11)$$

which is the network contribution to the entropy of the isomerization of the azo crosslinker. A quantitative comparison requires the determination of the microscopic elongation ratio, i.e. of Δr and $\langle r \rangle_0$. The average end-to-end distance $\langle r \rangle_0$ in the undisturbed state is given by

$$\langle r \rangle_0^2 = n l^2 C^\infty \qquad (12)$$

where n is the number of monomers per network chain, l is the length of a monomer unit ($= 2.5$ Å), and C^∞ is the characteristic ratio for polyisobutylene, equal to 6 (ref. 22).

The number of segments per chain is given by the number of monomer units $[M]$ and the crosslinker concentration c_v by

$$n = [M]/c_v$$

A reasonable estimate of Δr is much more difficult. The change of the azo crosslinker molecule is about 4.5 Å. The problem is to correlate this change with a change of the network chains. In addition only 10% of all junctions are of the azo type, thus complicating an estimation of Δr. Taking this into account the maximal change of the end-to-end distance for every network chain would be in the order of 0.5 Å.

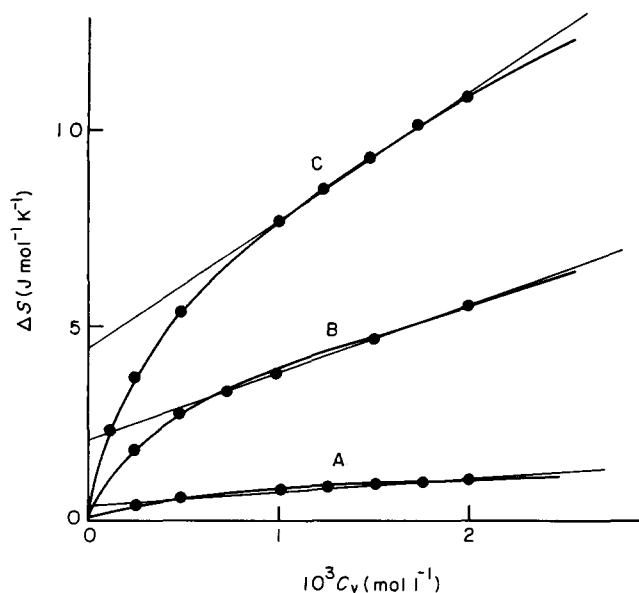In *Figure 9* the change in the network entropy per mole azo crosslinker is calculated for different values of Δr as a

Figure 9 Contribution of network to entropy in reaction calculated according to equation (11) for different values of Δr: (A) $\Delta r = 0.2$ Å, slope = 300; (B) $\Delta r = 1$ Å, slope = 1700; (C) $\Delta r = 2$ Å, slope = 3150

function of the concentration c_v. It is evident that in the concentration range $c_v = 0.75$–1.76×10^{-3} mol l^{-1} the function is quite linear, as is found experimentally. For a value of $\Delta r = 2$ Å the average slope in this concentration range corresponds well to the negative slope of d $\Delta S_{c \rightarrow t}^{0}/c_v$ obtained from the kinetic measurements. The values are 3150 and 3400 J l mol^{-2} K^{-1} respectively.

This value of 2 Å appears to be too large from considerations of the changes of the azo crosslinker alone. Nevertheless it should be taken into account that conformational hindrances of the segments linked directly to the crosslink will increase strongly the value of an effective $\Delta r'$. Consequently the local constraints of the chain segments near crosslink junctions will increase the effect of the isomerization on the network entropy and vice versa.

It has been pointed out by Flory and Erman[17] that the network junctions are the entities most vulnerable to the effects of diffuse entanglements and steric constraints. Direct experimental evidence of the increased steric constraints near junctions is given by ^{2}H n.m.r. experiments[1].

It has been shown that, in contrast to the isomerization of azo labels in free chains, for the isomerization of azo labels located at network junctions there is a marked effect on the isomerization kinetics in swollen gels. In the network case the dependence of the isomerization rate on the crosslink density can be interpreted in terms of the classical theory of rubber elasticity. The isomerization causes a decrease in the conformational entropy of the chains. The corresponding elastic retractive force induces a faster *cis–trans* isomerization.

The present results at first appear to be in contrast to those obtained by Eisenbach[8], where it was deduced from kinetic measurements that 'obviously crosslinking itself and also the degree of crosslinking retards the thermal

isomerization process'. A more detailed analysis of the data showed that this dependence reflects the different glass transition temperatures of the systems investigated, so that the observed rate constants primarily depend on the viscous properties of the surrounding polymer matrix and can be interpreted in terms of the free volume concept, where generally differences in the activation enthalpy are considered. In the present investigation the effect of the surrounding matrix diminishes because the 'glass transition temperature' of the gels is far below the temperature of measurement. Owing to the high mobility in the swollen state the chains immediately reach their conformations corresponding to thermal equilibrium. As a consequence the activation enthalpies are constant, which is not the case for the acrylate networks. Corresponding studies of the polyisobutylene networks in bulk and under deformation are currently being carried out.

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