

Electro-optical properties of polymeric "guest-host" system doped with 8-hydroxyquinoline azo dyes and its cobalt complexes

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Received April 12, 2009

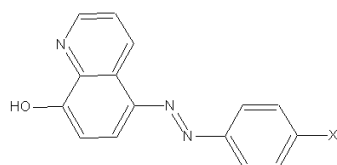
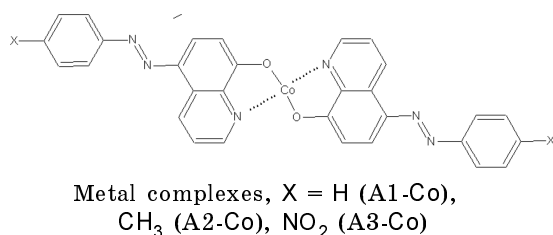
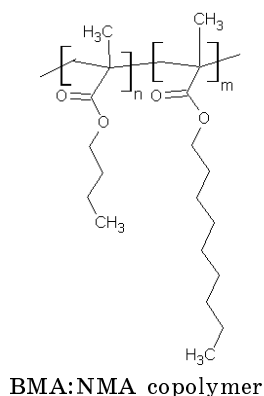
Polymeric composites based on the butyl methacrylate: nonyl methacrylate (3:1) copolymer doped with 8-hydroxyquinoline azo dyes with donor and acceptor substituents and the cobalt complexes thereof have been obtained. The influence of an external electric field on the polymeric film transmission of linearly polarized light in the long-wave part of the azo dye absorption range (corresponding to $\pi\pi^*$ azo fragment absorption range) and their metal complexes have been revealed. The influence of the electric field on the transmission is connected with the forces acting on dipole moments of azobenzene groups and metal ions.

Получены полимерные композиты на основе сополимера бутилметакрилат:нонилма-такрилат (3:1) с добавками азокрасителей на основе 8-оксихинолина с донорным и акцепторным заместителями и их комплексов с кобальтом. Обнаружено влияние внешнего электрического поля на пропускание полимерными пленками линейно поляризованного света на длинноволновом краю поглощения азокрасителей (соответствующем $\pi\pi^*$ полосе поглощения азофрагментов) и их металлокомплексов. Влияние электрического поля на пропускание света объясняется возникновением сил, действующих на дипольные моменты азобензольных групп и на ионы металла.

Films of polymeric compositions (PCF) containing azobenzene dyes [1–3] or azobenzene lateral groups [4–7] are of interest for their application as optically active media, in particular as polarization sensitive media for recording of optical holograms [8] and electro-optic modulators [9, 10]. The PCF containing azo dyes based on the 8-hydroxyquinoline are known to show a photoinduced optical anisotropy [11–17]. However, the electro-optical properties of PCF containing such dyes are not investigated to date. The aim of this work was to synthesize PC and to investigate the electro-optical characteristics of the films containing 8-hydroxyquinoline azo dyes at different

concentrations, depending on presence of metal ions in the chromophores at different dipole moments of azobenzene isomers. A model of the electrical field influence on the film transmission of the monochromatic polarized light is considered. For the studies, synthesized were the butyl methacrylate: nonyl methacrylate (BMA:NMA) (3:1 and 1:1 ratios), butyl methacrylate: vinyl butyl ether (1:1 ratio) copolymers as well as azo dyes, 8-hydroxyquinoline derivatives: 5-phenylazo-8-hydroxyquinoline (A1) and its complex with Co (A1-Co), 5-(4'-methoxyphenyl)azo-8-hydroxyquinoline (A2) and its complex with Co (A2-Co), 5-(4'-nitrophenyl)azo-8-hy-

droxyquinoline (A3) and its complex with Co (A3-Co).



The azo dyes were prepared according to the procedure [18]. The structures of the azo dyes were confirmed by the NMR spectroscopy. The Co complexes of the synthesized azo dyes were prepared by the exchange reaction between the cobalt nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and corresponding chelating agent in alcohol-NaOH solution used to regulate the system pH. The metal complex formation was confirmed by the IR spectroscopy. The copolymerization of the butyl methacrylate, nonyl methacrylate, vinyl butyl ether was carried out in DMF solution with azo isobutyronitrile (AIBN) as the free radical initiator (1 wt.% with respect to monomer) at 80°C during 10 hours. The BMA:NMA (3:1) copolymer was selected for investigations. Samples with the free surface (glass substrate — $\text{SnO}_2:\text{In}_2\text{O}_3$ conducting layer — polymeric film) were prepared. The concentrations of azo dyes and metal complexes were varied in the 1–10 wt. % with respect to the copolymer. The sample preparation procedure was described in [9]. The PC thickness was 2–3 μm .

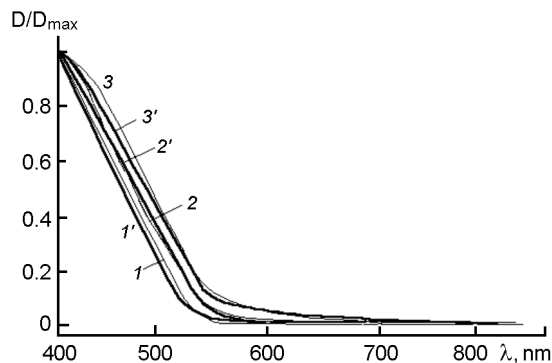


Fig. 1. Absorption spectra of BMA:NMA polymeric films with 5 wt. % A1 (1), A1-Co (1'), A2 (2), A2-Co (2'), A3 (3), A3-Co (3').

Measured were the optical density (D) spectra over the light wavelength range $\lambda = 400\text{--}900$ nm; the value $\delta I_E = (I_E - I_0)/I_0$, where I_0 and I_E are the monochromatic light intensities passed the PCF prior to and after the electrical field switching on, respectively. The polarized light was used to irradiate the samples. The sample was located between two polarizers with the polarization planes rotated by 90°. The value δI_E was determined after a long-term exposure (60 min) of the sample to polarized light with $\lambda > 400$ nm (the exposure time is selected larger than the typical settling time of photochemical processes in the system). The electric field ($E = 1 \cdot 10^8$ V/m) was produced using the corona discharge just as in [9, 19]. The δI_E value was determined as a function of the time (t) after the electrical field E switching on and switching off, and the wavelength λ . All measurements were carried out at room temperature.

The absorption spectra of the studied polymeric films are shown in Fig. 1. The normalized absorption spectra are weakly sensitive to the presence of metal ions in chromophores and to the chromophore concentration. The bathochromic shift of the absorption band at the transfer from A1 to A2 and A3 is connected with the presence of donor and acceptor substituents in the chromophore which reduce the excited state energy of organic dyes [20]. After the sample irradiation by polarized light from the azo compound absorption region (400–550 nm), the intensity of the polarized light passed through the sample is decreased when the electric field is switched on, and is restored to the original value (Fig. 2) when the field is switched off.

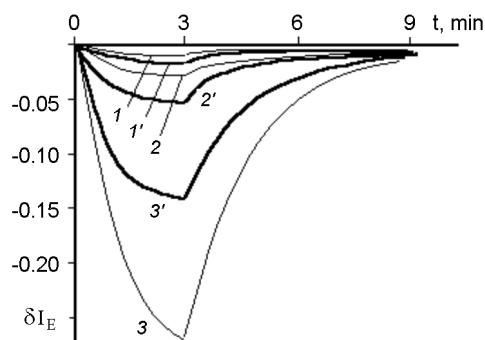


Fig. 2. Dependences of δI_E on time t after application of external electric field and its switching off after 3 min measured at $\lambda = 650$ nm for the BMA:NMA polymeric films with 5 wt. % A1 (1), A1-Co (1'), A2 (2), A2-Co (2'), A3 (3), A3-Co (3'). The samples were preliminarily irradiated with linearly polarized light during 60 min.

The light intensity change kinetics from I_0 to I_E and after the electric field is switched off can be described by simple correlations: $I(t) = I_0 + (I_E - I_0)(1 - \exp(-t/\tau_E))$ and $I(t) = I_0 + (I_E - I_0) \exp(-t/\tau_E)$. The time constant τ_E in these correlations is 150 ± 20 s. The electric field influence on the transmission of the linearly polarized light increases in the sequence A1, A1-Co; A2, A2-Co; A3, A3-Co. In Fig. 3, dependences $I_E/I_0(\lambda)$ are shown. The electrical field influence on the transmission of the linearly polarized light increases in the long-wave absorption range of the investigated PCF after a prolonged irradiation with polarized light from the azo dyes absorption range. The maximum $|\delta I_E|$ values have been obtained for azo dyes concentration 5 wt. % with respect of the BMA:NMA copolymer and those are three to four times higher than for PCF with 1 wt. % of azo dyes. The concentration increase to 10 % results in the film surface deterioration, the phase foliation and the increased light scattering therein.

In the studied PCF samples, the photoinduced optical anisotropy arises due to irradiation with a linearly polarized light causing the *trans-cis* isomerization of the azo dye molecules. An external electric field exerts an orienting effect on the photoinduced dipole moments of the azo compounds. This effect manifests itself as the electro-optical effect over the light wavelength range corresponding to the long-wave part of these azo dye absorption spectra. The time constant value τ_E exceeds significantly the geometrical capacitance charging duration of

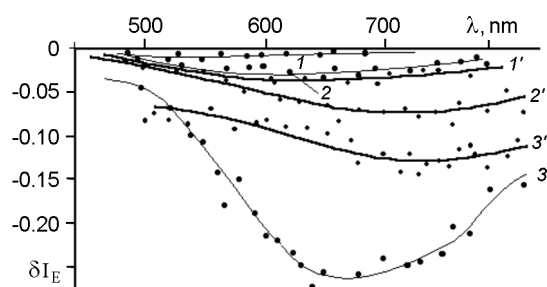


Fig. 3. Dependences of δI_E on λ for the BMA:NMA polymeric films with 5 wt. % A1 (1), A1-Co (1'), A2 (2), A2-Co (2'), A3 (3), A3-Co (3') after irradiation with linearly polarized light ($\lambda < 500$ nm) during 60 min.

the corresponding samples. This fact indicates that the dipole moments of azo molecule isomers in these films rotate slowly due to high viscosity of the polymeric matrix and steric hindrances caused by the presence of side groups in their structures.

The maximum influence of external electric field is observed within the visible spectral range close to long-wave absorption part of the azo chromophore groups. In the external electric field, the photoinduced dipole moments change their orientation with respect to the electric vector of the incident light wave. Such reorientation provokes a change of optical anisotropy of the studied films. The external electric field produces alignment of the photoinduced dipoles along the force lines of the field, the interaction between polarized light and these dipoles weakens and $\delta I_E < 0$. The $|\delta I_E|$ value increases in the sequence of PC films with A1, A2, A3, due to increasing dipole moments of azo dye molecule isomers. The same effect is observed for the cobalt-ion containing ones in PC films within the A1-Co, A2-Co sequence. The validity of the above suppositions about the photoinduced optical anisotropy mechanism in the studied PC films is confirmed by the model calculations using the Monte-Carlo method for the equilibrium configuration of the azo chromophore group isomer and the same isomer with connected ion Co^{2+} in the external electric field \mathbf{E} under account for the position of the Co^{2+} ion and the azobenzene group isomer dipole \mathbf{p} in the selected coordinate system. The increasing of azo chromophore dipole moment has been found to be able to level the influence of the electrical field interaction with Co^{2+} ion, that fact was observed experimentally in

the corresponding series of PC films with A1-Co, A3-Co.

Thus, the external electrostatic field effect on light transmission in the BMA:NMA films doped with 8-hydroxyquinoline derivative azo dyes after a long-term previous irradiation with linearly polarized light from the wavelength range corresponding to azo chromophore absorption region is caused by a reorientation of the photoinduced azo molecule isomers in the external electric field. The increasing dipole moments of the azo dyes by adding electron donor or acceptor substituents to the azo chromophores increase this effect. The increase of the azo dye concentration in the polymeric matrix from 1 % to 5 % leads to the intensification of the electro-optical effect, but the further increasing dye concentration cause the deterioration of the PC film optical homogeneity.

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Електрооптичні властивості полімерних систем "гість-хазяїн" з добавками азобарвників на основі 8-оксихіноліну та їх комплексів з кобальтом

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Одержано полімерні композити на основі співполімеру бутилметакрилат:нонілметакрилат (3:1) з домішками азобарвників на основі 8-оксихіноліну з донорним і акцепторним замісниками та їх комплексів з кобальтом. Виявлено вплив зовнішнього електричного поля на пропускання полімерними плівками лінійно поляризованого світла на довгохвильовій межі поглинання азобарвників (яка відповідає π^* смузі поглинання азофрагментів) та їх металокомплексів. Вплив електричного поля на пропускання світла пояснюється виникненням сил, які діють на дипольні моменти азобензольних груп і на іони металу.