

The Thermal Effect in the Photomechanical Conversion of a Photochromic Polymer

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Summary

The effect of radiation on the mechanical behaviour of the crosslinked copolymer of maleic anhydride and styrene containing photochromic azo groups was investigated. The analysis of results of the observed photomechanical conversion proved a considerable influence of the thermal effect in addition to the effect of photoisomerization of the photochrome. The interpretation of some photomechanical experiments described earlier may be obscured by a rise in temperature caused by the absorption of radiation.

Introduction

In photochromic polymers a light-induced reversible structural change (photoisomerization) of the photochromic group causes a change in mechanical response after irradiation of the polymer. Photochromic polymers that have been best investigated are systems containing photochromic aromatic azo compounds, i.e. derivatives of azobenzene (VAN DER VEEN, PRINS 1971, VAN DER VEEN 1972, CHUANG et al.), or spiropyrane photochromes (SMETS, EVENS 1973, SMETS, DE BLAUWE 1974, SMETS 1975).

In aromatic azo compounds irradiation is followed by geometrical isomerization from the stable trans to the cis configuration with respect to the azo bond $-N=N-$. In spiropyrane derivatives, radiation leads to the splitting of the C-O bond and to the rotation of one part of the molecule, accompanied by the formation of a coloured merocyanine form. The isomerization of the photochrome affects conformation of the polymer chain, and thus also mechanical properties of the photochromic sample. In the dark a back reaction takes place, by which the photochrome is returned to a thermodynamically more stable configuration, i.e. the trans isomer in the case of azobenzene, or the colourless form of spiropyrane.

Absorption of light has a twofold effect, namely,

(a) it causes the photoisomerization of the photochrome, (b) the absorbed light is transformed into heat. The rise in temperature leads to dilation of the material, and at the same time to an increase in the elastic modulus of the crosslinked polymer, which may also be affected by the temperature dependence of the reference chain dimensions in the network (FLORY et al.). These effects result in the so-called thermoelastic inversion, where the retractive force decreases at low elongations with increasing temperature (dilation predominates), while at larger elongations it increases (the increase in the modulus predominates). In this case, the rate of reaching the original force after the cessation of radiation is not controlled by back isomerization, but by heat transfer processes between the sample and its surroundings.

So far, the thermal effect in the photomechanical conversion has not been investigated in detail, although it may considerably exceed the effect due to photoisomerization even in the case of an efficient thermostating of the sample. The influence of the thermal effect has been proved by us experimentally by an investigation of the photochromic crosslinked copolymer of maleic anhydride and styrene, which contains light-sensitive azo groups P(MAH-STY-AAB) in side chains.

Experimental Part

The photochromic P(MAH-STY-AAB) was obtained by a reaction between the copolymer maleic anhydride-styrene with 4-aminoazobenzene (AAB). The polymer, containing 45 mol.% of azo groups, was crosslinked with 2% diaminodiphenylmethane. The sample swollen to equilibrium in diethyl phthalate was irradiated under various experimental conditions at various elongations (1) $\lambda = 1.25$, (2) $\lambda = 1.05$, and in the presence of a interference filter (IFF), or without such a filter ((b) or (a)). An interference filter with the highest transmittance at 365 nm was employed, because the absorption maximum of the photochromic sample lies at 360 nm (MATEJKA et al. 1978). The effect of radiation on a change in the retractive elastic force f at constant elongation λ was investigated. The thermal radiation of a mercury arc lamp was eliminated by means of a glass infrared filter (IRF), and the sample was thermostated at 298 K.

Results and Discussion

The most pronounced and fast change in f upon irradiation was observed in the experiment (1a) (i.e. $\lambda = 1.25$, without IFF, Fig. 1a). Within 3 min., the force at constant sample length increased by 1%. After the source of radiation had been switched off, f de-

creased again, but not to its original value, and an apparent new equilibrium was established within 5-10 min. If the sample was irradiated through IFF (experiment (1b)), the response of the polymer to light and the back relaxation in the dark were much slower (Fig. 1b). At a small elongation, $\lambda = 1.05$, the effect was qualitatively the same as in Fig. 1b and independent of the use of IFF.

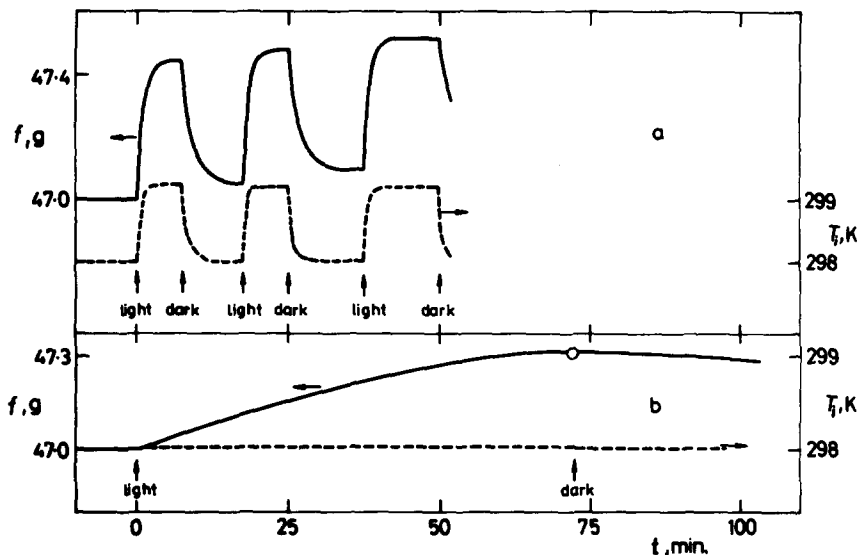


Fig. 1 The effect of radiation either on the refractive force f at constant elongation of the sample P(MAH-STY-AAB) swollen in diethyl phthalate or on the temperature inside the sample T_i $\lambda = 1.25$; temperature of the thermostated bath is 298 K ——— refractive force, ----- temperature inside the sample (a) without interference filter; (b) with interference filter.

In the experiment (1a), changes in the force occur too quickly compared with rate of the photochromic process, and therefore they cannot be due only to the photoisomerization of photochromic groups in the polymer. The back relaxation of the sample in the dark is by some two orders of magnitude faster than the thermal isomerization of photochromic groups determined experimentally (MATEJKA 1977). Also, the rise in force upon the irradiation is too fast. The calculations show that under the given experimental conditions, the stationary state in the trans-cis photoisomerization becomes established within a few hours. The establishment of the equilibrium within 3 min. indicates that the rise in force predominantly results from an effect

other than conversion of the photochrome.

The photochrome absorbs most efficiently radiation of wavelength 360 nm with the energy 330 kJ/einstein. The isomerization of azo groups consumes 40 kJ/einstein, which is the energy difference between the cis and trans form (CORRUCCINI, GILBERT). The rest of the absorbed energy is transformed into heat and dissipated in the polymer. If the intensity of radiation is sufficient, the temperature inside the gel increases. A sample of finite thickness is then heated even in the case of perfect external thermostating. This increase in temperature was experimentally confirmed by irradiation of a sample with a polymerized-in thermocouple. After irradiation of the sample without IFF (only with IRF) the temperature inside the polymer rose by 1.2 K. The time dependence of the temperature change in the sample corresponds to the dependence of the change in the retractive force (Fig.1a). With IFF, which lets only $\sim 30\%$ of energy pass through, no such rise in temperature could be observed.

The results obtained by the irradiation of the photochromic sample P(MAH-STY-AAB) may be interpreted as follows:

In the case (1a) (Fig.1a), the elongation of the gel is $\lambda > \lambda_{inv} = 1.07$ (λ_{inv} corresponds to the elongation in the thermoelastic inversion point); consequently, the force increases on heating due to the radiation absorption. In the experiment (1b) (Fig.1b), no fast increase in force could be recorded after irradiation, because the amount of energy incident upon the sample is low, and the polymer is not heated. The thermomechanical behaviour of the polymer in the experimental arrangement (2) may be explained by the fact that $\lambda \doteq \lambda_{inv}$. At this deformation, the force is temperature-independent, and the behaviour of the polymer irradiated with the use of IFF (experiment 2b) does not differ from that without IFF (experiment 2a). The slow change of force in this case similar to that in Fig.1b probably represents the photomechanical effect. The rates of the change in force correspond to the theoretically calculated rate of photoisomerization of azo groups and to the spectrally determined rate of back thermal isomerization. The apparently irreversible dependence of force shown in Fig.1a may be explained by the superposition of two processes, namely, of the fast thermal effect and of the slower isomerization. Because the duration of the radiation - darkness cycle is long enough to reach the thermal equilibrium, but too short for the photochrome to relax into the trans form, the difference in force at the beginning and at the end of the cycle characterizes the intensity of the photomechanical effect. Only after a much longer time does the force return to its original value.

In some earlier papers dealing with the photo-

mechanical effects (SMETS et al. 1973,1974,1975) there is also a striking difference between the rate of light-induced changes in the dimensions of the sample (subjected to a constant force) compared with the rate of the photochromic process itself which is supposed to be the cause of these changes. The change in dimensions in that creep experiment corresponds to a change in force in the case of our relaxation experiment. The poly(ethyl acrylate) sample crosslinked with a photochromic bis-spiropyrane contracted by 2% after irradiation; in the dark it immediately (within a few minutes) extended again to its original length. Such a back relaxation is faster by an order of magnitude than the respective thermally activated bleaching of the photochrome in the dark merocyanine-spiropyrane. In their latest paper SMETS et al. (1978) come to a conclusion that the contraction of the sample is not due to the photoisomerization spiropyrane-merocyanine, but to the interconversion between various isomers of the merocyanine form. They assume that the interconversion proceeds sufficiently quickly, thus explaining the fast course of mechanical changes. They also consider the possibility of thermal effect being operative here but only to a smaller extent.

With respect to time dependence these effects resemble the result shown in Fig.1a; similarly to our experiment the magnitude of the mechanical effect is proportional to the intensity of radiation. During the irradiation the contraction of the sample reaches its maximum when the concentration of the merocyanine form has reached only 40% of its maximum value. Further increase in the merocyanine content, and thus also potential possibilities of interconversion of the isomers do not affect the sample length any more. It is, therefore, not excluded that the mechanical changes described above may be connected with thermal effects caused by radiation absorption.

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