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## Synthesis and Electrooptical Properties of Metal-Containing Azopolymers

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*We propose new structures of polymeric composites with changeable optical characteristics (transmission and/or reflection of polarized light) under the influence of magnetic and/or electric fields. The new monomers 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-azobenzene, 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-2-nitroazobenzene, and 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-2-diethylamino-azobenzene, their complexes with Co, and polymers based on their base are synthesized. The influence of the electric field on the absorption spectra of films of the new metal-containing azopolymers is investigated. The effect of an electric field on the transmission of a linearly polarized light through the films is revealed. This effect is determined by the re-orientation of the dipole moments of azobenzene groups which is induced by a polarized light under the action of an electric field. The increase of the dipole moments of azobenzene groups due to the introduction of donor and acceptor substituents reduces the influence of Co ions on the electrooptical properties of polymeric films.*

**Keywords:** azobenzene; electrooptics; metallopolymers; photoisomerization; polycomplexes

## INTRODUCTION

Metallopolymers are new functional materials which are used for the application of coverings from the gaseous phase (the CVD-method), as

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effective and selective sorbents and hardeners, superconductors, and macroinitiators of the radical polymerization. Metallopolymers as a new generation of polymer materials are perspective for the development of anisotropic optic systems and films for solar batteries. The interest in these materials causes the elaboration of new methods of synthesis of metallopolymers.

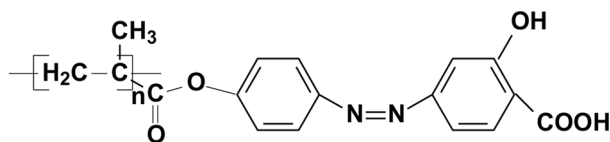
Monomeric and polymeric composites, hybrid systems, etc. have been found to be applicable in nonlinear optics. Nevertheless, polymers possess advantages over other systems due to their processability and other properties. The azobenzene system [1–5] exhibits non-linear optical properties, which make it suitable for variable kinds of applications, for example as the optical media for the registration of optical holograms [6], in xerography [7], etc.

The photoinduced polarization appears under the influence of a linearly polarized light in polymeric films. It can be changed by a thermal or mechanical treatment in external electric and/or magnetic fields under the light illumination. In the external electric field, the rotation of dipole moments occurs. Since the mechanism of the influence of electric and magnetic fields is connected with the orientational forces for the dipole moments of azobenzene groups, one can suppose that electrooptical properties should be observed in polymers with azogroups and metallic ions chemically bound with a polymeric chain.

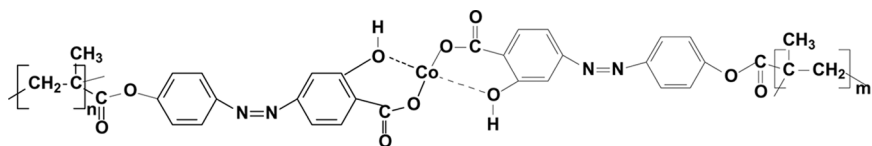
The aims of this work were the synthesis of new metal-containing azopolymers and the investigation of the optical properties of their films. The dependence of these properties on metal ions and substituents of the different nature in azobenzene fragments will also be studied.

Since the newly synthesized macrochelates have two parts, i.e. the azochromophore and a chelating group which “fasten” the metal in each polymer unit, they are expected to combine two functions. Under the influence of a polarized light, they exhibit anisotropic properties, and, under the influence of an external electromagnetic field, they modify electric and magnetic properties.

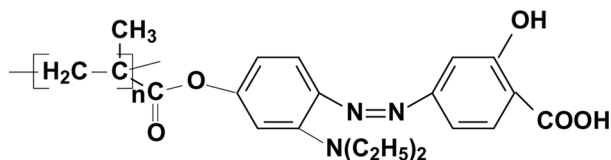
New polymer metal chelates with metals (Co, Ni) were synthesized.



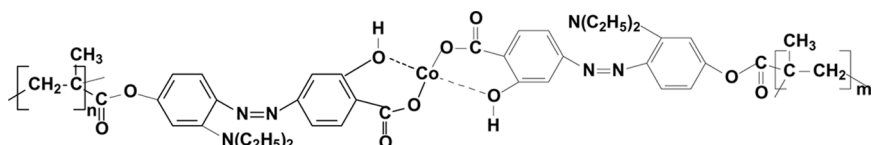
A1



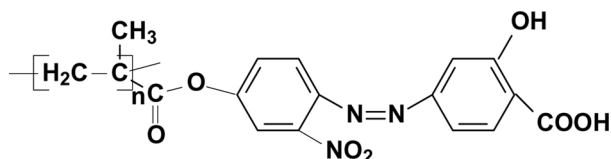
A1-Co



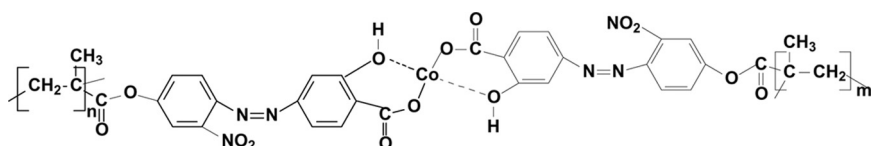
A2



A2-Co



A3



A3-Co

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

## EXPERIMENTAL

### 2.1. Monomer Synthesis

**Synthesis of 4-hydroxy-(4'-carboxy-3'-hydroxy)-azobenzene, 4-hydroxy-(4'-carboxy-3'-hydroxy)-2-nitroazobenzene, 4-hydroxy-(4'-carboxy-3'-hydroxy)-2-diethylaminoazo-benzene.** 4-amino-2-

hydroxybenzoic acid (15.3 g, 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 M) was 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 M) in a 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.**  $^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$ , ppm): 7.93–6.89 (3d, s, 7H, Ph-H), 11.4 (s, 1H, COOH), 10.19 (s, 1H, OH).

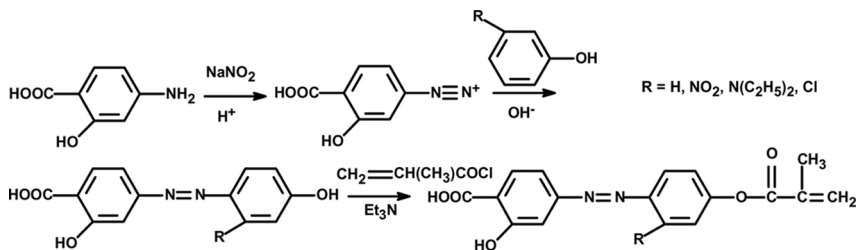
**4-hydroxy-(4'-carboxy-3'-hydroxy)-2-nitroazobenzene.**  $^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$ , ppm): 7.94–6.92 (2d, 2s, 6H, Ph-H), 11.37 (s, 1H, COOH), 10.24 (s, 1H, OH).

**4-hydroxy-(4'-carboxy-3'-hydroxy)-2-dimethylaminoazobenzene.**  $^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$ , ppm): 7.84–5.92 (2d, s, 6H, Ph-H), 1.24 (s, 6H, 2CH<sub>3</sub>), 3.51 (m, 4H, 2CH<sub>2</sub>), 14.75 (s, 1H, COOH), 11.41 (s, 1H, OH).

The synthetic route for target monomers is shown in Scheme 1.

## 2.2. Synthesis of Monomers

The synthesis of 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-azobenzene, as an example, is given below: the azocompound (2.58 g, 0.01 M) was dissolved in 25 mL of anhydrous THF, and freshly distilled triethylamine (1.53 mL, 0.011 M) was added to the solution. The reaction mixture was then cooled to 0–5°C. Methacryloyl chloride (1.07 mL, 0.011 M) in THF (5 mL) was gradually injected 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.



SCHEME 1

The resulting precipitate was filtered off. Purification was followed by recrystallization from methanol. Yield: 63–76%.

**4-methacroyloxy-(4'-carboxy-3'-hydroxy)-azobenzene.**  $^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$ , ppm): 8.12–6.92 (3d, s, 7H, Ph-H), 11.3 (s, 1H, COOH), 6.28 (s, 1H C=CH<sub>2</sub>, cis), 5.82 (s, 1H C=CH<sub>2</sub>, trans), 2.06 (s, 3H, =C–CH<sub>3</sub>).

**4-methacroyloxy-(4'-carboxy-3'-hydroxy)-2-nitroazobenzene.**  $^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$ , ppm): 8.13–7.02 (2d, s, 7H, Ph-H), 11.37 (s, 1H, COOH), 6.29 (s, 1H C=CH<sub>2</sub>, cis), 5.83 (s, 1H C=CH<sub>2</sub>, trans), 2.06 (s, 3H, =C–CH<sub>3</sub>).

**4-methacroyloxy-(4'-carboxy-3'-hydroxy)-2-diethylamino-azobenzene.**  $^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$ , ppm): 7.86–5.92 (2d, s, 7H, Ph-H), 1.24 (s, 6H, 2CH<sub>3</sub>), 3.50 (m, 4H, CH<sub>2</sub>), 14.75 (s, 1H, COOH), 6.28 (s, 1H C=CH<sub>2</sub>, cis), 5.82 (s, 1H C=CH<sub>2</sub>, trans), 2.08 (s, 3H, =C–CH<sub>3</sub>).

### 2.3. Synthesis of Chelates

New complexes of 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-azobenzene, 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-2-nitroazobenzene, 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-2-dimethylaminoazobenzene with Ni, Co, and Cu were synthesized by the exchange reaction between acetates of the corresponding metal (0.001 M) and monomers (0.002 M) in an 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 with Ni, Co, and Cu 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 a 10-wt.% DMF solution of a monomer with AIBN as the free radical initiator (10 wt.% with respect

**TABLE 1** Some Distinctive Absorption Bands of the Metallic Complexes of 4-methacroyloxy-(4'-carboxy-3'-hydroxy)-azobenzene

	$\nu_{as}(\text{COO}^-)$	$\nu_s(\text{COO}^-)$	$\nu(\text{COC})$	$\nu(\text{C=O})$
NiL <sub>2</sub>	1590	1380	1140	1715
CoL <sub>2</sub>	1600	1385	1140	1720
CuL <sub>2</sub>	1605	1385	1145	1725

of the monomer mass) at 80°C for more than 30 h in a thermostat. The polymerization mixture was poured into methanol. The solid precipitate was filtered, dissolved in DMF, reprecipitated into methanol, and then dried at 20°C overnight.

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

## 2.5. Spectral Measurements

Samples with free surface (glass substrate–conducting layer  $\text{SnO}_2:\text{In}_2\text{O}_3$ –polymeric film) were prepared and used in our investigations. The thickness of the polymeric films was 1–2  $\mu\text{m}$ . These samples were used for the following measurements: the spectra of the optical density  $D$  of polymeric films over the range of light wavelengths  $\lambda = 350\text{--}900\text{ nm}$ ; the value  $I_E/I_0$  where  $I_0$  and  $I_E$  are, respectively, the monochromatic light intensities before and after the application of the electric field. Nonpolarized and polarized light was used for the illumination of samples. In the latter case, the sample was located between two polarizers at an angle of ninety degrees. The electric field ( $E = 1 \times 10^8\text{ V/m}$ ) was produced by the corona discharge. The value  $I_E/I_0$  was determined as a function of the illumination duration ( $t$ ) by a polarized light and, after this illumination, a function of the light wavelength  $\lambda$ .

## RESULTS AND DISCUSSION

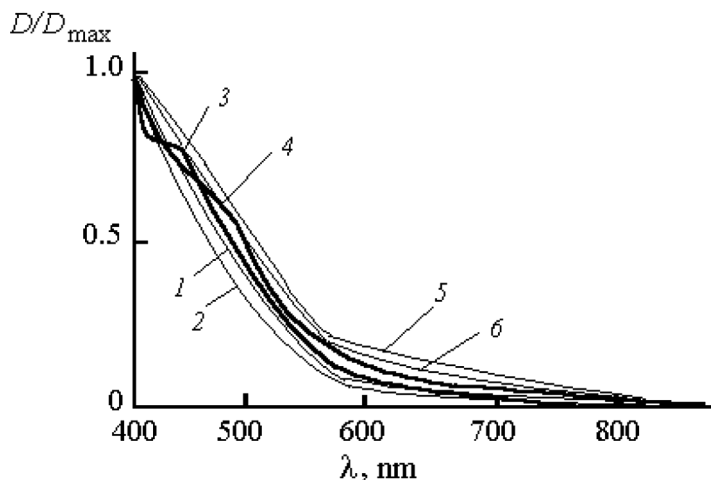
The absorption spectra of the investigated polymeric films are shown in Figure 1. The absorption is determined by the excitation of azobenzene groups by light and it is not sensitive to the presence of metallic ions in polymers. The bathochromic shift of the absorption band at the transfer from A1, A1-Co to A2, A2-Co and A3, A3-Co is connected with the influence of donor and acceptor substituents in chromophore which are able to reduce of the excited state energy of organic dyes [8].

The intensity of a nonpolarized light, which passed through the sample after the switching-on of the electric field, has decreased (Fig. 2) and has restored the original value after the switching-off of the electric field (Fig. 3).

The kinetics of the light intensity changes from  $I_0$  to  $I_E$  and, after the switching-off of the electric field can be described by the relations

$$I(t) = I_0 + (I_E - I_0)(1 - \exp(-t/\tau_E)) \quad (1)$$



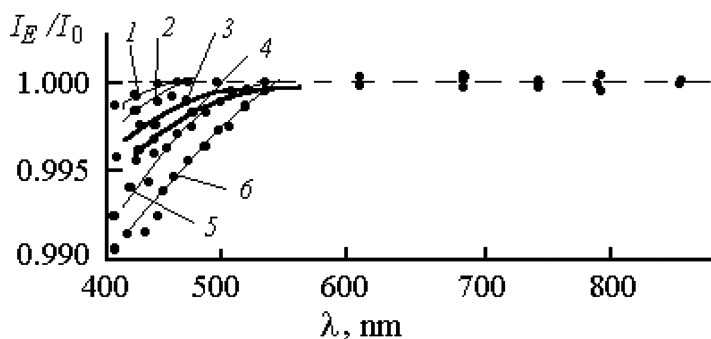


**FIGURE 1** Spectra of the optical density ( $D$ ) of polymeric films A1 (1), A1-Co (2), A2 (3), A2-Co (4), A3 (5), A3-Co (6).

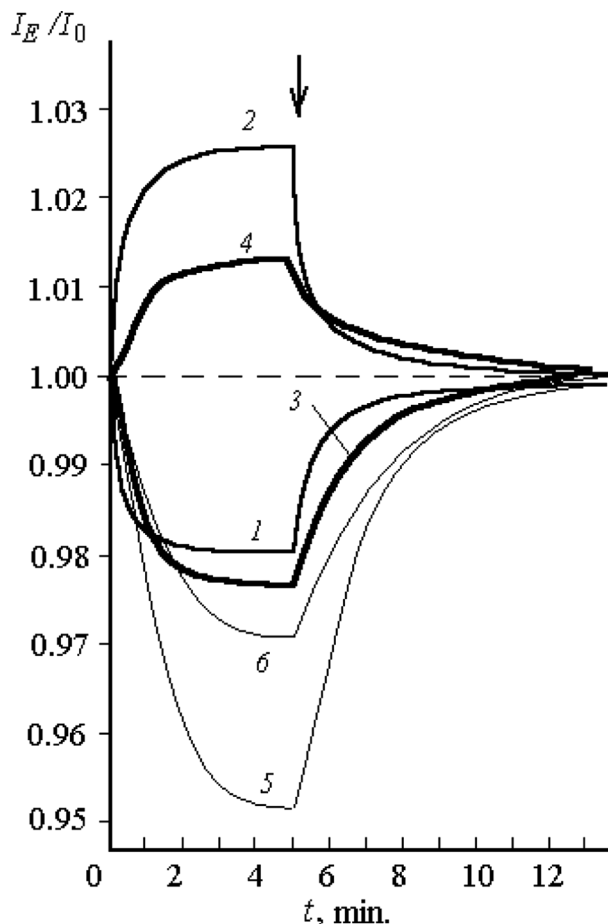
and

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

in which the time constant  $\tau_E$  amounts to  $60 \pm 10$  s for A1, A1-Co,  $90 \pm 10$  s for A2, A2-Co, and  $150 \pm 10$  s for A3, A3-Co. The influence of the electric field increases in the row A1, A1-Co; A2, A2-Co; A3, A3-Co, decreases with increase in  $\lambda$ , and is not observed for  $\lambda > 560$  nm.

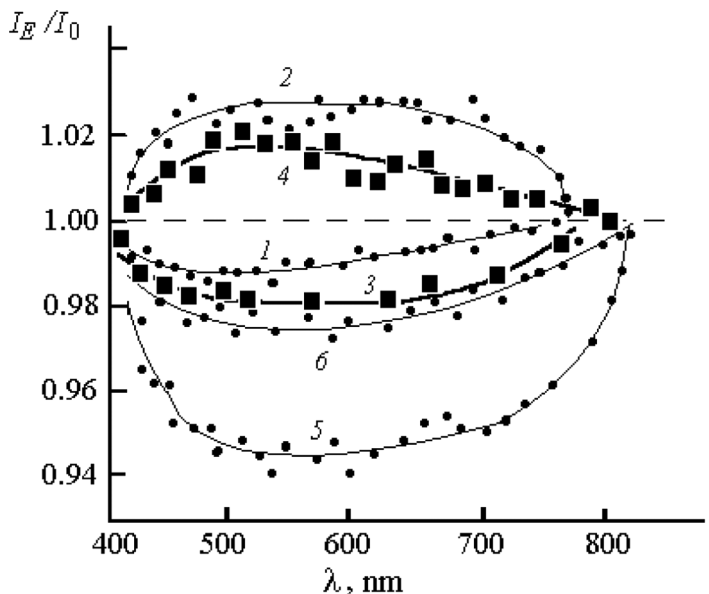


**FIGURE 2** Dependences of  $I_E/I_0$  for films A1 (1), A1-Co (2), A2 (3), A2-Co (4), A3 (5), A3-Co (6) under a nonpolarized light.



**FIGURE 3** Dependences of  $I_E/I_0$  on time  $t$  after the switching-on of  $E$  and the switching-off (the moment of the switching-on of the electric field is indicated by a vertical indicator) measured for  $\lambda = 544$  nm for samples A1 (1), A1-Co (2), A2 (3), A2-Co (4), A3 (5), A3-Co (6) after their illumination by a linearly polarized light during 60 min.

The influence of  $E$  on the light transmission comes into a particular prominence if samples are preliminarily illuminated by a polarized light (at  $\lambda < 550$  nm which is the absorption range of azobenzene groups). The most considerable changes of  $I_0$  at the switching-on of the electric field are observed after the illumination of samples by the light which passed through a polarizer during the time  $t > 30$  s. In Figure 4, we show the dependence  $I_E/I_0$  on  $\lambda$  which were measured



**FIGURE 4** Dependences  $I_E/I_0$  on  $\lambda$  measured in samples A1 (1), A1-Co (2), A2 (3), A2-Co (4), A3 (5), A3-Co (6) after their illumination by a linearly polarized light during 60 min.

after a long period of the illumination of samples by a polarized light with  $\lambda < 550$  nm.

The comparison of the curves in Figures 1–4 shows that the influence of the electric field on the light transmission after the long illumination by a polarized light was intensified in the long-wave band of absorption of the investigated compounds. The photoinduced optical anisotropy appears as a result of the illumination of the investigated samples by a linearly polarized light due to the *trans-cis*-isomerization of azobenzene groups. The electric field orients the photoinduced dipole moments of these groups and results in a rise of the electrooptical effect in the long-wave range of absorption of the investigated polymers.

The influence of  $E$  on the absorption of films even without preliminary illumination of samples by a linearly polarized light (Fig. 2) is related to the re-orientation of the dipole moments of azobenzene groups. The larger value of  $\tau_E$  for samples A3 and A3-Co in comparison to that for A2, A2-Co, and A1, A1-Co testifies that the re-orientation of the dipole moments of azobenzene groups A3, A3-Co, and A2, A2-Co occurs slowly over steric barriers which were caused by side substituents.

## CONCLUSIONS

The mechanism of the electrooptical effect for samples which were previously illuminated by a linearly polarized light is connected with the appearance and accumulation of the photoinduced dipole moments of the isomers of azobenzene groups. Since the absorption spectra of photoinduced isomers were displaced bathochromically relative to the absorption spectra of balanced azobenzene isomers [1,5], the maximum influence of the electric field was observed in the visible light range on the long-wave band of the absorption of azobenzene groups (Fig. 4).

Photoinduced dipole moments are re-oriented in an electric field relative to the electric vector of the exciting light wave, which results in a change of the optical anisotropy of the investigated films. In films A1, A2, and A2-Co, an external electric field involves the alignment of photoinduced dipoles along the field force lines, and the polarized light interacts with these dipoles. For  $\theta = \pi/2$ ,  $I_E/I_0 < 1$ . In film A1-Co, the polarized light is dissipated, and it is depolarized in the external electric field  $I_E/I_0 > 1$ . The last fact is related, perhaps, to a stronger interaction of  $\text{Co}^{2+}$  ions with  $E$  than the interaction of dipoles.  $\text{Co}^{2+}$  ions are bound with azobenzene fragments, but the direction of these bond does not coincide with the direction of a photoinduced dipole moment. The influence of the metallic ion in samples A2-Co and A3-Co in comparison to A1-Co is reduced under the increase of the dipole moment of an azobenzene group, and the re-orientation of this dipole moment at the external electric field prevails over the displacement of a  $\text{Co}^{2+}$  ion. Thus, the effect of the influence of an external electric field on the light transmission in the investigated films is related to the displacement of azobenzene groups and metallic ions from their balanced location due to the action of an external electric field. The increase of the dipole moment of azobenzene groups, for example, by the introduction of a donor or acceptor substituent enhances this effect and decreases the influence of metallic ions on the re-orientation of dipole moments.

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