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# A Photosensitive Polymer as Recording Material in Holography

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## Summary

A new reversible photochromic copolymer of maleic anhydride with styrene containing azo side groups was prepared. The system reacts to irradiation by a revers ible trans-cis photoisomerization of light-sensitive azo groups. Irradiation also causes a change in the refractive index, so that the polymer may be employed in recording optical information in the form of phase hologram. The resolution of the material is higher than 2000 lines/mm.

In spite of the large variability of organic compounds, according to available information only two groups of compounds have been utilized in the reversible recording of volume phase holograms. These are dimers of aromatic polycyclic hydrocarbons (TOMLINSON et al. 1972) and stilbene derivatives (ANONYM 1974). In this paper we describe a new reversible material for recording volume phase holograms (MATĚJKA et al. 1978).

## Photosensitive material

The photosensitive system is represented by a polymer with a covalently bound photochromic component. The macromolecular matrix consists of an alternating copolymer of maleic anhydride and styrene, P(MAH-STY), with 4-aminoazobenzene (AAB) as the photochrome. Polymeranalogous reaction of the amino group of 4-aminoazobenzene with the anhydride ring of the copolymer yielded a photochromic polymer P(MAH-STY--AAB) containing 1-72 mol-% of azo groups situated as side substituents of the main chain.

After irradiation of azo compounds there occurs geometrical trans-cis isomerization aroud the central double bond -N=N- (MARCKWALD 1899). Photoconversion to the cis isomer depends on the wavelength of the radiation used, on the solvent, temperature and other factors (BROWN 1971), while in the dark a thermally activated reverse reaction to the more stable trans isomer takes place.

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The isomerization of azo groups in systems under investigation caused by irradiation is reflected in a change of the UV spectrum, because the cis isomer absorbs at a shorter wavelength than the trans form.

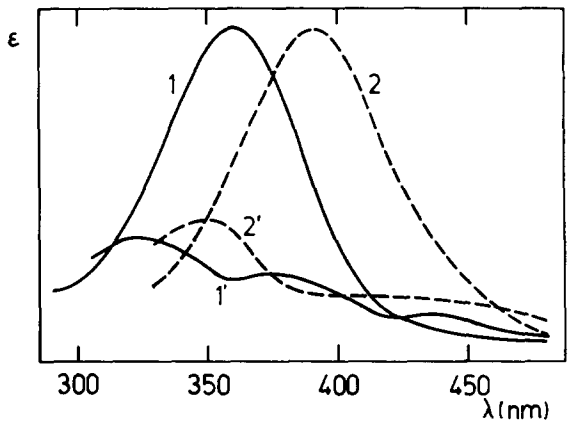


Fig. 1 Spectra of 4-aminobenzene and of copolymer P(MAH-STY-AAB) in tetrahydrofuran
1 - P(MAH-STY-AAB), 2 - AAB, 1', 2' - P(MAH-STY-AAB), or AAB after irradiation

Tetrahydrofuran solutions of P(MAH-STY-AAB) and of free AAB were irradiated at wavelength $\lambda$ = 365 nm and 400 nm, respectively. After binding of photochromic groups to the polymer, a hypsochromic shift of the respective absorption bands takes place, but the character of the reversible change of the spectrum after irradiation (at isomerization) is the same as with the free azo compound.

The trans ⟶ cis photoisomerization (Fig. 2, phase a) and reverse thermal cis ⟶ trans reaction occurring in the dark (Fig. 2, phase c) were investigated spectrally. Phase b is the domain of the photostationary state established during the irradiation. The trans ⟶ cis photoconversion, i.e. concentration of the cis isomer in the photostationary state, is lower in the polymer (80-85%) than in the free azo compound AAB (98%). The thermal cis ⟶ trans isomerization is kinetically of the first order and is slower in the polymer than in AAB: the rate constants k (P(MAH-STY-AAB)) = $0.41 \times 10^{-3} min^{-1}$ and k (AAB) = = $15.9 \times 10^{-3} min^{-1}$ at 20°C. (The respective reaction half-times are 28 h and 44 min.)

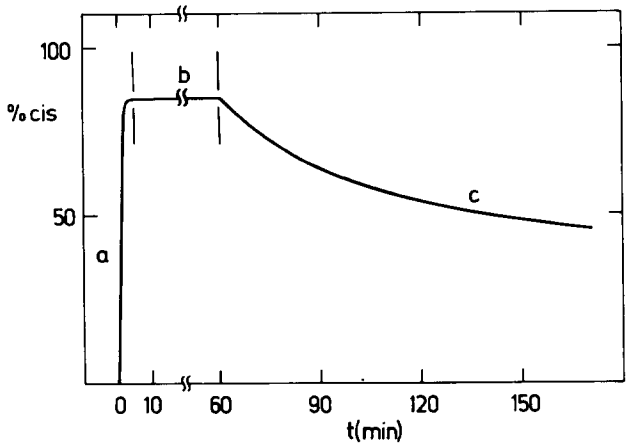


Fig. 2 The content of cis-isomer of the photochromic compound P(MAH-STY-AAB) during photoisomerization by irradiation at $\lambda$ = 365 nm (phase a), in the photostationary state (phase b) and during the reverse thermal isomerization at T = 40°C (phase c).

Holographic record

Holographic measurements were carried out with a transparent polymer film 50 μm thick and containing 25 mol-% of azo groups. The holograms were obtained with nonexpanded beams of an argon laser, $\lambda$ = 514.5 nm, and reconstructed at the same time with red light, $\lambda$ = 632.8 nm, incident on the sample at an angle fulfilling the Bragg condition. The recording beams were incident symmetrically to the normal; the angle between the beams was 40°. The beam intensity varied between 5 and 60 mW/cm²; it was found that the maximum diffraction efficiency of the hologram increased with increasing intensity, I. A diffraction efficiency $\eta$ = 1% was reached at the beam intensity 60 mW/cm² by a total exposure of 28 J/cm². In the case of a thin layer record, d=2 μm, $\eta$ = 0.035% was reached with the exposure 2 J/cm².

The record is not a permanent one and may be erased either spontaneously (temperature erasure), or by light (optical erasure). The process of thermal and optical erasure of the holographic record in P(MAH-STY-AAB) is shown in Fig.3. At 20°C, the diffraction efficiency decreases to half its value after c. 3 min. The hologram recorded with a higher intensity is more resistant towards erasure. In order to determine the resolution, holograms at an angle of 60° between the beams were also recorded. The resolution of the material was higher than 2000 lines/mm.

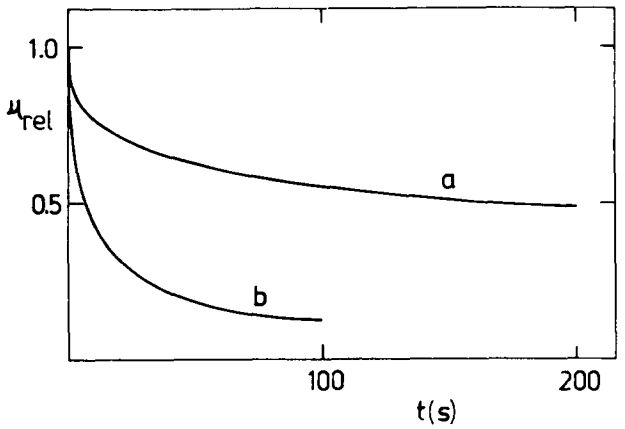


Fig. 3 Erasure of the hologram recorded in P(MAH-STY--AAB) (a) thermal at 20°C, (b) optical - with a beam having $\lambda$ = 514.5 nm and I = 60 mW/cm²

Preliminary experiments show that the polymer described above exhibits a much greater sensitivity in comparison with reversible materials described in literature. The study of the mechanism of holographic recording is in progress; results will be published later.

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