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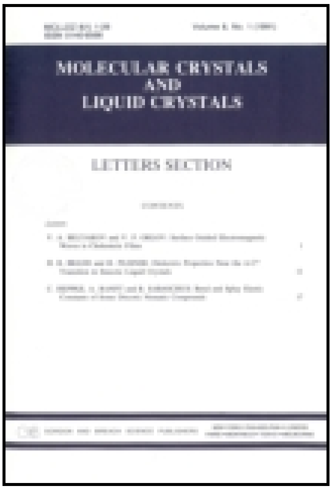

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Electrooptical Properties of Polymer Composites with Bisazobenzene Dyes and their Metal Complexes

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Electrooptical Properties of Polymer Composites with Bisazobenzene Dyes and their Metal Complexes

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Polymeric composites based on the copolymer - octyl methacrylate:acrylonitrile (1:1) with incorporated azo dyes: [4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}diazenyl) phenyl]amine, 1-[4-((E)-{4-[(E)-(4-amino phenyl)diazenyl]phenyl}diazenyl)phenyl] ethanone, 4-((E)-{4-[(E)-(4-aminophenyl)diazenyl] phenyl}diazenyl)benzoic acid and its complex with Co were synthesized and their electro-optical properties were investigated. The influence of the electric field on the absorption spectra of new polymer composites with azodyes and complex was investigated. The influence of electronic nature of substitutes in the bisazo chromophores on the electro-optical effect was investigated.

Keywords electro-optical effect; bisazoaromatic chromophore; azodyes; copolymer; complex; photoisomerization; dipole moment.

1. Introduction

There is considerable interest in the synthesis and characterization of azobenzene-containing polymers and polymeric composites (PC) because of their potential applications in photonic fields [1–7]. When irradiated with linearly polarized light the long molecular axis of the azobenzene will be aligned perpendicular to the electric field vector of the polarized actinic light through photochemical trans–cis–trans isomerization cycles. This process results in optical anisotropy, which can be monitored by the photoinduced birefringence measurements. Because of their unique properties, the polymers and polymer composites with azobenzene chromophores are expected to be one of the most attractive materials for reversible optical data storage media [8–13]. However, most of the investigations focused on the single azobenzene-based polymers, and few reports on the polymers with bisazobenzene chromophores have been presented [14–17]. Two azo groups in the bisazobenzene derivatives can undergo photoisomerization and consequently orientation exposed under polarized light, which may increase the efficiency of photoalignment and lead to novel optical properties [18–20]. It is known [21–23], for dyes and polymers containing bisazobenzene chromophores the considerable increase of the birefringence coefficient in comparison with monoazocompounds is observed. In addition for practical application of concerned optical medium the critical parameter is the relaxation medium time after electric field switching on and switching off. But in the literature the polymeric composites

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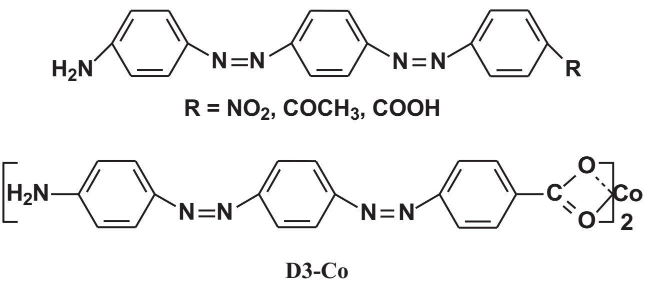

Scheme 1. Molecular structures of studied dyes and complexes.

with the value electrooptic effect is some percents are described. Therefore, novel materials search with enhanced properties is topical goal.

In this paper, we report our findings on the synthesis and behaviour of the polymeric composites with incorporated azo dyes: [4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl] phenyl} diazenyl)phenyl]amine, 1-[4-((E)-{4-[(E)-(4-amino phenyl)diazenyl]phenyl} diazenyl) phenyl]ethanone, 4-((E)-{4-[(E)-(4-aminophenyl)diazenyl] phenyl}diazenyl)benzoic acid and its complex with Co. The aim of this work was investigations of optical and electrical properties of metal-containing polymeric systems depending on electronic nature substitutes in the bisazo chromophores and metal ion availability.

The films of copolymer - octyl methacrylate:acrylonitrile (1:1) (**OMA:AN)** with incorporated azo dyes: [4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}diazenyl)phenyl]amine (**D1**), 1-[4-((E)-{4-[(E)-(4-amino phenyl)diazenyl]phenyl}diazenyl)phenyl]ethanone (**D2**), 4-((E)-{4-[(E)-(4-aminophenyl)diazenyl] phenyl}diazenyl)benzoic acid (**D3**) and its complex with Co **(D3-Co)** were synthesized:

The structures of the dyes, copolymer and metal complex were confirmed by NMR- and infrared spectroscopic data.

The copolymer selection OMA:AN for the creation of PC with unique photoelectric properties was obtained under early traced investigations [24]. In [24] the maximal effect of the electric field on the transmission of linearly polarized light through the PC was detected in copolymer film NMA:AN (nonylmethacrylate:acrylonitrile) which is explained the polymer flexibility and the polar groups availability.

2. Experimental

2.1. Synthesis of [4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}diazenyl)phenyl]amine (D1), 1-[4-((E)-{4-[(E)-(4-amino phenyl)diazenyl]phenyl}diazenyl)phenyl]ethanone (D2), 4-((E)-{4-[(E)-(4-aminophenyl)diazenyl] phenyl}diazenyl)benzoic acid (D3)

2-aminobenzoic acid or 4-nitroaniline (4-aminoacetophenone) (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 (0.1 mol) dissolved in a small amount of water added dropwise. The reaction mixture was stirred for 2 h, and then aminoazobenzene (0.1 mol) in ethanol 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: 75–91%.

[4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}diazenyl)phenyl]amine (**D1**):

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 8.32 (d, 2H, Ph-H), 8.03 (d, 2H, Ph-H), 7.93 (d, 2H, Ph-H), 7.67 (d, 2H, Ph-H), 7.52 (m, 4H, Ph-H, 2H, NH_2).

1-[4-((E)-{4-[(E)-(4-amino phenyl)diazenyl]phenyl}diazenyl)phenyl]ethanone (**D2**):

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 9.92 (s, 1H, NH_2), 8.03 (t, 4H, Ph-H), 7.93 (d, 2H, Ph-H), 7.65 (s, 2H, Ph-H), 7.5 (m, 4H, Ph-H, 1H, NH_2), 2.61 (s, 3H, CH_3).

4-((E)-{4-[(E)-(4-aminophenyl)diazenyl] phenyl}diazenyl)benzoic acid (**D3**):

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 8.34 (d, 2H, Ph-H), 8.05 (d, 2H, Ph-H), 7.91 (d, 2H, Ph-H), 7.64 (d, 2H, Ph-H), 7.5 (m, 4H, Ph-H, 2H, NH_2), 1.5 (s, 1H, COOH).

2.2. Synthesis of Chelates

Complex of 4-((E)-{4-[(E)-(4-aminophenyl)diazenyl] phenyl}diazenyl)benzoic acid with Co was synthesized by the exchange reaction between cobalt acetate (0.001 mol) and dye (0.002 mol) in alcohol-NaOH solution (20 mL) and purified by recrystallization from ethanol.

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

The formation of the metal complex was supported by the data from IR spectroscopy. The IR spectrum of the benzene fragment of the azodye D3 is similar to the IR spectrum of benzoic acid. Of greatest interest is the carboxyl group in so far as it takes part in the formation of the complex. The ν(OH) absorption is observed in the form of a broad band (2800–3200 cm^{-1}), which is typical of carboxylic acids whose molecules form hydrogen bonds in the solid state. In the 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. The IR spectrum in this region changes significantly as a result of complex formation. In place of the absorption band of the carboxyl there are two absorption bands for the carboxylate group, namely ν_{as}(COO–) and ν_s(COO–) at 1610 and 1400 cm^{-1} respectively.

The difference $\Delta = \nu_{as} - \nu_s$ amounts to more than 200 cm^{-1}, indicating a monodentate mode of coordination of the carboxylic group of synthesized ligand.

2.3. Polymerization

Copolymer was synthesized by free-radical polymerization in DMF. The polymerization was carried out in 10 wt.% DMF solution of monomers with AIBN as free radical initiator (1 wt.% with respect of monomers mass) at 80°C for more than 8 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.

Copolymer - octyl methacrylate:acrylonitrile:

^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm): 4.05 (m, 2H, CH_2), 2.85–1.75 (m, 3H, $2CH_2$), 1.65 (s, 3H, CH_3), 1.3 (s, 12H, $6CH_2$), 1.06 (m, 1H, CH_2), 0.89 (s, 3H, CH_3).

2.4. Characterization Methods

Infrared spectra were taken using 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.

2.5. 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 mη. The spectra of optical density (D) over the range of light wavelength $\lambda = 400$–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 before and after switching on the electrical field, respectively, were measured. 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 δI_E was determined after a long-term exposure (60 min) of the sample by polarized light with $\lambda > 400$ nm (the exposure time is selected larger than the typical time of the establishment of photochemical processes in the system). The electric field ($E = 1 \times 10^8$ V/m) was produced by the corona discharge. The value of δI_E was determined depending on the time (t) after the electrical field E switching on and switching off. All measurements were carried out at room temperature.

3. Results and Discussion

3.1. Spectral Properties

The polymeric films absorption is determined by light excitation of azobenzene groups and it is not sensitive on the presence of metallic ions in polymeric compozite.

The electric field had a more appreciable effect on the light transmission when the samples were preirradiated by polarized light in the absorption range of azobenzene groups ($\lambda < 550$ nm). The most significant change in I_0 induced by an external electric field is observed after exposure of samples to light transmitted through the polarizer during $t >$ 20 min. 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 ($\lambda = 400$–750 nm).

The kinetics of light intensity changes from I_0 to I_E and when the electric field is switched off it can be described by the simple correlations: $I(t) = I_0 + (I_E - I_0)(1 - \exp(-t/\tau_E))$ and $I(t) = I_0 + (I_E - I_0)\exp(-t/\tau_E))$, in which τ_E is the average time constant of the electro-optical effect relaxation.

The value of $|\delta I_E|$ increases (figure 1) in series of PC films with D1, D2, D3, owing to dipole moments of azo dyes molecules isomers increase, which cause the strengthening of these dipoles interaction with external electric field.

Therefore, external electrostatic field effect on light transmission by the PC films with D1, D2, D3 bisazo dyes additions after their long-term previous illumination with linearly polarized light for wavelength corresponding to azo chromophores absorption region is caused by a re-orientation of the photo induced azo molecules isomers in the external electric field.

The growth of the azo dyes dipole moments by adding electron-donor or acceptor substituents to the azo chromophores or metal ion involves increase of this effect.

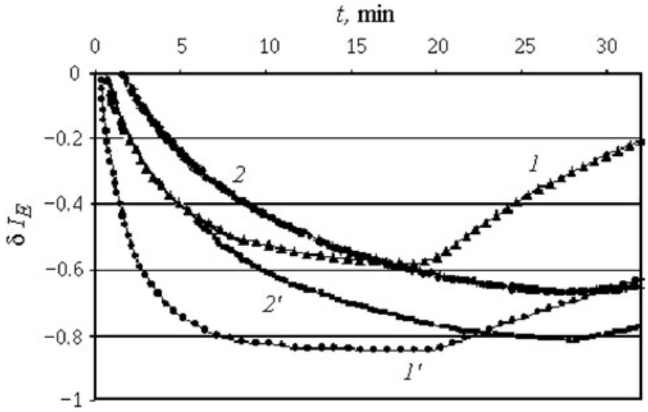

Figure 1. The dependencies of δI_E on time t after application of the external electric field and its switching off after 20 min illuminated with linearly polarized light measured for $\lambda = 470$ nm in the polymeric films based OMA:AN with 5 mass.% D3 (*1*) ($\tau_E = 4$ min), D3-Co (*1'*) ($\tau_E = 2{,}4$ min), and 27 min measured for $\lambda = 665$ i 720 nm in the polymeric films based OMA:AN with 5 mass.% D2 (*2*) ($\tau_E = 8{,}1$ min), D1 (*2'*) ($\tau_E = 7{,}3$ min). The samples were preliminarily illuminated with linearly polarized light during 20 min.

Unusually large-scale values $|\delta I_E|$ - more 80% - for investigated PC with incorporated azodyes and metallocomplex on basis of copolymer OMA:AN can be explained the presence of two azo groups which undergo the photoinduced isomerization and polar nitrile groups of acrylonitrile in copolymer which increase of example dipole moment. The effect strengthening is practicable due to the process adjustment of structural-soft polymeric matrix which is accompanied the dipole orientation of azochromophore and polar nitrile groups too.

4. Conclusions

The films of copolymer - octyl methacrylate:acrylonitrile (1:1) with incorporated azo dyes: [4-((E)-{4-[(E)-(4-nitrophenyl)diazenyl]phenyl}diazenyl)phenyl]amine, 1-[4-((E)-{4-[(E)-(4-amino phenyl)diazenyl]phenyl}diazenyl)phenyl]ethanone, 4-((E)-{4-[(E)-(4-aminophenyl)diazenyl] phenyl}diazenyl)benzoic acid and its complex with Co were synthesized and characterized.

The influence of substitutes electronic nature in the bisazo chromophores and metal ion availability on the electro-optical effect was investigated.

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

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 polymeric composites.

Thus, the peculiarities of electro-optical effect occurrence in PC with bisazo chromophores were investigated and the considerable light intensity variation by electric field switching on were detected.

Therefore, polymeric composites and complexes that consist two chromophore groups are perspective for optical storage application.

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