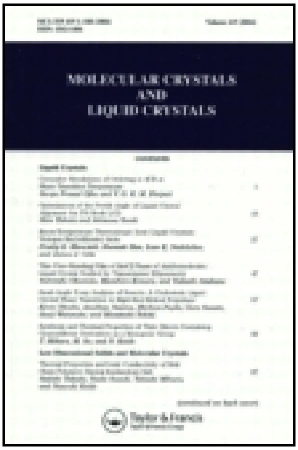

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Synthesis and Electrooptical Properties of Metal-Containing Azopolymers. The Influence of Steric Factors on the Electro-Optical Effect in Polycomplexes of Azobenzene Derivatives with Cobalt

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Synthesis and Electrooptical Properties of Metal-Containing Azopolymers. The Influence of Steric Factors on the Electro-Optical Effect in Polycomplexes of Azobenzene Derivatives with Cobalt

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We propose new structures of metal-containing azopolymers with changeable electro-optical properties in consequence of different coordination metal ions. The new monomers – 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene, 4-methacroyloxy-2′-carboxy-azobenzene and their complexes with Co and polymers based of these ones are synthesized. The influence of the electric field on the absorption spectra of new metal-containing azopolymers films are investigated. Electro-optical properties of polymeric films is determined by the re-orientation of dipole moments of azobenzene groups photo induced by polarized light in the electric field. Increase of structural inflexibility by the photo isomerization of azobenzene groups decrease the electro-optical effect value.

Keywords: azobenzene; dipole moment; electrooptics; metallopolymers; photo isomerization; polycomplexes

1. INTRODUCTION

Azobenzene functionalized polymers are interesting because it combine the properties of anisotropy with photoresponsive behavior that give rise to applications in areas such as optical storage, optical switching, diffractive optical elements, non-linear optical devices, LC displays etc. [1–3].

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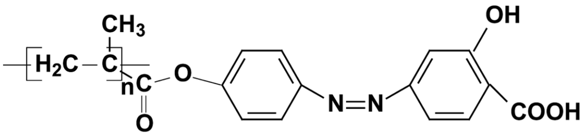
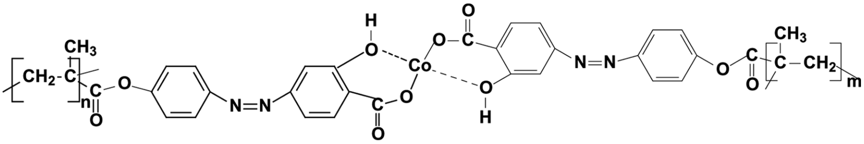
Under the action of linearly polarized light, which is absorbed by azobenzene groups and leads to changes in isomeric structures, polarization is induced in the films. The photoinduced polarization appears under influence of linearly polarized light in polymeric films. It can be changed by thermal or mechanical treatments in external electric and\or magnetic fields, under light illumination. The rotation of dipole moments occurs in the external electric field. Since the mechanism of the influence of electric and magnetic fields is connected with the aligning forces for dipole moments of azobenzene groups [4–6] one can suppose that the electro-optical effect depends on steric factors which complicates the displacement of electric dipoles and metal ions. It mean for the selection of substances used in optoelectronics.

The aims of this work were the synthesis of new metal-containing azopolymers and investigation the optical and electrical properties of their polymeric films depending on structural peculiarities of cobalt ions coordination.

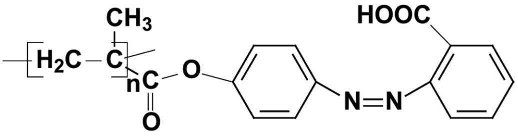
Polymer metal chelates with cobalt were synthesized.



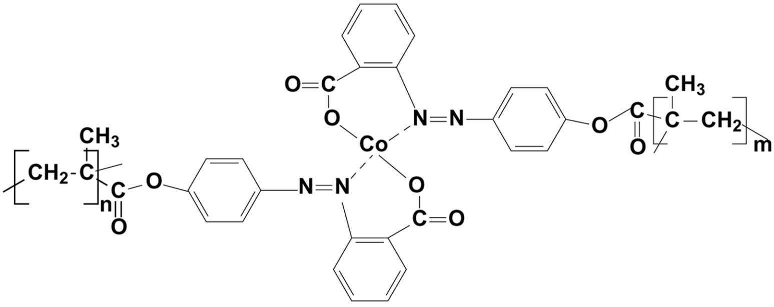
A1



A1-Co



A2



A2-Co

The structures of the monomers and metal complexes were confirmed by the data of NMR- and infrared spectroscopes.

2. EXPERIMENTAL

2.1. Synthesis of Azocompounds

Synthesis of 4-hydroxy-(4′-carboxy-3′-hydroxy)-azobenzene and 4-hydroxy-(2′-carboxy)-azobenzene

4-amino-2-hydroxybenzoic acid (0.1 mol) or 2-aminobenzoic acid (0.1 mol) was dissolved in a solution of concentrated hydrochloric acid: water (50:50) (100 mL). The mixture was cooled to 0°C in an ice-water bath, and then sodium nitrite (6.8 g, 0.1 mol) dissolved in a small amount of water added dropwise. The reaction mixture was stirred for 2 h, and then phenol (9.4 g, 0.1 mol) in NaOH solution (100 mL) was added slowly. The resulted solution was stirred for 4 h at 0–5°C and for an additional 10 h at room temperature. The precipitate formed was collected by vacuum filtration and finally dried. The product was purified by recrystallization from ethanol. Yield: 87–92%.

4-Hydroxy-(4′-carboxy-3′-hydroxy)-azobenzene

^{1}H NMR (400 MHz, DMSO, δ, ppm): 7.93-6.89 (3d, s, 7H , Ph-H), 11.4 (s, 1H, COOH), 10.19 (s, 1H, OH).

4-Hydroxy-(2′-carboxy)-azobenzene

^{1}H NMR (400 MHz, DMSO, δ, ppm): 7.79-6.90 (2d, m, 8H, Ph-H), 11.0 (s, 1H, COOH), 10.14 (s, 1H, OH).

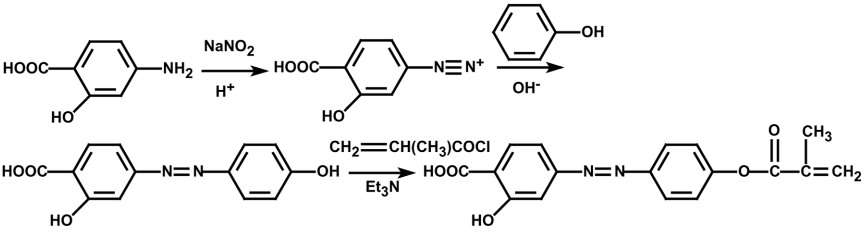
2.2. Synthesis of Monomers

The synthetic route for the target monomers is shown by Schemes 1, 2.

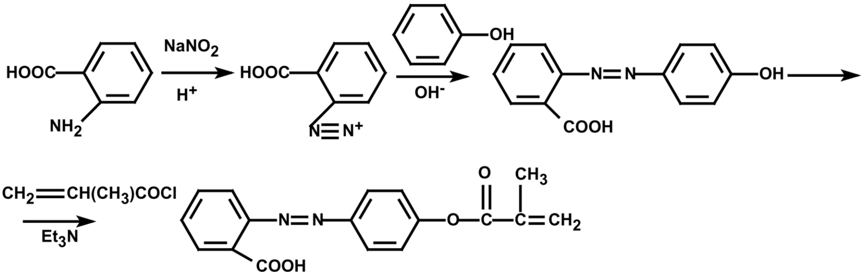
The synthesis of 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene, as an example, is given below: azocompound (2.58 g, 0.01 mol) was dissolved in 25 mL anhydrous THF, and freshly distilled triethylamine (1.53 mL, 0.011 mol) was added to the solution. The reaction mixture was then cooled to 0–5°C. Methacryloyl chloride (1.07 mL, 0.011 mol) in THF (5 mL) was injected gradually to the above solution via a glass syringe while the solution temperature was kept below 5°C. The reaction mixture was stirred overnight at room temperature. The resulting precipitate was filtered off. Purification was followed by recrystallization from methanol. Yield: 63–76%.

4-Methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene

^{1}H NMR (400 MHz, DMSO, δ, ppm): 8.12-6.92 (3d, s, 7H , Ph-H), 11.3 (s, 1H, COOH), 6.28 (s, 1H C=CH_2, cis), 5.82 (s, 1H C=CH_2, trans), 2.06 (s, 3H, =C-CH_3).



SCHEME 1 Synthesis of 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene.



SCHEME 2 Synthesis of 4-methacroyloxy-(2′-carboxy)-azobenzene.

4-Methacroyloxy-(2′-carboxy)-azobenzene

^{1}H NMR (400 MHz, DMSO, δ, ppm): 8.08–6.9 (2d, m, 8H , Ph-H), 11.0 (s, 1H, COOH), 6.34 (s, 1H C=CH$_2$, cis), 5.87 (s, 1H C=CH$_2$, trans), 2.06 (s, 3H, =C-CH$_3$).

2.3. Synthesis of Chelates

New complexes of 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene and 4-methacroyloxy-(2′-carboxy)-azobenzene with Co were synthesized by the exchange reaction between acetates of the corresponding metal (0.001 mol) and monomers (0.002 mol) in alcohol-NaOH solution (20 mL) and purified by recrystallization from ethanol.

The structures of the obtained complexes of 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene and 4-methacroyloxy-(2′-carboxy)-azobenzene with Co have been studied by infrared spectroscopy (Table 1).

2.4. Polymerization

Polymers were synthesized by free-radical polymerization in DMF. The polymerization was carried out in 10 wt.% DMF solution of monomer with AIBN as free radical initiator (10 wt.% with respect of monomer mass) at 80°C for more than 30 hours in thermostat. The polymerization mixture was poured into methanol. The solid precipitate was filtered, dissolved in DMF, and reprecipitated into methanol and then dried at 20°C overnight.

The synthesized polycomlexes were characterized by ^{1}H NMR spectroscopy. The obtained results were in agreement with the proposed structures.

2.5. Spectral Measurements

Samples with free surface (glass substrate – conducting layer SnO$_2$:In$_2$O$_3$ – polymeric film) were prepared and used in our

TABLE 1 Some Distinctive Absorption Bands of Metallic Complexes of 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene (I) and 4-methacroyloxy-(2′-carboxy)-azobenzene (II)

CoL$_2$	ν_{as} (COO$^-$)	ν_s (COO$^-$)	ν (COC)	ν (C=O)
I	1600	1380	1140	1715
II	1590	1370	1135	1720

investigations. The thickness of the polymeric films was 1–2 mη. These samples were used for the following measurements: the spectra of optical density D of the polymeric films over the range of light wavelength $\lambda = 350$–$900\,\mathrm{nm}$; the value I_E/I_0, where I_0 and I_E are the monochromatic light intensities respectively before and after application of the electric field. Nonpolarized and polarized light was used for illumination of the samples. In the latter case the sample was located between two polarizers at an angle of ninety degrees. The electric field ($E = 1 \times 10^8\,\mathrm{V/m}$) was produced by the corona discharge [7]. The value δI_E was determined in dependence on time (t) of the illumination with polarized light and after this illumination, light wavelength λ, angle θ between directions of polarized axes of the polarizer and analyzer. All experiments carried out at room temperature $T = 293\,\mathrm{K}$, the influence of depolarization properties of the layer SnO_2:In_2O_3 [8] is graded.

3. RESULTS AND DISCUSSION

The absorption spectra of the investigated polymeric films are shown on Figure 1. The absorption is determined by light excitation of azobenzene groups and it is not sensitive on the presence of metallic ions in polymers. The electric field had a more appreciable effect on

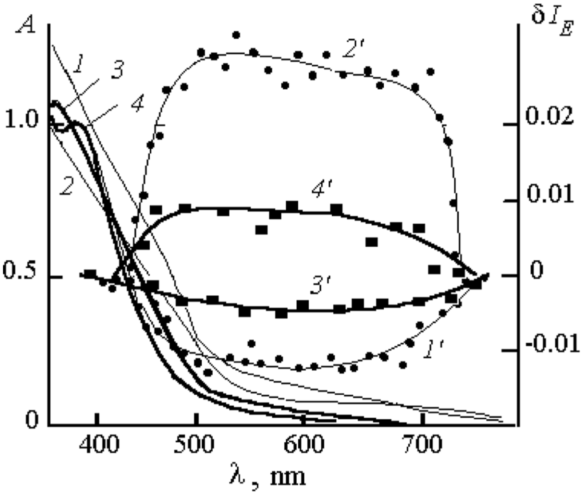


FIGURE 1 Spectra of optical density (D) and dependences of δI_E of λ of the polymeric films A1 (1, 1′), A1-Co (2, 2′), A2 (3, 3′), A2-Co (4, 4′) measured for $\theta = \pi/2$ after their illumination by linearly polarized light ($\lambda < 500\,\mathrm{nm}$) during 60 min.

the light transmission when the samples were pre irradiated by polarized light in the absorption range of azobenzene groups ($\lambda < 550\,\text{nm}$). The most significant change in I_0 induced by an external electric field is observed after exposure of the samples to light transmitted through the polarizer (exposure time $\text{t} > 30\,\text{s}$) and when an analyzer with $\theta = \pi/2$ is used [7]. Figure 1 shows the dependences of δI_E on λ, measured for $\theta = \pi/2$ after a long-term exposure of the samples by polarized light with $\lambda < 550\,\text{nm}$. The influence of electric field on the light transmission is increased after long-term irradiation by polarized light in the long-wave part of the absorption range of investigated polymeric films.

At comparison A1, A2 with A1-Co, A2Co is changed the mark of δI_E and the time constant (τ_E) is increased after the external electric field is switched on and is switched off.

The kinetics of light intensity changes from I_0 to I_E and after the electric field is switched off can be described by the simple correlations:

$$I(t) = I_0 + (I_E - I_0)(1 - \exp(-t/\tau_E)) \tag{1}$$

and

$$I(t) = I_0 + (I_E - I_0)\exp(-t/\tau_E), \tag{2}$$

in which time constant τ_E averages $60 \pm 10\,\text{s}$ for A1, A1-Co, $90 \pm 10\,\text{s}$ for A2, A2-Co (Fig. 2).

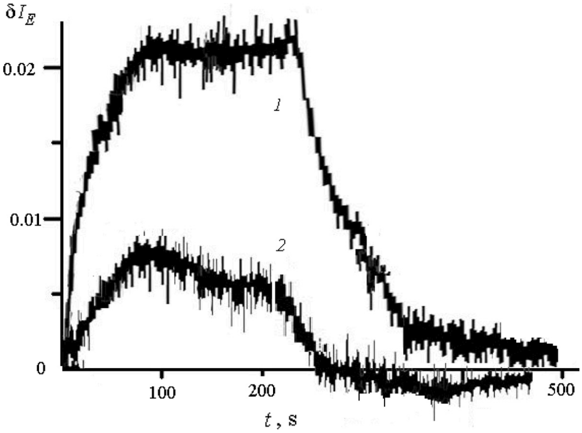


FIGURE 2 Dependences of δI_E on time t after switching on E and switching off, measured for $\theta = \pi/2$ and $\lambda = 625\,\text{nm}$ for the samples A1-Co (1), A2-Co (2) after theirs illumination by linearly polarized light during 60 min.

The increase of τ_E can be explained by the influence of steric factors at rotations of azobenzene isomers.

4. CONCLUSIONS

In our structures photoinduced optical anisotropy arises as a result of irradiation by linearly polarized light, which causes *trans-cis* isomerization of azobenzene groups. An external electric field orientates the light-induced dipole moments of these groups, causing the electro-optic effect at wavelengths near the long-wave absorption edge of the polymers (Fig. 1).

In films A1, A2 an external electric field involves alignment of photoinduced dipoles along the field force lines and the polarized light interacts with these dipoles and for $\theta = \pi/2$ the value $\delta I_E < 0$. In films A1-Co, A2-Co the polarized light is dissipated and it is depolarized in the external electric field $\delta I_E > 0$. The last one perhaps [9] is related to the more strong interaction of Co^{2+} ions with E than the interaction of dipoles and Co^{2+} ions are bonded with azobenzene fragments but the direction of this bond does not coincide with the direction of the photoinduced dipole moment. Consequently, the change of orientation angle of photoinduced dipoles in the external electric field in the samples A1-Co, A2-Co over the bond with metallic ions back in films A1, A2.

The influence of the metallic ion in the samples A1-Co in comparison to A2-Co is reduced over the increase of forces of elasticity which are prevented from the rotation of dipole moments of azobenzene groups [9]. At comparison A1-Co with A2-Co the δI_E is decreased and the τ_E is increased because of steric difficulties in films A2-Co which is determined the immediate bond Co ion with azobenzene groups.

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