Photomechanical effects in crosslinked photochromic polymers

L. Matějka, M. Ilavský, K. Dušek and O. Wichterle
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06
Prague 6, *Czechoslovakia*
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The effect of radiation on photochromic crosslinked polymers containing azo group side chains is investigated. After irradiation at constant sample length, the swollen gels of light-sensitive polymers exhibit a reversible increase in the elastic retractive force. The light induced conformational changes are also accompanied by changes in the swelling equilibrium and temperature of the sample due to absorption of radiation and this added complication to the interpretation of the data. Interactions of the polymer with the solvent and the heat effect were eliminated by determining the temperature dependences of the elastic retractive force for the irradiated and unirradiated rubbery dry networks. The photomechanical effect increased with an increase in the content of photochromic groups and for the polymer with 5.4 mol % of azo groups, the photoinduced contraction of the sample amounted to 1%.

INTRODUCTION

In light-sensitive polymers containing photochromic components, irradiation leads to a photoisomerization of the photochrome, and under suitable conditions it also may lead to a change in the conformation of the macromolecule. In solution, for example, this effect is reflected in a change in viscosity after irradiation[1-5], while in solid samples there is a change in macroscopic dimensions and mechanical characteristics[6-16].

In 1971, Van der Veen and Prins[6] published a paper on the photomechanical transformation of energy in a system crosslinked gel-solution of a low-molecular weight photochrome. They found that a sample of crosslinked poly(2-hydroxyethyl methacrylate) swollen in a solution of a photochromic bis-azo compound, chrysophenine, is reversibly contracted by 1.2% after irradiation. The photochrome is adsorbed on the polymer chain and the radiation affects the adsorption equilibrium and the conformation of the polymer causing the gel to de-swell. Smets *et al.*[10-13] studied photomechanical effects on dry and swollen crosslinked gels with a covalently bound photochrome. For poly(ethyl acrylate) crosslinked with photochromic bis-spirobenzopyrane, they observed after irradiation a contraction by 2.5–6% if the sample was kept under constant load. In crosslinked polymers the effect of the photomechanical energy conversion may also be considerably affected by a purely thermal effect, i.e. by an increase in the temperature of the sample[15]. Photomechanical effects have also been observed by other authors[9,14,16], and a review has been published recently by Williams and Daly[17] covering this topic.

We have already[4] revealed the effect of radiation on the conformation of the linear photochromic copolymer of maleic anhydride with styrene containing covalently bound aminoazobenzene P(MAH–STY–AAB). Azo groups in side chains undergo *trans–cis* isomerization after irradiation. For a polymer with 72 mol % of photochromic groups we recorded a photoinduced decrease in viscosity of ~30% in dioxan solution. This paper reports the results of a study of the radiation effects on P(MAH–STY–AAB) networks. The investigation of photomechanical effects is supplemented by the results of photoisomerization in other photochromic crosslinked systems based on poly(2-hydroxy-ethyl methacrylate) and poly(butyl acrylate) with azo groups in side chains.

EXPERIMENTAL

Sample preparation

The copolymer of butyl acrylate (BA) with methacryloylamidoazobenzene (MAAB)–P(BA–MAAB) containing 0.19, 1.1 and 5.4 mol % of azo groups was obtained by the copolymerization of components with 1–2.2% of ethylene dimethacrylate as the crosslinking agent. The reaction initiated with 0.1–0.5% of dibenzoyl peroxide proceeded at 360 K for 72 h. Photochromic MAAB was obtained by reacting an equimolar mixture of methacryloylchloride with 4-aminoazobenzene (AG Fluka) (ref. 18).

The copolymer of maleic anhydride with styrene containing azo groups, P(MAH–STY–AAB), was crosslinked with 4,4′-diaminodiphenylmethane[4]. Mechanical measurements were performed with a sample containing 45 mol % of azo groups and 2% of 4,4′-diaminodiphenylmethane.

The crosslinked copolymer of 1-[4-(2-methacryloyloxyethyloxy)phenylazo]-2-hydroxynaphthalene with 2-hydroxyethyl methacrylate P(HEMA–MAN) was obtained by the coupling of 2-hydroxynaphthalene with the crosslinked diazotized copolymer of 4-[2methacryloyloxyethyloxy] aniline with 2-hydroxyethyl methacrylate. The monomers used in the preparation of the latter copolymer were HEMA, 4-[2-methacryloyloxyethyloxy]acetanilide and ethylene dimethacrylate. A mixture of these monomers (in the ratio 100:1:0.3) was diluted with 30% glycerol and heated with

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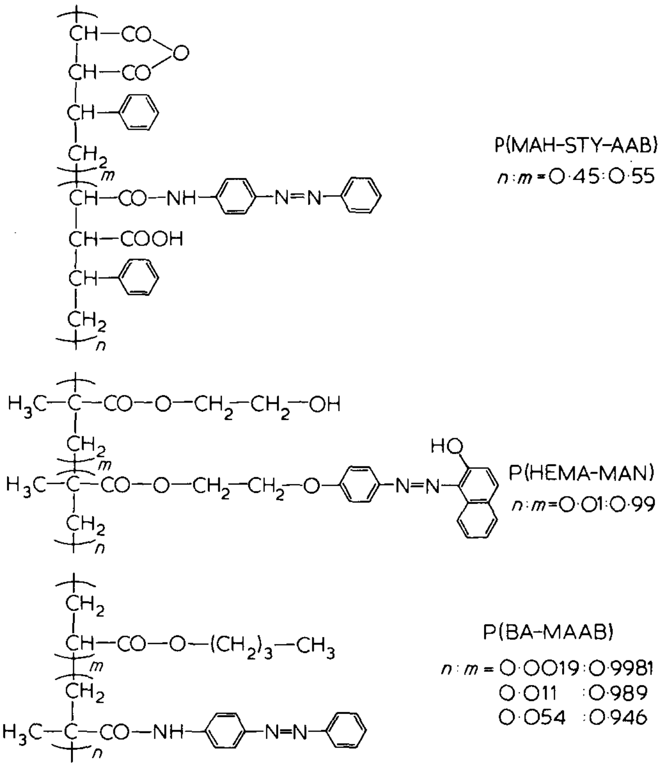

Scheme 1

0.5% of azobisisobutyronitrile at 323 K for 4 h. The films obtained, 0.65 mm thick, were then washed with water and heated in 0.1 N NaOH at 373 K for 3 h in order to saponify the acetylamine group. The gel was equilibrated with 1 N HCl and then diazotized at 273 K with an equivalent amount of $NaNO_2$ and placed in an alkaline solution of 2-hydroxynaphthalene in a water/ethanol mixture for coupling. Then the gel was washed with 0.01 N NaOH and water.

4-(2-Methacryloylethyloxy)acetanilide was prepared according to the following procedure: An equimolar amount of methacryloyl chloride was added dropwise at 273 K to a 50% solution of 4-(2-hydroxyethyloxy)acetanilide. After standing at 298 - for 30 min, the reaction mixture was poured into a twentyfold amount of water at 273 K with vigorous stirring. After recrystallization from a 60% aqueous solution the m.p. of the analytically pure product was found to be 392 K.

The composition of chains in the crosslinked gels, is shown in Scheme 1.

Mechanical characteristics

In mechanical measurements in a unidirectional elongation the elastic retractive force f was recorded by means of a thermostatically controlled force transducer connected to an amplifier (Hottinger–Baldwin Messtechnik, FRG accuracy ±0.001 N). The sample fixed between two clamps was placed in a thermostatically controlled vessel (±0.1 K) with a specially adjusted window allowing the passage of radiation. The deformation measurements at various elongations $\lambda = l/l_0$ (l and l_0 are the lengths of deformed and undeformed sample, respectively, measured with an accuracy ±0.001 cm) were performed both on swollen [P(MAH–STY–AAB), P(HEMA–MAN)] and dry [P(BA–MAAB)] networks in the rubbery state. For swollen photochromic systems the time dependences of the retractive force $f(t)$ were measured in darkness-irradiation cycles. For P(BA–MAAB) networks measured in the dry state, thermoelastic experiments were performed, i.e. the dependence of the equilibrium force f_e on temperature was measured in the range 293–368 K on irradiated and unirradiated samples. The temperature coefficient of linear elongation $\alpha_l = (1/l_0)\,(\mathrm{d}l_0/\mathrm{d}T)_p$ was also determined from the dependence of temperature change of the initial length of the sample using the same instrument.

Irradiation of samples

The light from the 500 W mercury lamp was focused on the sample by means of a converging lens and the relative radiation intensity was indicated using an Sb–Cs photodiode type F-4. The following light filters were used: an interference filter (VEB Zeiss, Jena) for 365 nm for P(MAH–STY–AAB), band filters VG 6 and UG 1/3.5 g with the respective maximal transmittance at 520 and 370 nm for P(HEMA–MAN) and P(BA–MAAB) samples, respectively. The thermal radiation of the mercury lamp was screened by means of a glass infra-red filter. The temperature near the polymer surface was checked during the irradiation; the temperature inside the gel was determined once during the irradiation by using a thermocouple fixed by polymerization in the bulk of the sample.

RESULTS AND DISCUSSION

Irradiation of samples with photosensitive groups [P(MAH–STY–AAB), P(HEMA–MAN), P(BA–MAAB)] induces a change in the elastic retractive force at constant length of the elongated sample. However, such force changes are not due only to conformational changes of the polymer chains as a result of the isomerization of bound photochromic groups. In addition to the purely photomechanical effect, a thermal effect is also operative, i.e. a rise in the sample temperature during the irradiation. Swollen gels also exhibit a change in the swelling equilibrium due to a change in temperature. The swollen gel is a complicated system and an unequivocal interpretation of the results is difficult. The polymer–solvent interaction is affected not only by temperature, but also by a change in the chemical nature of the polymer caused by the isomerization of the azo component. The effect of the interaction between polymer and solvent is absent in the study of the dry elastic network of the copolymer P(BA–MAAB). In order to rule out the influence of the thermal effect, we measured the temperature dependences of the equilibrium elastic force f_e of the irradiated and unirradiated samples. From the results a pure photomechanical effect can be obtained.

Photoisomerization in swollen gels

The crosslinked copolymer P(MAH–STY–AAB) swollen in diethyl phthalate was irradiated at the elongation $\lambda = 1.25$ and 1.05 with and without an interference filter (IFF). In the experimental arrangement without IFF and at $\lambda = 1.25$, the irradiation of the sample causes a reversible increase in the force f by 1% (*Figure 1a*). Force changes are much faster than the isomerization reaction, however, and analysis has shown[15] that the decisive role in this case is played by the heat effect and not by the photoisomerization of the photochrome.

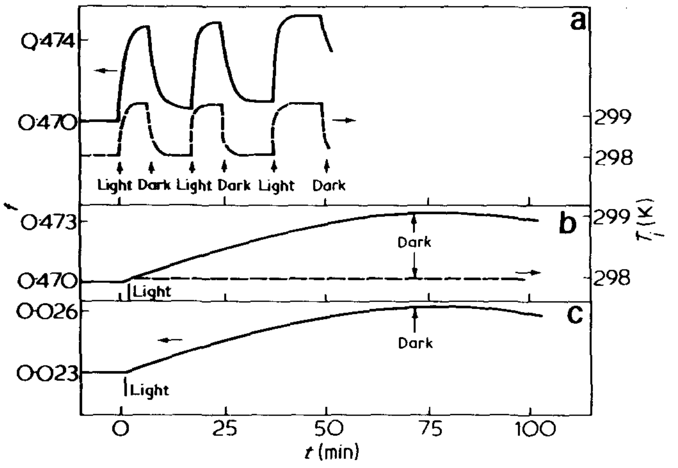

Figure 1 Effect of radiation on the retractive force f (in Newtons) at constant length of the sample of P(MAH–STY–AAB) swollen in diethyl phthalate and on the temperature inside the sample, T_i. (——) retractive force, (– – – –) temperature. (a) λ = 1.25 without interference filter, (b) λ = 1.25 with interference filter, (c) λ = 1.05 without interference filter

At a sufficient intensity of radiation the sample is heated by the absorption of radiation during the experiment even in the case of perfect external thermostatic control. It was found experimentally that the rise in temperature inside the gel due to irradiation without IFF is 1.2 K (*Figure 1a*). According to the theory of elasticity of Gaussian networks, three effects may be expected to be operative at a constant deformed sample length: (a) an increase in the modulus with temperature causing an increase in the retractive force, (b) an increase in the initial sample length with temperature, resulting in a decrease in force, (c) the effect of increasing temperature on the reference dimensions in the network expressed through a change in the so-called dilation factor $\langle\alpha_i^2\rangle = \overline{r_i^2}/\overline{r_0^2}$, where $\overline{r_i^2}$ and $\overline{r_0^2}$ are the mean squared distances between ends of elastically active network chain in the undeformed isotropic and reference states[19], respectively. The simultaneous action of these effects (especially (a) and (b)) leads to thermoelastic inversion[20], i.e. a decrease in force with increasing temperature at small elongations (effect (b) prevails) and an increase in force with increasing temperature at large elongations ((a) prevails). Effect (c) participates in the value of λ_{inv} at which inversion takes place.

In the experiment without IFF (*Figure 1a*), the elongation $\lambda = 1.25$ is larger than $\lambda_{\mathrm{inv}} = 1.07$, and therefore the force increases with increasing temperature. With IFF, the sample is not heated (*Figure 1b*), so that the thermal effect is eliminated. The slow process of force changes in *Figure 1b* is therefore given only by the photomechanical effect. At $\lambda = 1.05$ the thermal effect is not operative because elongation of the sample corresponds approximately to the thermoelastic inversion point. The increase and decrease in force, which in this case is again given only by the photoeffects, is slow (*Figure 1c*) and independent of the use of IFF. Its rate corresponds to the same order of magnitude as is the isomerization rate of the photochrome[21] in the system.

Superposition of the fast thermal and the slower photoisomerization effect results in an apparent irreversibility of the process if the sample is irradiated in the absence of IFF (*Figure 1a*). During the dark period of a light–dark cycle the photochrome cannot relax into the stable *trans* configuration and the force does not reach its original value. The difference in force at the beginning and after the end of one cycle may therefore be interpreted as the photomechanical effect. Only after some time in the dark does the force return to its initial value.

The investigation of swollen gels P(MAH–STY–AAB) was supplemented by an investigation of the photoisomerization effect on swelling equilibria in the water-swollen P(HEMA–MAN) network. The gel of the copolymer P(HEMA–MAN) was irradiated at the elongation $\lambda = 1.004$, and its response to the radiation is shown in *Figure 2*. The overall increase in force at constant sample length is 50%, but under the given experimental conditions the absolute value is very low. The fast initial decrease in force by 1% is due to the thermal expansion of the sample caused by irradiation. The elongation $\lambda = 1.004$ is below λ_{inv} and consequently, the force decreases if the sample is heated. The slower increase which follows represents photomechanical conversion.

We ruled out an explanation of the force increase due to deswelling of the sample caused by heating during the irradiation despite the interaction parameter χ of the system PHEMA–water (at $T < 323$ K) which increases with increasing temperature[22]. The gel–water system is heated by less than 2 K by the irradiation, and the analysis shows that the corresponding effect of the change in the χ parameter on the degree of swelling and modulus may cause a 5% increase in force at the most. Also, the effect of temperature change in the reference dimensions of the chain calculated from the known temperature dependence of $\overline{r_0^2}$ (ref. 23) is not essential in this case and accounts only for a ~0.4% increase in force.

It may be inferred, therefore, that the contraction of the sample upon irradiation is due mainly to changes in chain conformation and swelling equilibrium induced by *trans–cis* photoisomerization.

Photoisomerization in the dry elastic copolymer P(BA–MAAB)

We investigated samples containing 0.19, 1.1 and 5.4 mol % of azo groups, but the photomechanical effect could be recorded only for the polymer containing the highest number of photochromic groups.

The temperature dependences in *Figure 3* show that the elastic force is higher for the irradiated polymer at all

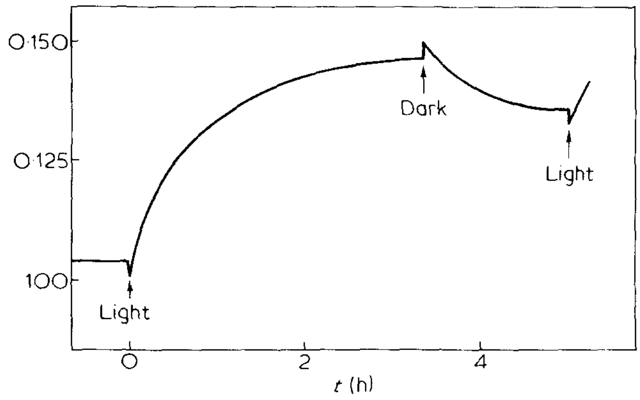

Figure 2 Effect of radiation on the force f (in Newtons) at constant length of the crosslinked copolymer P(HEMA–MAN) swollen in water at 298 K λ = 1.004

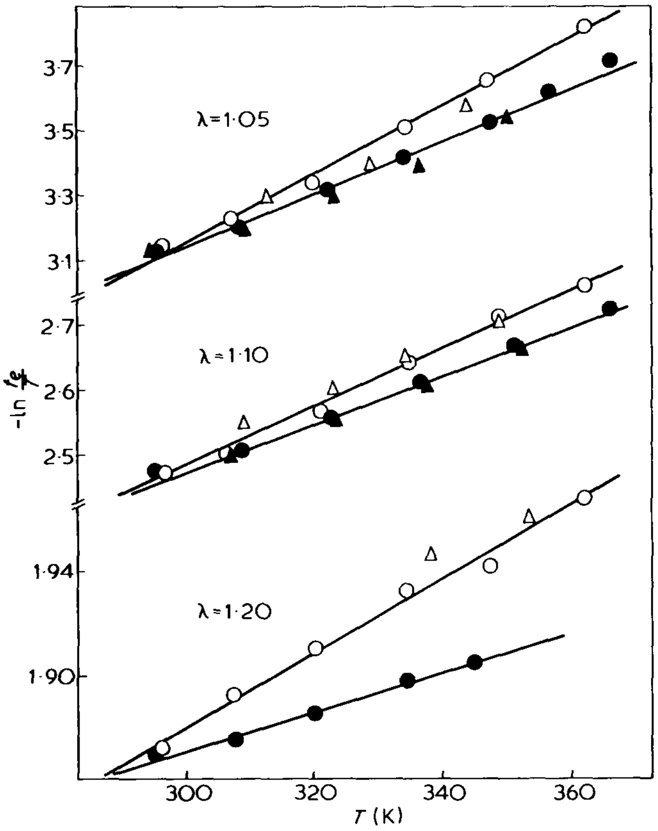

Figure 3 Thermoelastic properties of the irradiated and unirradiated copolymer P(BA–MAAB) at various deformations in the dark: ○, increasing temperature; △, decreasing temperature. During irradiation: ●, increasing temperature; ▲, decreasing temperature

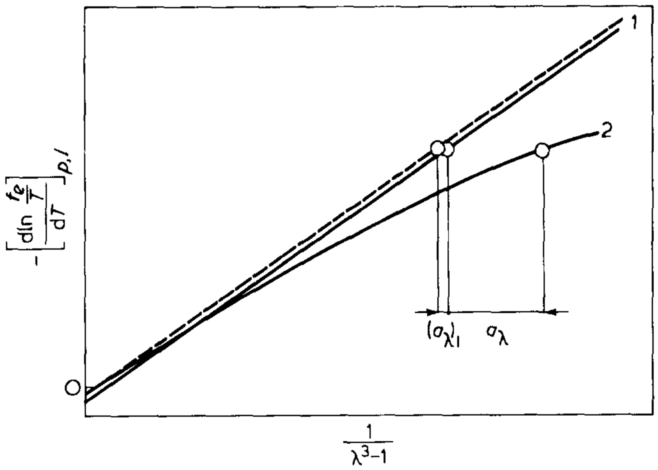

Figure 4 The dependence of the temperature coefficient of force on the deformation function $1/(\lambda^3-1)$ for irradiated and unirradiated P(BA–MAAB). Schematic illustration of the data in *Figure 3*. (——) experimental dependences: (1) in the dark, (2) after irradiation; (— — — —) theoretical dependence obtained by transformation of curve 2 using factor $[a_\lambda + (a_\lambda)_1]$

elongations below and above the thermoelastic inversion point $\lambda_{\text{inv}} = 1.08$. The fact that f_e is higher for the irradiated network irrespective of λ allows us to conclude that the photoinduced changes in the thermoelastic behaviour are not caused by heating of the sample (direct temperature measurement inside the irradiated gel showed that with the band filter the sample was heated by ~0.1 K), but represent the photomechanical conversion of energy.

For the equilibrium retractive force f_e of the deformed dry network, the theory of elasticity of Gaussian networks gives the equation[19]

$$f_e = A(v/l_0)(\overline{r_i^2}/\overline{r_0^2})\,\mathrm{R}T(\lambda-\lambda^{-2}) \qquad (1)$$

in which v is the concentration of elastically active network chains, R is the gas constant, A is a factor still discussed in the literature[19]. The equation allows a relation to be derived which was subsequently used in the determination of the temperature coefficient of unperturbed dimensions d ln $\overline{r_0^2}/\mathrm{d}T$:

$$-[\delta\ln(f_e/T)/\delta T]_{p,l} = \mathrm{d}\ln\overline{r_0^2}/\mathrm{d}T + 3\alpha_l/(\lambda^3-1) \qquad (2)$$

We found that the coefficient dln $\overline{r_0^2}/\mathrm{d}T$ remains almost unchanged after the irradiation (*Table 1*), while the slope of the dependence of $-[\delta\ln(f_e/T)/\delta T]_{p,l}$ vs. $1/\lambda^3-1$), (*Figure 4*), which should correspond to the volume expansion coefficient $\beta(=3\alpha_l)$, decreases sharply. On the other hand, the independently determined coefficient β is the same for both the irradiated and unirradiated sample (*Table 1*). For the unirradiated sample the slope in *Figure 4* is equal to the experimentally determined coefficient β, the slope of the irradiated sample is lower than β and the dependence in *Figure 4* is curved. It is assumed therefore that the decrease in the slope and its curvature caused by irradiation are due to the light-induced contraction of the sample by Δl_0, which also brings about a change in elongation λ. The pure photomechanical effect is given by the difference between the thermoelastic curves for the irradiated (*Figure 4*, curve 2) and unirradiated (*Figure 4*, curve 1) sample, and it may be expressed through the transformation factor a_λ (which transforms the elongation λ), by which curve 2 is transformed into curve 1. The value of a_λ was used in the determination of the shortening of the sample Δl_0, assuming that the temperature coefficient of reference dimensions dln $\overline{r_0^2}/\mathrm{d}T$ is not changed on irradiation (*Table 2*, values A).

However, the assumed independence of the temperature coefficient on irradiation may not be strictly obeyed (*Table 1*). Taking into account the possible change for the sample with the highest concentration of azo groups, a correction shown in *Figure 4* is obtained so that the pure photomechanical effect is given now by $a_\lambda + (a_\lambda)_1$ and not by a_λ (*Table 2*).

Table 1 Values of the temperature coefficient of unperturbed dimensions and of the temperature coefficient of volume expansion β for the irradiated and unirradiated copolymer P(BA–MAAB)

	d ln $\overline{r_0^2}/\mathrm{d}T \times 10^3$ (K^{-1})		
Sample	A_1	A_2	A_3
dark	−0.1 ± 0.05	−0.35 ± 0.05	−0.5 ± 0.1
irradiation	−0.1 ± 0.10	−0.4 ± 0.10	−0.3 ± 0.2
	$\beta \times 10^4$ (K^{-1})		
Sample	A_1	A_2	A_3
dark	7.8 ± 0.1	7.9 ± 0.1	10.4 ± 0.1
irradiation	7.8 ± 0.1	7.8 ± 0.1	10.4 ± 0.1

A_1, A_2, A_3 are samples containing 0.19, 1.1, and 5.4 mol %, respectively of azo groups; $\beta(=3\alpha_l)$ determined from the temperature dependence of the initial sample length

Table 2 Values of the light-induced contraction of the sample P(BA–MAAB) containing 5.4 mol % of azo groups

	$(\Delta l_0/l_0) \times 100$	
Deformation λ	A	B
1.05	−0.9 ± 0.4	−1.0 ± 0.4
1.10	−0.6 ± 0.2	−0.9 ± 0.2
1.20	−0.6 ± 0.2	−1.6 ± 0.2

$\Delta l_0 = l_0^0 - l_0$; l_0^0, l_0 is the length of the underformed sample after irradiation, and in the dark, respectively, A—calculated from the shift a_λ; B—calculated from the shift $[a_\lambda + (a_\lambda)_1]$

The results suggest that the intensity of the photomechanical effect of the dry network P(BA–MAAB) increases with an increase in the content of photochromic groups. An analysis of the results shows that the sample containing 5.4 mol % of azo groups undergoes a photoinduced contraction by ~1%, which represents the pure photomechanical conversion of energy.

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