

## PHOTOMECHANICAL EFFECTS IN PHOTOCHROMIC SYSTEMS

G. Smets, J. Braeken and M. Irie

Department of Chemistry, K. Universiteit Leuven, Belgium

**Abstract** - Indoleninospirobenzopyrans (ISBP) undergo under ultraviolet irradiation ring opening with production of strongly coloured merocyanines, which can return thermally or photochemically to the colourless spirobenzopyrans. Their decolouration rate in stretched polymer matrices depends on their molar volume, the physical properties of the matrix and on the orientation of the polarized light with respect to the stretch orientation. In polyvinyl alcohol they exhibit reverse photochromism, i.e. the coloured merocyanines are stable and decolourize under visible light irradiation. These merocyanines, dissolved in stretched polyvinyl alcohol, develop strong absorption dichroism, resulting from their molecular orientation.

On the basis of these properties the photochemical contraction of ethyl acrylate networks cross-linked with ISBP-bismethacrylate has been further examined. The influence of the bismethacrylate concentration and the influence of the relative elongation have been studied, as well as the reversibility of the contraction/elongation cycles and their activation energies. Using monochromatic light of different wavelengths, it is possible to bind the photoresponse of the system with the absorption spectrum of the merocyanine in the visible. The influence of the orientation of the merocyanines was analyzed using polarized light. Shrinking is stronger with parallel polarized light than perpendicular with respect to the stretch orientation. The contraction dichroism of stretched samples equals 1.5 ( $D_{\parallel} / D_{\perp}$ ), while the decolouration rate dichroism amounts to about 1.14.

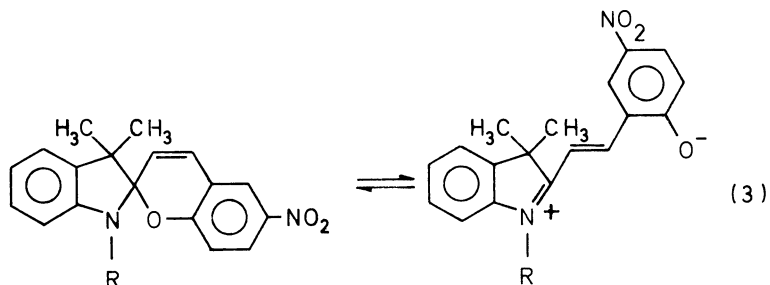
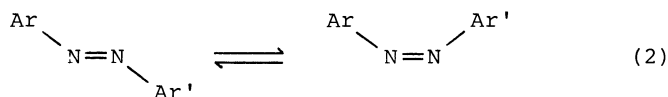
## INTRODUCTION

Reversible photoisomerization reactions are typical examples of photochromic systems, in which a photosensitive chromophore A is transformed under irradiation into an isomer B, which can return to the initial state either thermally, or photochemically (eq.1).



If such photoisomerization reactions are carried out in a polymeric matrix instead of in solution, one observes very often a strong decrease of their quantum yield and a modified photostationary equilibrium, especially if the reaction takes place below the glass transition temperature of the matrix. These polymeric effects are most strongly pronounced when the chromophores are bound chemically to the polymer; they are indeed related with the reduction of chain segment mobility (1,2). The matrix rigidity may influence the different deactivation processes involved in these photochemical reactions, but it affects most strongly the thermal reverse reactions. The isomerization reactions which have been considered most from these points of view in the literature are those which involve an appreciable change of configuration of the photochrome, e.g. rotation of one moiety of the molecule with respect to the other one. They are the reversible cis  $\rightleftharpoons$  trans isomerization of aro-

matic azo compounds (3 to 7) and the ring opening/closure of spiroopyran derivatives (2,8 to 11) as shown in the following equations 2 and 3.

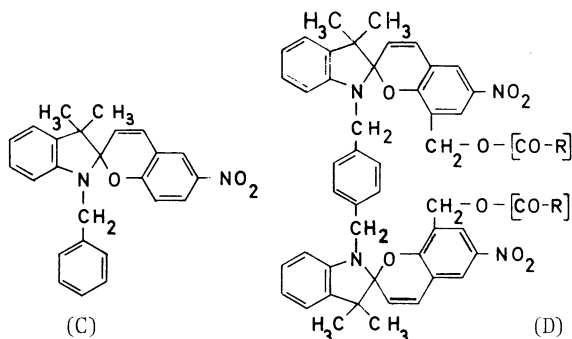


Actually the second class of compounds afforded more pronounced effects, and was therefore examined previously in more details. Recently as a consequence of preliminary observations (12) we focussed our main interest on orientation phenomena, namely from two points of view: influence of polymer orientation on photochromic behaviour, and inversely influence of benzospiroopyran photochromes on matrix behaviour.

In the present paper we wish to report on both aspects, and insist especially on the so called photomechanical effects, i.e. the photocontractile behaviour of some photochromic rubbers.

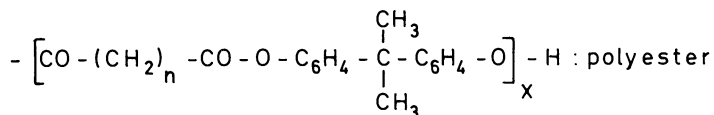
#### INFLUENCE OF POLYMER ORIENTATION

It was observed that the decolouration behaviour of spirobenzopyran photochromes dissolved in a given polymer depends on their molecular size and on their molecular orientation by stretching the matrix (13,14,15). Comparison was made between 1'-benzyl-6-nitro-DIPS, i.e. 1'-benzyl-6-nitro-3',3'-dimethyl-spiro(2H-1-benzopyran-2,2'-indoline) (C) and corresponding xylylene-bis-DIPS diesters (D).



-CO-R:

-CO-Et : bispropionate



For oligomers,  $n=4$  (adipate) and  $x$  carries between 2 and 8; for photochromic polyesters,  $n$  was equal to 5 (pimelate) and  $x$  amounts to 20-25. In order to

obtain reproducible and conclusive kinetic results, one has to take in consideration slow relaxation phenomena occurring in films on stretching; therefore annealing and prolonged storage are required before making kinetic measurements. Stretching of a film of poly-bisphenol-A-pimelate ( $\bar{M}_n$ : 32.000) or polyethyleneglycol tere/isophthalate (50/50) ( $\bar{M}_n$ : 21.000) containing 5 weight percent bisphotochrome propionate, affects considerably the first rapid decolouration phase as well as the second phase that becomes very slow at high elongation (Fig.1).

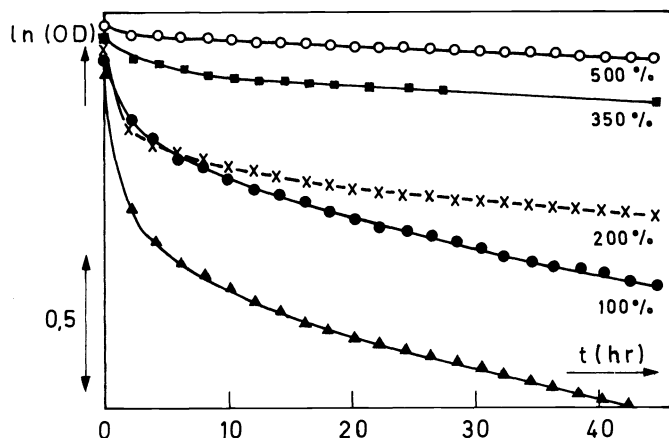


Fig.1. Decolouration of bisphotochrome propionate. Influence of film stretching.

Such molecular orientation effect on colour fading occurs only temporarily with the mono-photochrome C and vanishes indeed progressively on storage (14). However as soon as the molecular size of the photochrome becomes sufficiently high by increasing the length of the ester groups attached in position 8 (formula D,  $x > 2$ ) thermal fading becomes very slow and practically insensitive to stretching of the matrix in which the photochrome is dissolved. Its decolouration behaviour is similar, sometimes even better than that of polyester in which the photochrome is built within the polymeric backbone.

TABLE 1. Thermal decolouration of photochrome oligomers. Influence of polymer stretching.

Irrad. time	temp.	Photochrome	Matrix	Unstretched		Stretched	
				% decol. after 20 hr	$\text{K} \times 10^7 \text{ sec}^{-1}$	% decol. after 20 hr	$\text{K} \times 10^7 \text{ sec}^{-1}$
80	25°	polyester <sup>a</sup>	-	38	20	33	18
15	66°	polyester	-	7	5	6.4	5
120	60°	oligomer-20 <sup>b</sup>	PET-I <sup>c</sup>	4.5	3	3.7	2.8
120	65°	oligomer-20	PSt <sup>d</sup>	3.5	3.5	2.5	2.5

a.  $\bar{M}_n$  : 16.000

c. polyethylene-tere/iso-phthalate (50/50)

b. molecular weight 2020 (vap.p.osmom.)

d. polystyrene

The orientation of photochromes in stretched polymer films, and especially in stretched polyvinylalcohol (PVOH) can be easily demonstrated by dichroism measurements. Indeed in highly polar medium as PVOH, the equilibrium spiro-pyran  $\rightleftharpoons$  merocyanine is strongly shifted to the right, and the planar merocyanine can be more easily oriented than the parent spiro-pyran; therefore PVOH is particularly suitable for such measurements. By irradiating with polarized light parallel and perpendicular with respect to the stretch direction, one can evaluate easily the dichroism ratio by measuring the absorbance in both directions  $D = A // A_{\perp}$ . As an illustration, a film of PVOH contain-

ing 0.5% 6-carboxy-8-nitro-DIPS ( $\lambda_{\max}$  553 nm) shows a strong dichroism on stretching. The dichroism ratio increases strongly with the elongation (Fig. 2), and reaches a plateau value, that depends itself on the wavelength of measurements.

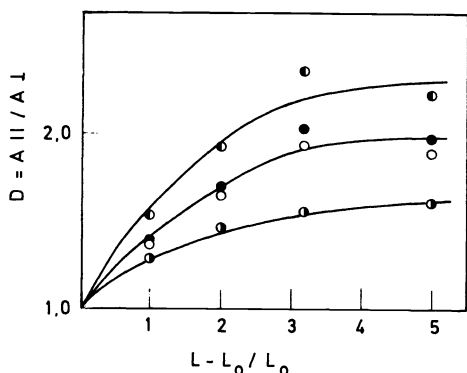


Fig. 2. Influence of film stretching on the dichroism of 6-carboxy-8-nitro-DIPS in polyvinylalcohol.  
 ○ 370 nm; ● 440 nm; ○ 500 nm; ● 590 nm.

This wavelength dependence may result from the existence of several isomers with different absorption maxima, and different orientation of their transition moments.

In conclusion, kinetics of decolouration of open ring merocyanines and dichroism experiments can clearly show the orientation of the merocyanines in the stretch direction. They provide valuable informations for the interpretation of the effect of polarized light on the photocontraction, which will be considered in the second part.

#### PHOTOCHEMICAL CONTRACTION OF PHOTOCROMIC NETWORK

As well as the polymeric matrix can induce orientation of spirobenzopyran photochromes and affect considerably their rate of thermal fading, reciprocally ring-opening followed by cis-trans isomerization should influence the molecular shape of the macromolecules. Indeed when one moiety of the photochrome rotates with respect to the other one, then a large part of the chain has to

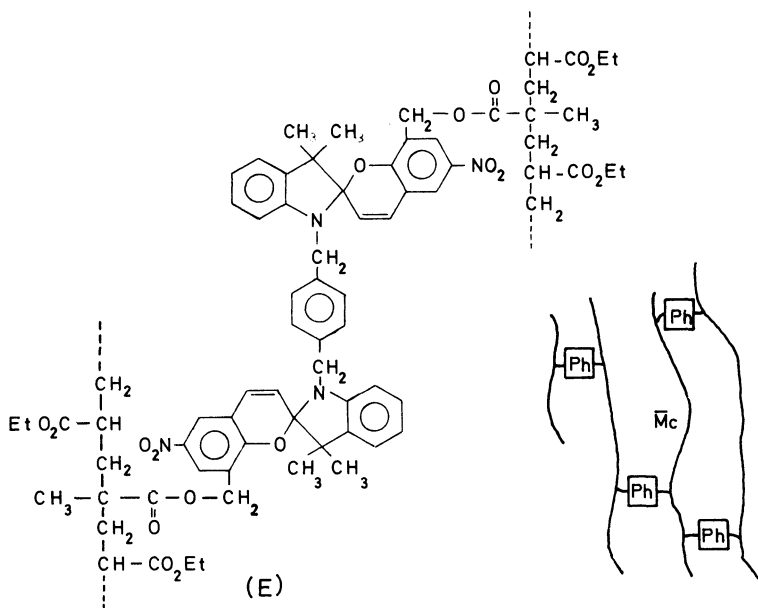


Fig. 3. Photochromic polyethyl acrylate rubber.

follow the motion and has to swing into a new position. In the case of a photochromic cross-linked rubber, contraction/expansion cycles could be envisaged, and this hypothesis was strengthened by the reversible photomechanical properties observed by Van der Veen and Prins (16,17) with gels of cross-linked 2-hydroxyethyl methacrylate containing small amount of chrysofenins, and by Agolini and Gray (18) with poly-(4,4'-diphenylazopyromellitimide). Similarly Smets and De Blauwe (12) reported photocontraction of cross-linked spirobenzopyran rubber networks which were obtained by copolymerization at 35°C of ethyl acrylate (EA) with variable amounts of bis-photochrome dimethylacrylate as cross-linking agent (BPC), i.e. 1,1'-( $\alpha,\alpha'$ -p-xylyl)-bis-[3',3'-dimethyl-8-methacryloxymethyl-6-nitro-spiro(2H-1-benzopyran 2,2'-indoline)]. The chemical structure of these DIPS-rubbers (formula E) is characterized by the presence of photochromic cross-links between polyethyl acrylate chains (Fig.3).

This system has been further examined in more details in order to elucidate its intimate mechanism.

The copolymerizations were carried out in benzene solution (50% vol.) in the presence of diisopropyl peroxydicarbonate (IPP) as radical initiator. Their syntheses and molecular characteristics are given in Table 2.

TABLE 2. Photochromic PEA-rubbers

Polymer	mmoles BPC <sup>e</sup>	nitrogen <sup>a</sup> %	$\bar{M}_c$		Tg <sup>d</sup>
			calc. <sup>b</sup>	exp. <sup>c</sup>	
a	0.76	0.56	10.000	11.500	-11
b	0.66	0.47	11.900	14.900	-13
c	0.54	0.42	13.300	21.000	-14
d	0.44	0.39	14.400	34.500	-15

a) elemental analysis

b) calculated from the nitrogen content

c) by swelling experiment in acetone

d) DSC-measurements

e) number mmoles BPC for 100 mmoles EA and 0.096 mmoles IPP

In this table serious discrepancies exist between the swelling  $\bar{M}_c$ -values and those calculated on the basis of the nitrogen content for an ideal network (in which the number of chains should be twice the number of BPC-junctions); they increase considerably with decreasing the cross-linker concentration. It is likely due to the presence of cross-linker that did react only with one function, and to network imperfections e.g. loose ends.

On irradiation of stretched sheets of these photochromic rubbers G. Smets and F. De Blauwe (12) observed previously an apparent photocontraction which was related with the ring opening and cis-trans isomerization of the benzopyran system. They have shown that the maximum shrinking corresponds to about 2.5% relative contraction; it depends on the stress, the temperature and the degree of cross linking of the rubber. The phenomenon was reversible, and permitted contraction/elongation cycles corresponding to alternate light/dark periods. They assumed that contraction corresponds to an entropy increase of the polymer chain, due to the higher flexibility of the open-ring merocyanine compared to the stiffness of the parent ring-closed spiroopyran. The set-up used for these experiments is shown in Fig.4; the temperature increase in the film compartment never exceeds 0.2°C.

The elastic properties of these rubbers is illustrated in Fig.5 which represents the variation of  $f$ , tensile force per unit cross-section measured in the unstrained state, as a function of  $(\lambda - \frac{1}{\lambda^2})$  according to the equation

$$f = \frac{\rho RT}{\bar{M}_c} \left( \lambda - \frac{1}{\lambda^2} \right)$$

where  $\lambda$  is the mean fractional extension  $L/L_0$  of the rubber sample,  $\rho$  the polymer density and  $\bar{M}_C$  the mean molecular weight between two neighbouring cross-links (19). At constant elongations,  $f$  increases with decreasing  $\bar{M}_C$ .

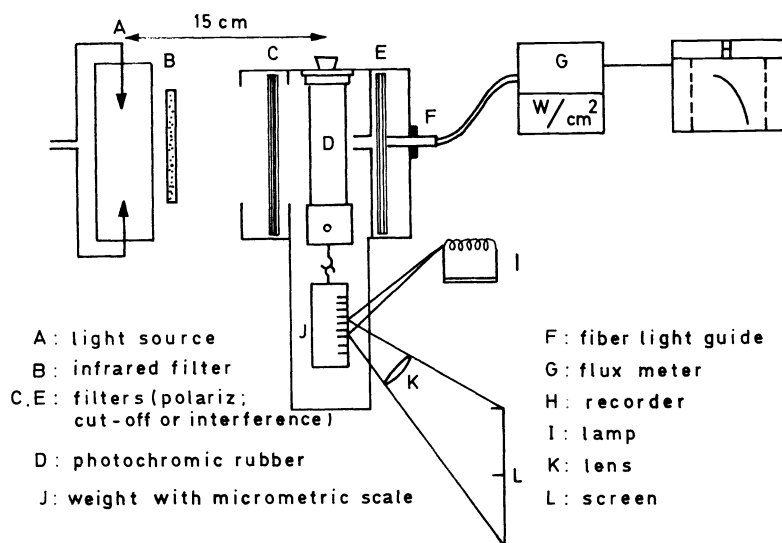


Fig.4. Experimental schema

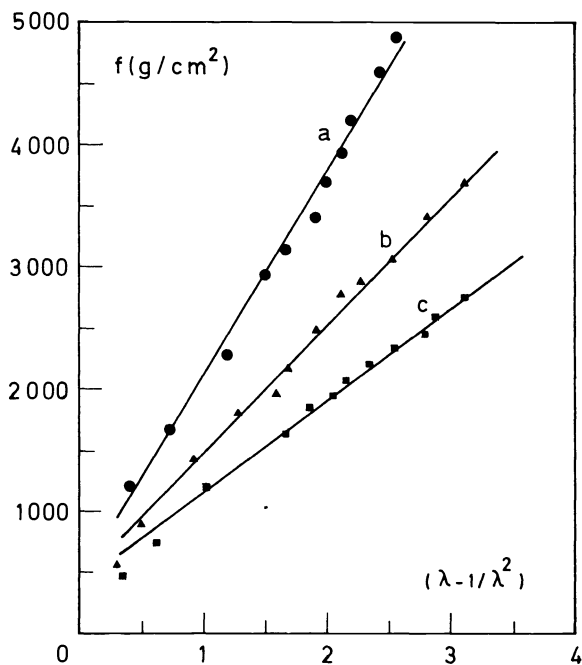


Fig.5. Elastic behaviour of PEA rubbers.  
 a:  $\bar{M}_C$  34.500; b:  $\bar{M}_C$  14.900; c:  $\bar{M}_C$  11.500

On irradiation of stretched samples ( $\lambda_{\text{irr.}} > 290$  nm) contraction as well as colouration (551 nm) are observed. The contraction reaches soon (1-2 min.) its final asymptotic value; on cutting off the light the contraction decays rapidly, and the initial length is restored after two minutes. Alternate shrinking/length recovery cycle can be repeated many times; they are nicely reproducible and show no apparent fatigue. This photocontraction depends on

the degree of cross-linking (Fig.6); by plotting the relative contraction  $-\Delta L/L$  against the tensile force, curves are obtained presenting a maximum, that is highest for the highest  $\bar{M}_c$  values.

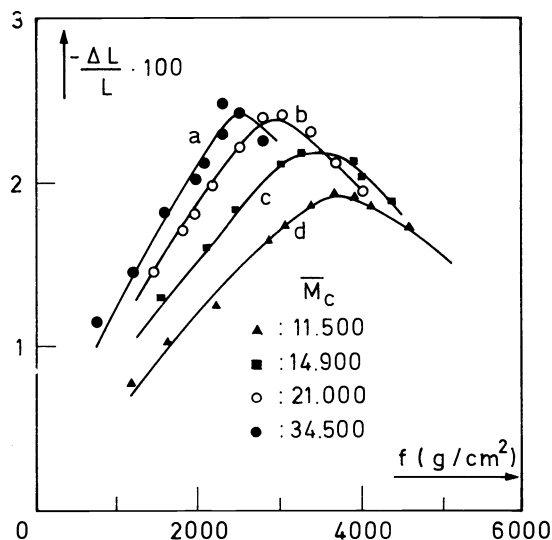


Fig.6. Photocontraction of PEA rubbers. Influence of tensile force and  $\bar{M}_c$ .

On following simultaneously colour fading and length recovery during the dark period, it appeared however surprisingly that only a minor decrease (less than 3%) of optical density is noticed during the complete length recovery. This means that only a small percent of photochromic cross-links should intervene in these contraction phenomena, or that there is no direct correlation between the decoloration of merocyanine and length recovery. Moreover the rate of shrinking, i.e. the photomechanical response, is higher when the film has been already strongly coloured previously, than on the first irradiation cycle (Fig.7). This statement suggests strongly that the merocyanine absorption plays an important role in the contraction.

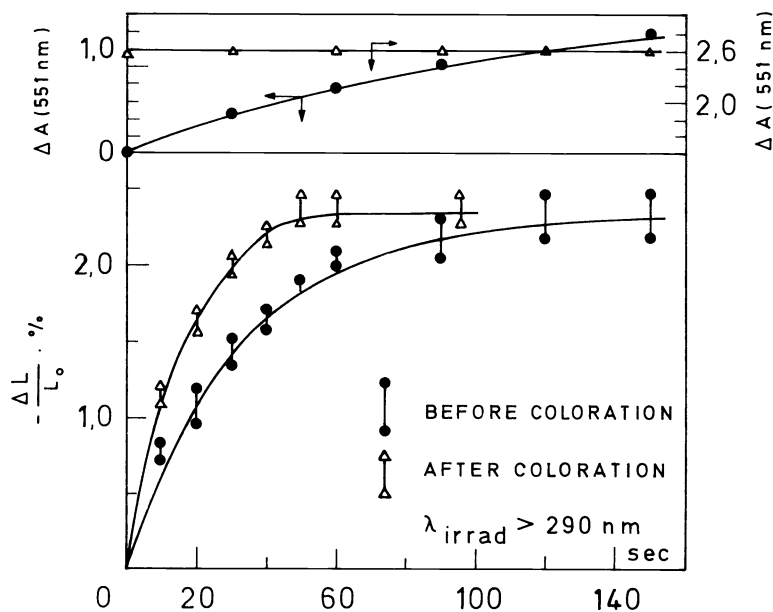


Fig.7. Variation of optical density ( $\Delta A$ ) and photocontraction.

In order to clear up the reaction mechanism, the activation energy of thermal length recovery has been determined for two different samples with  $\bar{M}_c$  equal to 11.500 ( $R_3$ ) and 21.000 ( $R_5$ ). Therefore recovery half-times have been measured, each value resulting from five successive shrinking/elongation cycles. As observed previously by De Blauwe and Smets (12) the contraction decreases on increasing the temperature, as expected. It depends markedly on the  $\bar{M}_c$  values; at around 15°C the final contraction (plateau) amounts 2.73% at  $\bar{M}_c$  21.000 instead of 1.9 percent for  $\bar{M}_c$  equal to 11.500. The contraction rate is also greater at high  $\bar{M}_c$ ; one-half minute is only required for reaching already 80-90% contraction for sample  $R_5$ .

The synoptic Table 3 illustrates the experimental results; it shows the increase of relative contraction with the duration of irradiation (columns 4 and 5). After 60" the photostationary contraction was obtained, unless indicated. Columns 6 and 7 give the decrease of relative contraction with the time in the dark, while  $\tau_{1/2}$  indicates the half-time of length recovery (dark).

An equivalent activation energy of 6 to 7 kcal was found for both photochromic rubbers.

On the other hand, thermal decolouration kinetics have also been followed for the  $R_5$  sample at different temperatures between 13 and 46°C. The Arrhenius diagram indicates an activation energy of 26.8 kcal/mole. The enormous difference between both activation energy values implicates that the thermal fading of merocyanine to spiroopyran cannot be the determining factor of the length recovery in the dark.

TABLE 3. Influence of the temperature on shrinking/elongation

Polymer	t°/C	L cm	$-\frac{\Delta L}{L} \cdot 100$				$\tau_{1/2}$
			Light		Dark		
			15"	60"	15"	60"	
$R_3$ $M_c=11.500$	15.3	6.7	0.88	1.91	1.38	0.55	28.3
	22	8.4	0.71	1.74(90")	1.02	0.22	21
	31.5	7.61	0.71	1.58	0.91	0.16	17
	38.4	8.26	0.57	1.43	0.66	0.13	12
	49.3	7.54	0.53	1.07(90")	0.32(10")	0(30")	8
$R_5$ $M_c=21.000$	14.6	6.7	1.46	2.73	2.02	0.7	34
	25	6.56	1.46	2.51	1.48	0.18	23
	35.3	6.38	1.85	2.44	1.22	0.24(30")	15
	47	6.16	1.83	2.22	0.41	0(30")	10

All these new data made it necessary to select the irradiation wavelength by using cut-off-light filters or interference filters, if one desires to elucidate unambiguously the contraction/elongation mechanism.

When irradiation with visible light ( $\lambda_{irr.} > 472$  nm) is used excluding absorption by the parent spirobenzopyran, a similar contraction/length recovery diagram is obtained, notwithstanding some bleaching of the merocyanine. A contraction of about half the preceding value may result from a difference of absorbed light intensity. When light of 400 nm  $> \lambda > 290$  nm wavelength is used, the contraction reaches a stationary value of only 0.2% after 60", while the colouration reaction spirobenzopyran  $\rightarrow$  merocyanine still continues. Thus the colouration process does not contribute significantly to the contraction, the low absorption of the merocyanine in the ultraviolet region being likely responsible for the small contraction (Fig.8).

On further irradiation with visible light ( $\lambda > 472$  nm) a sharp increase of contraction is observed, and an equivalent stationary value is obtained as in the previous experiment.



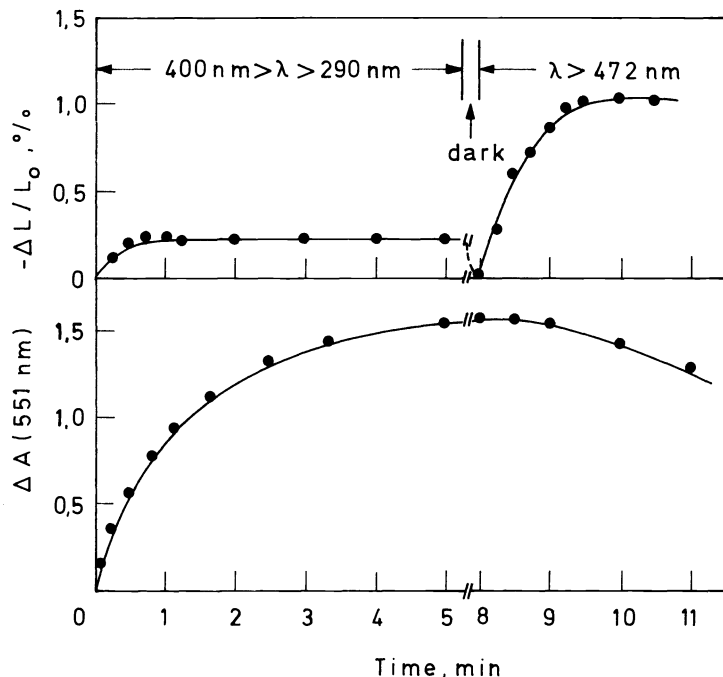


Fig.8. Colouration/contraction under UV and visible light irradiation.

On the other hand it was found that the photostationary contraction, obtained by irradiation with visible light ( $\lambda > 472 \text{ nm}$ ), is directly proportional with the light intensity, the corresponding diagram passing through the origin. The contraction spectrum, i.e. the dependence of film shrinkage on irradiation wavelength, has been measured using monochromatic light by means of interference filters with super high pressure mercury lamp Q 900. The contractions obtained after 2 minutes irradiation were normalized against the contraction at 578 nm, taking account of the differences of light intensity at the different wavelengths. It can be seen from Fig.9 that the contraction

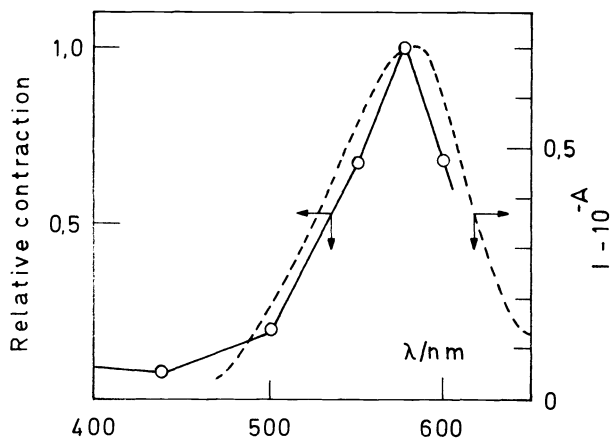


Fig.9. Contraction (—) and absorption (---) spectra of photochromic rubbers.

spectrum fits very well the light absorption spectrum of the merocyanine, which is represented by the dotted line. This result shows unambiguously that the light absorption of the merocyanine causes the contraction of film. Moreover the efficiency of ultraviolet light is poor, though the spirobenzopyran absorbs strongly in this region (367 nm), i.e. the photoisomerization

spiropyran  $\rightleftharpoons$  merocyanine is not the cause of the contraction.

An interesting point in these photomechanical systems is the problem of the energy conversion efficiency  $\phi_E$ , which is equal to the ratio of the contraction work to the absorbed light energy

$$\phi_E = \frac{981 w(g) \Delta L(cm)}{I(\text{watt/cm}^2) (1-10^{-A}) s(\text{cm}^2) . C . t}$$

In this expression  $w$  is the load,  $\Delta L$  the contraction,  $I$  the absorbed light intensity,  $S$  the irradiated surface and  $t$  the time during which contraction work has been performed.  $C$  is a correction factor taking account of the reflection on the film surface. All values can be accurately determined except  $t$ , for which a value of 60" has been adopted. The mean values of  $\phi_E$  are given in Table 4 for 4 different irradiation wavelengths; it is sensibly equal to 0.86 without clear wavelength dependence.

TABLE 4. Energy conversion. Dependence on irradiation wavelength.

irrad. wavelength	work erg	$I_{\text{abs}}$ erg	$\phi_E\%$
502	$4.66 \times 10^3$	$5.90 \times 10^3$	0.79
551	$1.29 \times 10^3$	$1.58 \times 10^5$	0.82
578	$1.53 \times 10^3$	$1.65 \times 10^5$	0.93
600	$1.17 \times 10^3$	$1.33 \times 10^5$	0.88

It must however be pointed out that the contraction/time curves are not linear, with a steep initial part. Calculated on the first contraction phase, a value of  $\phi_E$  around 2% can be estimated (Fig.10).

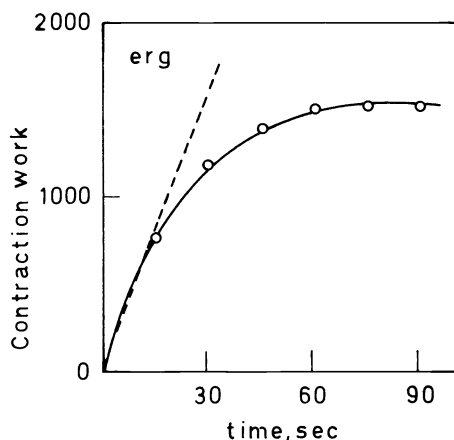


Fig.10. Irradiation time ( $\lambda$  578 nm) contraction work dependence.

Another problem that arises for the interpretation of these shrinking/elongation phenomena is the possible orientation of the light sensitive merocyanines with respect to the stretching direction. Irradiation with polarized light, parallel and perpendicular to the stretching direction should indeed influence the contractile behaviour of previously coloured films. From Table 5 it is obvious that the contraction under stretch parallel polarized light is higher than with stretch perpendicular one (exper. a & b); the ratio of both contractions  $\Delta L_{\parallel} / \Delta L_{\perp}$  increases with the tensile force. The direction of the UV light used for the formation of the merocyanine also intervenes, though to a less degree, in the contraction observed under the influence of visible light (exp. a & c). In the same table, relative rates of

TABLE 5. Effect of polarized light on contraction and decoloration rate ( $\lambda_{irr} > 472$  nm)

	Coloration 367 nm	Contraction $\frac{-\Delta L}{L_0}$ , %			Relative decoloration rate	
	Direct	Direct	116 g	160 g	116 g	160 g
a	↑	↑	3.1	3.8	1.0	1.0
b	↑	→	2.3	2.5	0.71	0.74
c	→	↑	2.6	3.1	1.0	0.98
d	→	→	2.0	2.4	0.75	0.73

decolouration under influence of polarized light are also given. Here also the rate decreases by changing from parallel to perpendicular polarized light, i.e. merocyanines oriented in the stretch direction undergo more easily ring closure to spiropyran formation.

Worthwhile to mention is that the dichroism of the merocyanines increases proportionally with the stretching ratio. It depends on the monitoring wavelength, as well as on the orientation of irradiation (merocyanine formation) with respect to the stretch direction (Fig.11).

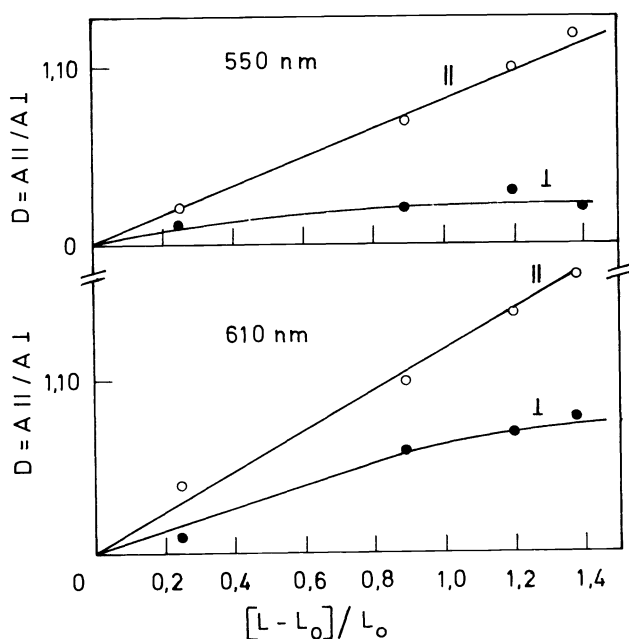


Fig.11. Dichroism dependence on stretching ratios.

The experimental contraction ratio  $\Delta L_{||} / \Delta L_{\perp}$  is however larger than the observed dichroism ratio. This statement suggests that the merocyanines responsible for contraction and involved as cross-links between the polymer chains constitute only a part of those intervening in the absorption dichroism.

#### CONCLUSIONS

The experimental results described above have unambiguously demonstrated that i. the contraction is induced by the photoexcitation of the merocyanine chromophores, and increases linearly with the absorbed light intensity. The mean energy conversion efficiency is low (0.85%) but attains 2% in the initial stages of the contraction.

ii. the irradiation wavelength dependence of the contraction corresponds narrowly with the absorption spectrum of the merocyanines.  
 iii. the rates of ring opening/closure in the spiropyran  $\rightleftharpoons$  merocyanine equilibrium are not controlling the rates of dilatation/contraction. The contribution of ring opening/closure is of secondary importance, except for the first formation of the merocyanine.

iv. the activation energy of contraction is only 6-7 kcal, while that of thermal decolouration amounts to 27 kcal.

The interpretation of these results can be twofold.

a. It is well known that open-ring merocyanines exist in the form of different isomers (20,21) of which the rates of interconversion in solid polymer matrices are larger by two or three orders of magnitude than that of ring closure, the equilibrium enthalpy being equal to 4 kcal/mole (22,23). When the conversion of one isomer (the most stable) into another is due to light absorption, a change in conformation of the chain segments directly connected with the chromophore can result, and be responsible for contraction. Cutting off the light, the stereoisomer equilibrium will be restored and the most stable isomer reformed, with concomitant length recovery. This interpretation is supported by the low activation energy value. Evidently the change of conformation of the chains will depend on the chemical structure and the viscoelastic properties of the polymer, and should be especially marked if the isomerization takes place within the chain.

b. Another interpretation is conversion of the energy stored by the chromophore in local heat effects, which would also result in shrinking of stretched rubber samples. Such effect could result from an insufficient heat exchange between the sample and the cell compartment, and depend on the specific heat capacity and the density of the polymer. Notwithstanding the experimental difficulty of measuring simultaneously "in situ" temperature increase and contraction under irradiation, several separate experiments have shown that heat effects indeed occur, and are responsible for thermal contraction, of which the contribution increases with the duration of irradiation. During the rapid contraction phase (about 80% of final contraction), i.e. during the first 20-30 seconds irradiation, the thermal contraction represents about one-third of the total contraction.

In conclusion, we assume that the photochemically induced shrinking/length recovery phenomena observed with photochromic PEA-rubbers are related mainly with the photochemical interconversion of the different merocyanine isomers, and, for a smaller extent, with local thermal effects.

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#### REFERENCES

1. G. Smets, Pure Appl. Chem. **42**, 509 (1975).
2. G. Smets and G. Evens, Pure Appl. Chem., Macromol. Chem. **8**, 357 (1973).
3. W. J. Priest and M. M. Sifain, J. Polymer Sci. A-1, **9**, 3161 (1971).
4. H. Kamogawa, M. Kato and H. Sugiyama, J. Polymer Sci. A-1, **6**, 2967 (1968).
5. C. S. Paik and H. Morawetz, Macromolecules **5**, 171 (1972).
6. D. Ta-hi Chen and H. Morawetz, Macromolecules **9**, 463 (1976).
7. H. Kamogawa, Progr. Polym. Sci. Japan **7**, 1 (1974).
8. J. B. Flannery, J. Am. Chem. Soc. **90**, 5660 (1968).
9. G. Smets, Pure Appl. Chem. **30**, 1 (1972).
10. Z. G. Gardlund, J. Polymer Sci. B, **6**, 57 (1968).
11. Z. G. Gardlund and J. J. Laverty, J. Polymer Sci. **7**, 719 (1969).
12. G. Smets and F. De Blauwe, Pure Appl. Chem. **39**, 225 (1974).
13. A. Aerts, Ph. D. Thesis, K. Univ. Leuven 1976.
14. G. Smets, J. Thoen and A. Aerts, J. Polymer Sci. Symposium **51**, 119 (1975).
15. G. Smets, J. Polymer Sci., Chem. Edit. **13**, 2223 (1975).
16. G. Van der Veen and W. Prins : 23rd IUPAC Congress Boston 1971, Macromol. Preprints **1**, p.70.
17. G. Van der Veen : Ph. D. Thesis, Univ. Groningen (The Netherlands) 1972.
18. F. Agolini and F. P. Gray, Macromolecules **3**, 349 (1970).
19. L. R. G. Treloar : The Physics of Rubber Elasticity, 3rd ed. Clarendon Press, Oxford 1975 p.80 & foll.
20. O. Chandé, Cah. Phys. **50**, 17 (1954); **51**, 6 (1954); **52**, 3 (1954).
21. J. Arnaud, C. Wippler and F. Beauré d'Augères, J. Chim. Phys. **64**, 1165 (1967).
22. M. Kryszewski and B. Nadolski, J. Polymer Sci., Chem. Ed. **13**, 345 (1975).
23. M. Kryszewski and B. Nadolski, Pure Appl. Chem. **49**, 511 (1977).