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SYNTHESIS AND ELECTROOPTICAL PROPERTIES OF SIDE-CHAIN POLYMETHACRYLATES AND POLYCOMPLEXES CONTAINING AZOBENZENE MOIETIES WITH DIFFERENT LENGTH SPACERS

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Abstract. We propose new structures of metal-containing azopolymers with changeable electro-optical properties depending on different length spacers. The new monomers – 4-{4-[4-(methacroyloxy)butoxy]phenyl} diazenyl benzoic acid, 4-{4-[4-(methacroyloxy)octyl]oxy]phenyl} diazenyl benzoic acid and their complexes with Co and polymers based on these ones were synthesized. The influence of the electric field on the absorption spectra of new metal-containing azopolymers was investigated. Electro-optical properties of polymeric films are determined by the re-orientation of dipole moments of azobenzene groups photo induced by the polarized light in the electric field. Increase of structural flexibility due to the photo isomerization of azobenzene groups increases the electro-optical effect value.

Keywords: electrooptics, azobenzene, metallopolymers, polycomplexes, photo isomerization, dipole moment.

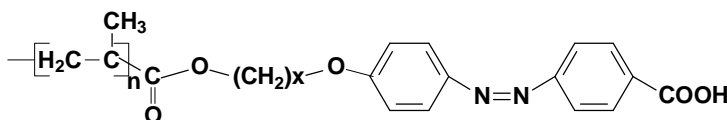
1. Introduction

Azobenzene containing polymers have received great attention in recent years because of their combined properties of anisotropic liquid crystals, photoresponsive materials and flexible polymers [1-8]. The liquid crystalline properties of azo polymers are related to the rod-like *trans*-azo mesogens, and the photoinduced fast and reversible isomerization between the *trans*- and *cis*-isomers of the azo groups upon exposure to UV or visible light provides them with fascinating photoresponsive properties, which can lead to photoinduced reorientation of azo groups in the polymers and triggers significant

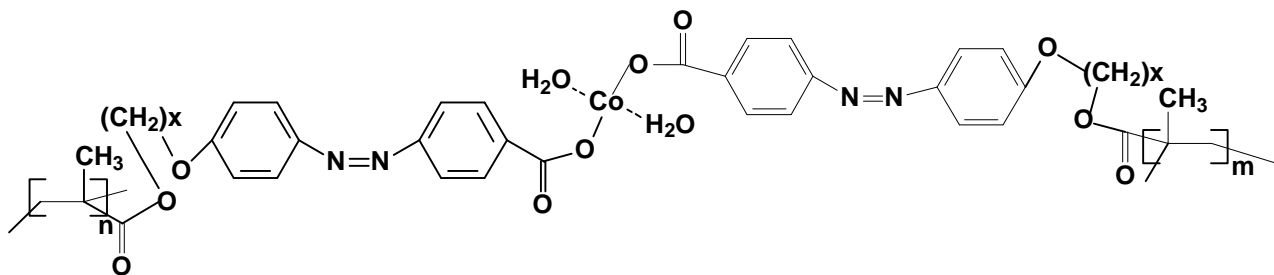
changes in their physicochemical properties. Many potential applications have been proposed for these polymers, such as optical data storage, liquid crystal displays, molecular switches, nonlinear optical devices, and photomechanical systems. So far, a great number of azo-containing polymers have been developed for different purposes, including side-chain liquid crystalline polymers with azo mesogens as side groups [9-14], photoresponsive polymers with azo units located in the main chains, [15, 16] and photoresponsive polymers networks [17-20]. One of the main focuses in this rapidly developing area is the rational design and efficient synthesis of novel azo-containing side-chain polymers in order to provide advanced functional materials with potential applications in desired areas. In general, the molecular structure of an azo-containing sidechain polymers can be divided into three main parts, *i.e.*, the polymer backbone, the pendant photoactive azo mesogens, and the flexible spacer connecting them.

In this paper, we present our findings on the synthesis and photo physical properties of the side chain polymethacrylates and their polycomplexes containing substituted azobenzene units as mesogens attached directly to the polymeric backbone with different length spacers. The aim of this work was to investigate optical and electrical properties of metal-containing polymeric systems depending on spacers length.

The polymers – poly-4-{4-[4-(methacroyloxy)butoxy]phenyl} diazenyl benzoic acid, poly-4-{4-[4-(methacroyloxy)octyl]oxy]phenyl} diazenyl benzoic acid and polycomplexes with Co were synthesized:



x = 4, 8



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

2. Experimental

2.1. Materials

Tetrahydrofuran (THF, 99 %) was refluxed over sodium and then distilled. *N,N*-Dimethylformamide (DMF, 99.5 %) was dried with anhydrous magnesium sulfate (MgSO_4) and then distilled under vacuum. Triethylamine (99 %) was dried with anhydrous sodium sulfate (Na_2SO_4) and then distilled. Thionyl chloride (99.5 %) was purified by distillation prior to use. Azobisisobutyronitrile (AIBN, chemical purity (CP)) was recrystallized from ethanol.

2.2. Syntheses

2.2.1. Synthesis of azocompounds

4-hydroxy-(4'-carboxy)-azobenzene: 4-amino-benzoic acid (0.1 mol) was dissolved in a solution of concentrated hydrochloric acid: water (50 : 50) (100 ml). The mixture was cooled to 273 K in an ice-water bath, and then sodium nitrite (6.8 g, 0.1 mol) dissolved in a small amount of water was 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 273–278 K and for additional 10 h at room temperature. The precipitate was formed and was collected by vacuum filtration and finally dried. The product was purified by recrystallization from ethanol. Yield 87 %.

4-hydroxy-(4'-carboxy)-azobenzene: ^1H NMR (500 MHz, DMSO, δ , ppm): 8.08 (d, 2H, Ph-H), 7.84 (d, 2H, Ph-H), 7.79 (d, 2H, Ph-H), 6.92 (d, 2H, Ph-H).

10.89 g (0.045 mol) 4-hydroxy-(4'-carboxy)-azobenzene was dissolved in a dry DMF (70 ml), 6 g (0.06 mol) calcined K_2CO_3 and 4.88 g (0.045 mol) 4-chlorobutanol-1 were added. The reaction was carried out in a flat-bottom flask with a backflow condenser by mixing on the magnetic stirrer over a period 25 h. The

DMF solution was evaporated partially by a rotary evaporator after the reaction has finished. The precipitate was formed and was collected by vacuum filtration and finally dried. The product was purified by recrystallization from ethanol. Yield 87 %.

4-[-(4-hydroxybutoxy)phenyl]diazanyl benzoic acid: ^1H NMR (500 MHz, DMSO, d , ppm): 8.07 (d, 2H, Ph-H), 7.86 (m, 4H, Ph-H), 6.95 (d, 2H, Ph-H), 3.65 (2H, $-\text{CH}_2-$), 3.45 (2H, $-\text{CH}_2-$), 1.73 (2H, $-\text{CH}_2-$), 1.55 (2H, $-\text{CH}_2-$).

4-{4-[(8-hydroxyoctyl)oxy]phenyl}diazanyl benzoic acid: ^1H NMR (500 MHz, DMSO, d , ppm): 8.07 (d, 2H, Ph-H), 7.86 (m, 4H, Ph-H), 6.95 (d, 2H, Ph-H), 3.73 (2H, $-\text{CH}_2-$), 3.48 (2H, $-\text{CH}_2-$), 3.07 (2H, $-\text{CH}_2-$), 2.88 (2H, $-\text{CH}_2-$), 2.45 (2H, $-\text{CH}_2-$), 2.10 (2H, $-\text{CH}_2-$), 1.75 (2H, $-\text{CH}_2-$), 1.51 (2H, $-\text{CH}_2-$).

The synthesis of 4-{4-[4-(methacroyloxy)butoxy]phenyl}diazanyl benzoic acid, as an example, is given below: azocompound (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 273–278 K. 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 278 K. 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-{4-[4-(methacroyloxy)butoxy]phenyl}diazanyl benzoic acid: ^1H NMR (500 MHz, DMSO, d , ppm): 8.07 (d, 2H, Ph-H), 7.86 (m, 4H, Ph-H), 6.95 (d, 2H, Ph-H), 3.73 (2H, $-\text{CH}_2-$), 3.48 (2H, $-\text{CH}_2-$), 3.07 (2H, $-\text{CH}_2-$), 2.88 (2H, $-\text{CH}_2-$), 2.45 (2H, $-\text{CH}_2-$), 2.10 (2H, $-\text{CH}_2-$), 1.75 (2H, $-\text{CH}_2-$), 1.51 (2H, $-\text{CH}_2-$), 5.95 (s, 1H, C=CH₂), 6.32 (s, 1H, C=CH₂), 1.20 (s, 3H, $-\text{CH}_3$).

4-{4-[4-(methacroyloxy)octyl]oxy]phenyl}diazanyl benzoic acid: ^1H NMR (500 MHz, DMSO, d , ppm): 8.07 (d, 2H, Ph-H), 7.86 (m, 4H, Ph-H), 6.95 (d, 2H, Ph-H), 3.73 (2H, $-\text{CH}_2-$), 3.48 (2H, $-\text{CH}_2-$), 3.07 (2H, $-\text{CH}_2-$), 2.88 (2H, $-\text{CH}_2-$), 2.45 (2H, $-\text{CH}_2-$), 2.10 (2H, $-\text{CH}_2-$), 1.75 (2H, $-\text{CH}_2-$), 1.51 (2H, $-\text{CH}_2-$), 5.95 (s, 1H, C=CH₂), 6.32 (s, 1H, C=CH₂), 1.20 (s, 3H, $-\text{CH}_3$).

2.2.2. Synthesis of chelates

Complexes of monomers with Co were synthesized by the exchange reaction between cobalt acetate (0.001 mol) and monomer ligand (0.002 mol) in alcohol-NaOH solution (20 ml) and purified by recrystallization from ethanol.

2.3. Polymerization

Polymers and polycomplexes were synthesized by free-radical polymerization in DMF. The polymerization was carried out in 10 wt % DMF solution of monomers with AIBN as a free radical initiator (10 wt % with respect to the monomers mass) at 353 K for more than 8 h (for monomeric complexes) and 20 h (for monomers) in a thermostat. The polymerization mixture was poured into methanol. The solid precipitate was filtered, dissolved in DMF, and reprecipitated into methanol and then dried at 293 K overnight.

2.4. Characterization Methods

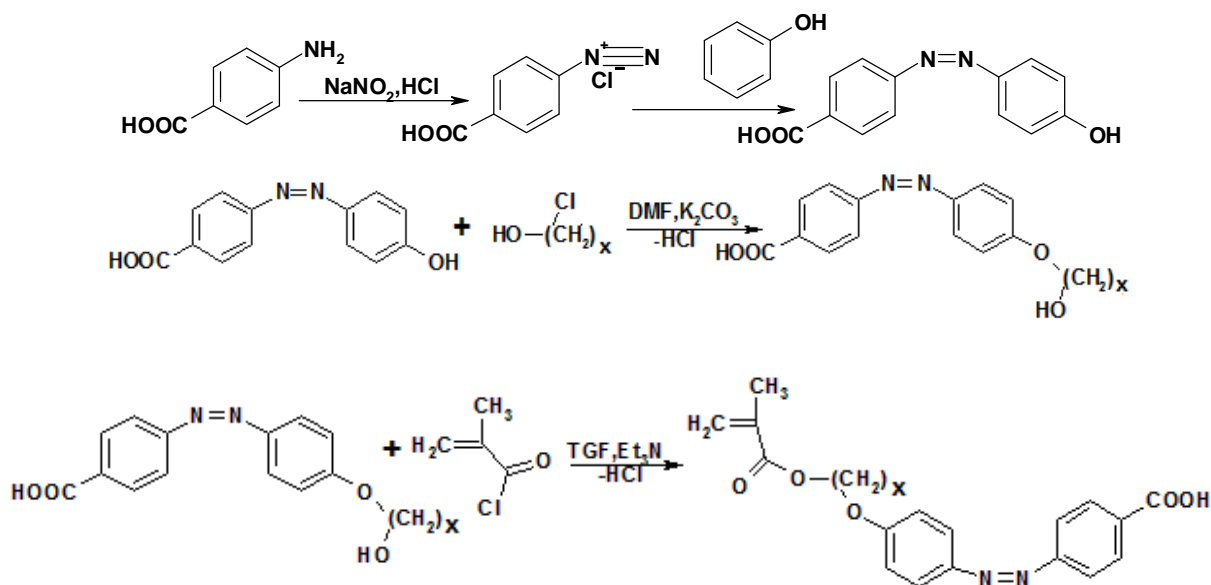
Infrared spectra were taken in a Fourier transform infrared (FTIR) spectrophotometer (Perkin-Elmer 1600) using KBr pellets. ^1H (500 MHz) spectra were recorded on a Bruker 500-MHz FT-NMR spectrometer with dimethyl sulfoxide- d_6 (DMSO- d_6) and CDCl_3 as solvents and tetramethylsilane as an internal standard. 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 was registered by a KSVIP-23 spectral measurement and data processing complex. The electronic absorption spectra were recorded using a spectrophotometer Shimadzu "UV-VIS-NIR Shimadzu UV-3600".

2.5. Spectral Measurements

Samples with the 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 2–4 μm . The spectra of optical density (D) over the range of light wavelength $l = 400\text{--}900\text{ nm}$; the value $dl_E = (I_E - I_0)/I_0$, where I_0 and I_E are the monochromatic light intensities passed before and after switching on the electrical field, were measured respectively. The polarized light was used for illumination of the samples. The sample was located between two polarizers at an angle of ninety degrees. The value dl_E was determined after a long-term exposure (60 min) of the sample by polarized light with $l > 400\text{ nm}$ (the exposure time is selected larger than the typical time of the establishment of photochemical processes in the system). The electric field ($E = 1 \cdot 10^8\text{ V/m}$) was produced by the corona discharge. The value of dl_E was determined depending on the time (t) after the electrical field E switching on and switching off, and the wavelength l . All measurements were carried out at room temperature.

3. Results and Discussion

Synthesis of azopolymers and polycomplexes was carried out in three steps. The synthetic route for the target monomers is shown in Scheme 1. At the first stage of synthesis 4-hydroxyazobenzene containing carboxylic group was obtained. Azo compounds were synthesized according to the classical scheme of diazotiation of 4-aminobenzoic acid and their further azocoupling with phenol.



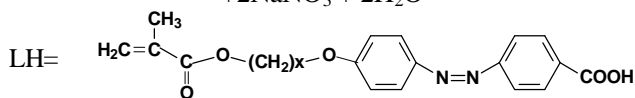
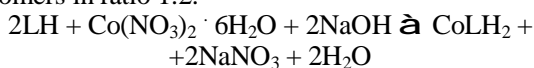
Scheme 1

The next stage of the synthesis was insertion of the alkyl spacer. The reaction was carried out by the Williamson method by boiling the obtained dye with 4-chlorobutyl alcohol or 8-chlorooctyl alcohol in DMF in the presence of K_2CO_3 for 25 h, respectively.

Purity of corresponding azo dyes was controlled by thin-layer chromatography and these substances were identified according to NMR-spectroscopy data. Synthesized materials are well-solved in majority of organic solvents, as well as stability to light and air.

The azo compounds were then acylated with methacryloyl chloride in the presence of triethylamine in the tetrahydrofuran solution.

The complexes were obtained by an exchange reaction between equimolar amounts of cobalt acetate and monomers in ratio 1:2.



$x = 4, 8$

The structures of the obtained complexes with Co have been studied by the infrared spectroscopy.

The formation of the metal complex was supported by the data from IR spectroscopy. IR spectrum of benzene fragment of azo dye was similar to IR spectrum of benzoic acid. The greatest interest was the carboxyl group in so far as it takes part in the formation of the complex. Absorption $\nu(\text{OH})$ was observed in the form of a broad band ($2800\text{--}3200\text{ cm}^{-1}$), which is typical for carboxylic acids which molecules form hydrogen bonds in the solid state. In IR spectra of the complex there are no absorption bands for the nitrate ions, indicating the formation of chelate compounds with the composition CoL_2 . IR spectrum in this region changes significantly as a result of complex formation. In place of the absorption band of the

carboxyl there were two absorption bands for the carboxylate group, namely $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ at 1595 and 1395 cm^{-1} respectively. The difference $\Delta = \nu_{as} - \nu_s$ amounts to more than 200 cm^{-1} , indicating a monodentate mode of the carboxylic group coordination of the synthesized ligand.

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 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.

Therefore, the mechanism of electric field influence is connected with occurrence of forces which rotate dipole moments, the important parameter is the time of media relaxation after electric field switching on and switching off. It can be achieved if polymer has liquid-crystal properties, for example thanks to the spacer in the polymer side chain.

The polymeric films absorption is determined by light excitation of azobenzene groups and it is not sensitive to the presence of metallic ions in polymers (Fig. 1). The bathochromic shift absorption for A4–A8 was observed (Fig. 2), that is testified by the development of aggregation in these polymers (class of J-aggregates) because of the capability of hydrogen bonds formation between substituents (carboxylic group) in azobenzene chromophores of the “head-to-head” type. The fulfillment of the Bouguer-Lambert-Beer law was observed and the bathochromic shift absorption for A4-Co, A8-Co was not observed, therefore the carboxylic groups in azobenzene chromophores take part in the complex formation.

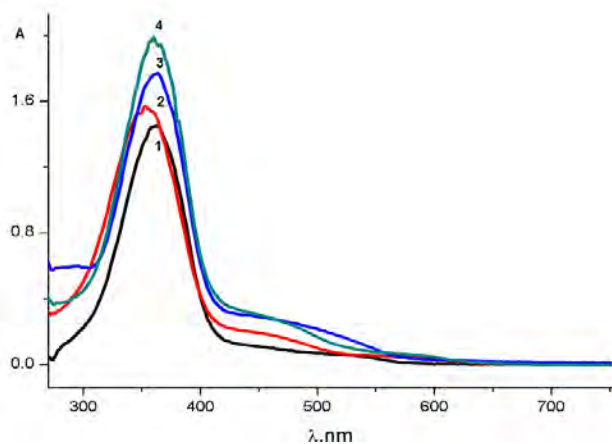


Fig. 1. The spectra of the optical density of solutions A4 (1), A8 (2), A4-Co (3) and A8-Co (4) in DMF ($C = 10^{-4}\text{ mol/l}$)

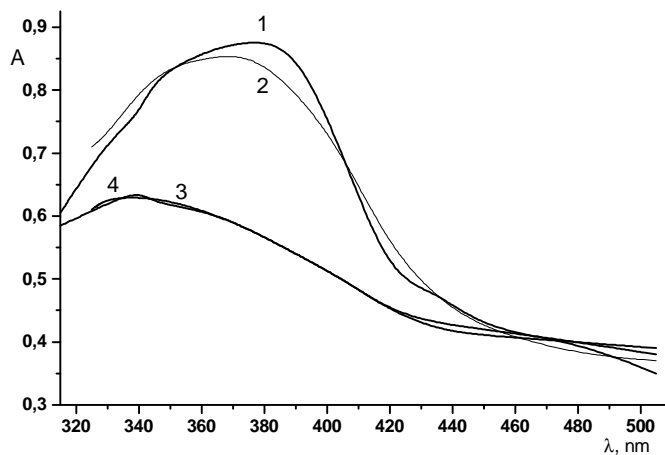


Fig. 2. The spectra of the optical density of films A4 (1), A8 (2), A4-Co (3) and A8-Co (4)

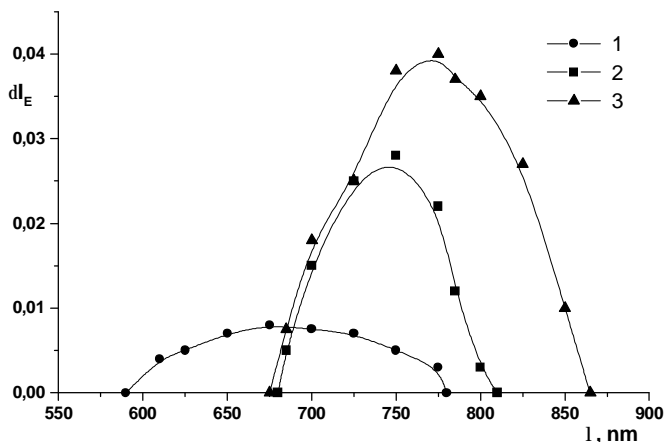


Fig. 3. Dependences of dl_E on l after switching on E and switching off, measured for $l = 625$ nm for the samples A8 (1), A8-Co (2) and A4-Co (3) after their illumination by the linearly polarized light during 60 min

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 in the wavelength near the long-wave absorption edge of the polymers (Figs. 3 and 4).

Figs. 3 and 4 show the results from measurements of dl_E in relation to l and t . After prolonged irradiation with polarized light E has an effect on the transmission of light in the long-wave region of absorption of the investigated compounds films. In films A4, A8, A4-Co, A8-Co an external electric field involves alignment of photoinduced dipoles along the field force lines and the polarized light interacts with these dipoles and the polarized light is dissipated and it is depolarized in the external electric field $dl_E > 0$. The last one perhaps is related to the stronger interaction of Co^{2+} ions with electric field 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.

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

The electric field had a more appreciable effect on the light transmission when the samples were pre irradiated by the polarized light in the absorption range of azobenzene groups ($l < 550$ nm). The most significant change in I_0 induced by an external electric field is observed after exposure of samples to light transmitted

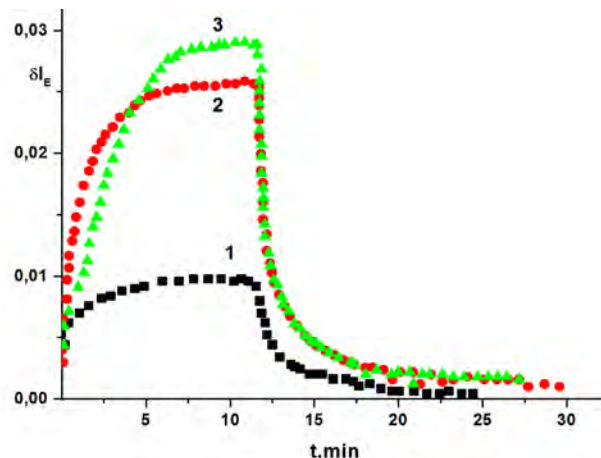


Fig. 4. Dependences of dl_E on time t after switching on E and switching off, measured for $l = 625$ nm for the samples A8 (1), A8-Co (2) and A4-Co (3) after their illumination by the linearly polarized light during 60 min

through the polarizer during $t > 30$ min. The influence of electric field on the light transmission increases after long-term irradiation by the polarized light in the long-wave part of the absorption range of investigated polymeric films ($l = 400\text{--}800$ nm).

Investigated polymers are relaxing very rapidly (Fig. 2) after switching off the electrical field. This effect can be explained by the flexible alkyl spacer present in their structure.

The value of dl_E increases (Fig. 3) in the order A8 – A8-Co – A4-Co, because in the films of polycomplexes with cobalt the polarized light experiences more intense scattering and depolarization in the external electric field. One can suppose that this feature is to be attributed to a stronger interaction between the electric field and Co^{2+} ions than that with the dipoles.

The value of dl_E for similar polycomplexes without the spacer does not exceed 2 % [21], probably through the inflexible structure of polycomplexes which complicate the azochromophore isomers reorientation in the electric field. In addition, the electrooptic effect for these polycomplexes was observed in the absorption range to $I_{\max} \sim 680$ nm but for A4-Co $I_{\max} \sim 860$ nm.

4. Conclusions

Side chain polymethacrylates and their polycomplexes containing substituted azobenzene units as mesogens attached directly to the polymeric backbone were synthesized and characterized.

In investigated polymeric samples the electro-optical effect mechanism is presented as a result of the

appearance and accumulation of light-induced dipole moments of azobenzene groups. The photoinduced dipoles change the orientation regarding the electrical vector of the incident light wave in the external electric field, which results in the change of optical anisotropy of these films.

Growth of the “spacer” length (A4, A8) and the capability of formation of hydrogen bonds between substituents in azobenzene groups involve decrease of the effect time and increase of optical characteristics changes of the films in the external electric field: the value $|dI_{E_{\max}}|$ increases by several times and value I_{\max} increases upon 60–160 nm.

Therefore, azo polymers and complexes based on them which include the flexible alkyl spacers in the side chain support the considerable electrooptic effect in the broad spectral range including near infrared range and are perspective for optical storage application.

From the present results, one can conclude that the films of the azobenzene polycomplexes with metallic ions can be considered as attractive for application in information media sensitive for external electromagnetic influences. Media for electro-optical and magneto-optical light modulators as well as for polarization holography can exemplify such media. In these media, the effect of a constant external electric field on a light transmission was attributed to the displacement of the azobenzene groups and metallic ions from their equilibrium state under the field influence. The results of the present investigation seem to be important for development of information media.

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СИНТЕЗ І ЕЛЕКТРОПТИЧНІ ВЛАСТИВОСТІ ПОЛІМЕТАКРИЛАТІВ І ПОЛІКОМПЛЕКСІВ, ЯКІ МІСТЯТЬ АЗОБЕНЗОЛЬНІ ЗАМІСНИКИ З РІЗНОЮ ДОВЖИНОЮ СПЕЙСЕРА В БІЧНОМУ ЛАНЦЮГУ

Анотація. Запропоновані нові структури металовмісних азополімерів із змінними електрооптичними властивостями в залежності від різної довжини спейсера. Синтезовані нові мономери – 4-[4-[4-(метакроїлокси)бутоксифеніл]діазеніл бензойна кислота, 4-[4-[4-(метакроїлокси)октил]оксифеніл]діазеніл бензойна кислота, їх комплекси з кобальтом і полімери на їх основі. Досліджено вплив електричного поля на поглинання нових металовмісних азополімерів. Встановлено, що електро-оптичні властивості полімерних плівок визначаються переорієнтацією дипольних моментів азобензольних груп, які індуковані впливом поляризованого світла в електричному полі. Показано, що збільшення структурної гнучкості внаслідок фотоізомеризації азобензольних груп збільшує величину електрооптичного ефекту.

Ключові слова: електрооптика, азобензол, металополімери, полікомплекси, фотоізомеризація, дипольний момент.