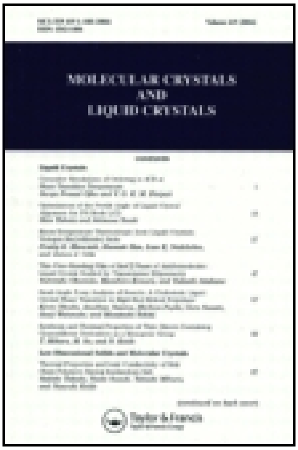

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Influence of the Chromophore Concentration on the Electro-Optical Effect in Polycomplexes of Azobenzene Derivatives

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Influence of the Chromophore Concentration on the Electro-Optical Effect in Polycomplexes of Azobenzene Derivatives

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The new polymeric composites with azobenzene chromophores are synthesized, and the influence of the chromophore concentration on the photoelectrical effect in films of these materials are investigated. The influence of the external electric field on the absorption spectra of azopolymer films are studied. Electro-optical properties of polymeric films are determined by the re-orientation of the dipole moments of azobenzene groups photoinduced by polarized light in the electric field. The photoelectric effect grows owing to the increase of the azobenzene chromophore concentration.

Keywords: azobenzene chromophore; azopolymer; dipole moment; electro-optical effect; photoisomerization; polycomplexes

1. INTRODUCTION

The polymeric systems with azobenzene chromophores doped or covalently attached have been investigated for potential technological applications such as optical information storage and processing, diffractive optical elements, LC displays, etc. [1–3]. Some of the recent research interest in the azo dye-containing polymeric films involves polarization splitters, nonlinear optical devices, integrated optical devices like channel waveguides, etc. [4–5].

Under the action of linearly polarized light, which is absorbed by azobenzene groups and leads to changes in isomeric structures, the polarization is induced in the films. It can be changed by thermal or

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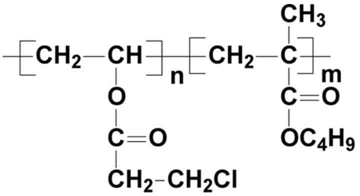
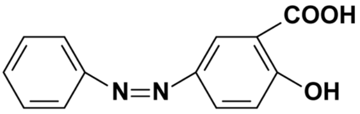
mechanical treatments in external electric and/or magnetic fields, under light illumination. The rotation of dipole moments occurs in the external electric field. Since the mechanism of the influence of an electric field is related to the aligning forces for the dipole moments of azobenzene groups, one can suppose that the electro-optical effect is observed in polymers with azochromophore and metallic ions chemically bound with a polymeric chain.

The aims of this work were the synthesis of new metal-containing polymeric composites and the investigation of optical and electrical properties of their polymeric films depending on the concentration of chromophore azobenzene groups in the polymeric matrix.

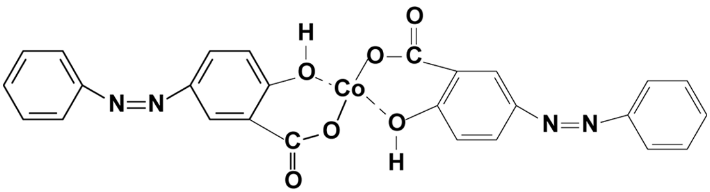
The copolymer β-chloroethyl vinyl ether with butyl methacrylate (1:3) having good film-forming and optical properties, model compound – azo dye 3-carboxy-4-hydroxy-azobenzene (M1) and its metal complex with cobalt (M1-Co), poly-4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene (A1), and polycomplex of 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene with Co (A1-Co) were synthesized:



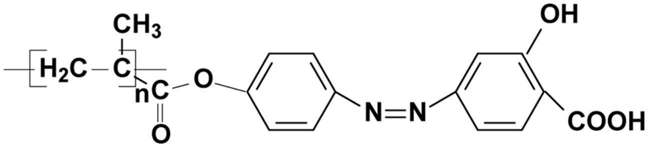
P1



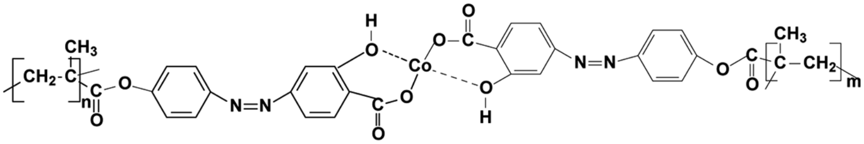
M1



M1-Co



A1



A1-Co

The structures of the monomers and metal complexes were confirmed by the data of NMR- and infrared spectroscopies. The copolymer composition has been determined by the element analysis.

2. EXPERIMENTAL

2.1. Materials

All the chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. The structures of all the precursors and final products were confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were measured on samples dissolved in DMSO.

2.2. Synthesis of Azocompounds

4-hydroxy-(4′-carboxy-3′-hydroxy)-azobenzene and 4-methacroyloxy-(4′-carboxy-3′-hydroxy)-azobenzene were prepared as previously reported [6]. The synthesis of 3-carboxy-4-hydroxy-azobenzene was executed by the common routine.

2.3. Synthesis of Complexes

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

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

CoL_2	ν_{as} (COO^-)	ν_s (COO^-)	ν (COC)	ν (C = O)
I	1600	1380	1140	1715
II	1610	1390	1170	1680

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

2.4. Polymerization

(Co)polymers were synthesized by free-radical polymerization in DMF. The (co)polymerization was carried out in 10-wt % DMF solution of a monomer with AIBN as a free radical initiator (10 wt.% with respect of the monomer mass for azocompounds and 1 wt.% for β-chloroethyl vinyl ether with butyl methacrylate) at 80°C for more than 30 h (8 h for copolymerization, respectively) 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 polymers and polycomplexes were characterized by ^1H NMR spectroscopy. The obtained results were in agreement with the proposed structures. Elem. Anal. Calculated for the copolymer β-chloroethyl vinyl ether with butyl methacrylate (1:3): Cl, 6.24%. Found: Cl, 6.6%.

2.5. Instruments for Characterization

The synthesized azopolymers and organic intermediates were characterized by ^1H NMR spectroscopy. The ^1H NMR (400 MHz) spectra were recorded on a "Mercury-400" spectrometer using DMSO as a solvent. Chemical shifts are in ppm from the internal standard tetramethylsilane (TMS). The thickness of the polymer films was 2–4 μm as measured with an MII-4 interference microscope. The intensity of light passed and its variation were registered by a KSVIP-23 spectral measurement and data processing complex.

2.6. Spectral Measurements

Samples with the free surface (glass substrate – conducting layer $SnO_2{:}In_2O_3$ – polymeric film) were prepared and used in our investigations. The thickness of the polymeric films was 2 – 4 μm. These samples were used for the following measurements: the spectra of optical density D of the polymeric films over the range of light wavelengths $\lambda = 350–900\,\text{nm}$; and the ratio I_E/I_0, where I_0 and I_E are the monochromatic light intensities, respectively, before and after the application of the electric field. The 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 value of δI_E was determined after a long-term exposure (60 min) of the samples by polarized light with $\lambda = 532\,\text{nm}$. The electric field ($E = 1 \cdot 10^8$ V/m) was produced by the corona discharge.

3. RESULTS AND DISCUSSION

The absorption spectra of the investigated polymeric films are shown on 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 increase of the concentrations of azo dye (M1) and its complex (M1-Co) in the polymeric matrix (P1) reduces the growth of D, but does not influence the dependence $D/D_{\max}$ on λ. For samples with A1, the dependences are analogous. The influence

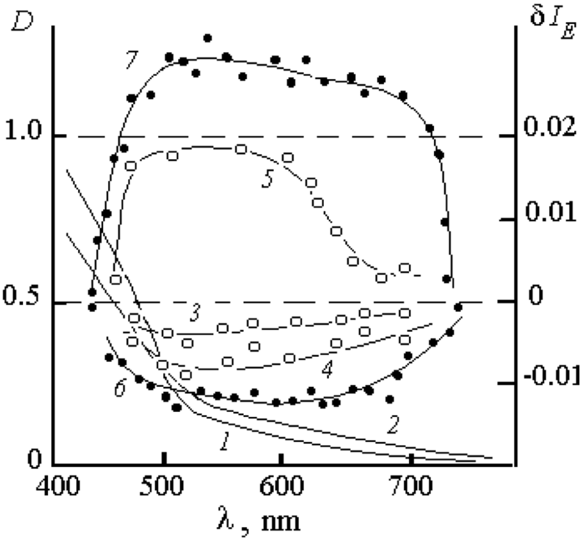


FIGURE 1 Spectra of optical density (D) versus λ for the polymeric films P1 + 10 mass.% M1 (*1*), A1 (*2*), and the dependences of δI_E on λ for the polymeric films P1 + 5 mass.% M1 (*3*), P1 + 10 mass.% M1 (*4*), P1 + 5 mass.% M1-Co (*5*), A1 (*6*), and A1-Co (*7*) measured at $T = 293\,\text{K}$.

of the electric field on polymeric samples P1 is not observed, but it is present in films P1 with additions M1 and M1-Co and increases with the concentration of these additions. The electric field had a more appreciable effect on 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 the exposure of the samples to light transmitted through a polarizer during $t>30\,\text{min}$. The influence of the electric field on the light transmission increases after the long-term irradiation by polarized light in the long-wave part of the absorption range of the polymeric films under study ($\lambda = 400$–$750\,\text{nm}$). The light intensity changes from I_0 to I_E when the electric field is switched-on and from I_E to I_0 after the electric field is switched-off and can be described by the simple relations: $I(t) = I_0 + (I_E - I_0)(1 - \exp(-t/\tau_E))$ and $I(t) = I_0 + (I_E - I_0)\exp(-t/\tau_E))$.

While comparing the properties of films P1 and films with additions M1 and M1-Co with those of azopolymer (A1) and polycomplex (A1-Co), it is seen that the value of $|\delta I_E|$ increases still more. This is caused by the growth of the chromophore concentration in the polymeric matrix.

The value of $|\delta I_E|$ increases in series of polymeric films with A1 and A1-Co, decreases with increase in the wavelength λ, and is not observed for $\lambda > 560\,\text{nm}$. Complexes and polycomplexes with Co have a positive sign of δI_E.

4. CONCLUSIONS

In the investigated polymeric samples, the electro-optical effect is observed as a result of the appearance and the accumulation of the light-induced dipole moments of azobenzene groups. The photoinduced dipoles change their orientation regarding the electrical vector of an incident light wave at an external electric field, which results in a change of the optical anisotropy of these films.

The increase of the chromophore concentration in the polymeric matrix contributes to the intensification of the electro-optical effect. Therefore, azopolymers and complexes based of them which contain chromophore groups in every polymeric unit are perspective for optical storage applications.

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