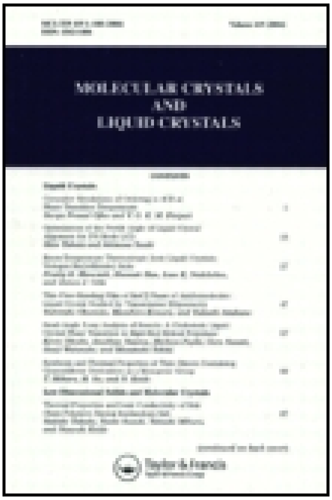

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Spacer Length Influence on the Electrooptic Effect of Methacrylic Azopolymer Series

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Methacrylic azopolymers with different spacer lengths in side chains have been synthesized. The spectra and kinetics of the electrooptic effect which arises in azopolymer films after their irradiation by linearly polarized light are investigated. The photo-induced optical anisotropy in the films appears due to a change of the concentration ratio of trans- and cis-isomers of azobenzene fragments. This explains the nature of the electrooptic effect. Owing to a mobility increment of azobenzene fragments by means of the spacer extension, the electrooptic effect becomes more pronounced, and its relaxation time decreases.

Keywords: azopolymer; electro-optical modulator; fragment mobility, information medium; photoisomer

1. INTRODUCTION

Azobenzene-containing polymers are widely studied due to their potential application in many fields which include the optical data storage, liquid crystals displays, and holographic surface relief gratings [1–5]. The photoresponsive properties of the polymers are based on the *trans*-to-*cis* and *cis*-to-*trans* photoisomerizations of azobenzene which lead to considerable changes in their molecular shape and dipole moments [6,7].

Induced polarization changing is possible under the external thermal or mechanical action (heating, light illumination, external electric field). In the external electric field, the rotation of azobenzene isomers takes place. The mechanism of the electric field influence is

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determined by the appearance of directive forces which influence the dipole moments of azofragments [8]. Nevertheless up to date, the issue about the influence of a spacer length (cluster of atoms which connects side azobenzene fragments with the main chain) on electrooptic properties of methacrylic polymer films was not investigated. This question is important for the creation of new electrooptic holographic media. Therefore, the goal of our exploration was the generation of azopolymers with different spacer lengths and the investigation of electrooptic properties of films of such azopolymers.

2. EXPERIMENTAL

2.1. Materials

The general structure of methacrylic azopolymers is shown in Chart 1. All the chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Standard distillation procedures were applied. The structures of all the precursors and final products were confirmed by solution ^{1}H NMR spectroscopy. All ^{1}H NMR spectra were taken in $CDCl_3$. The synthesis of all polymers was similar, and only the steps toward making methacrylic azopolymers are detailed.

Monomer Synthesis

The synthetic route for the target azomonomers (M) is shown on Scheme 1. The corresponding monomers were synthesized by general methods. The azocompound (0.06 mole) and triethylamine (9.0 ml) were dissolved in THF (200 ml). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (6.0 ml, 0.06 mole) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resulting mixture was stirred at room temperature overnight. Then the solution was poured into distilled water (1 l), and the obtained residue was filtered and air-dried. Recrystallization of monomers was carried out in ethanol.

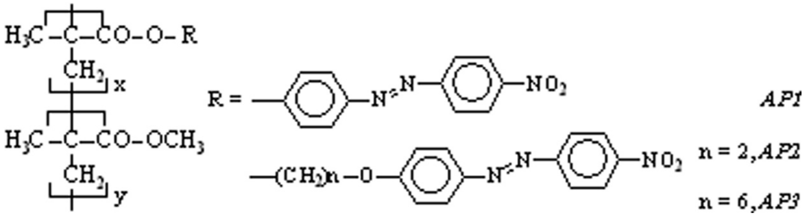
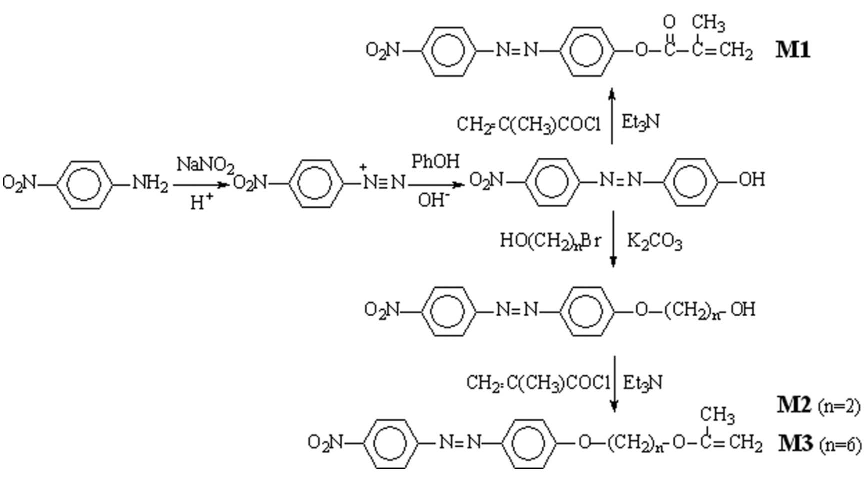


CHART 1 Investigated azopolymers.



SCHEME 1 Azomonomer synthesis.

For the purpose of the insertion of an alkyl spacer into the azomonomer structure, the azocompound was alkylated by bromine derivative of alcohols over potassium carbonate. The obtained product was methacrylated as stated above (Scheme 1).

The azomonomers obtained in this way are characterized by the good solubility in DMF, acetone, chloroform, and dioxane.

4′-Methacryloxy-4-Nitroazobenzene (M1)

Orange crystals; yield 69%; mp 145°C (by DSC). ^{1}H NMR ($CDCl_3$), δ (ppm): 8.43 (d, 2H, Ph-**H** *ortho* to NO_2), 8.07 (d, 2H, Ar), 8.03 (d, 2H, Ar), 7.40 (d, 2H, Ar), 6.34 (s, 1H, $=CH_2$), 5.91 (s, 1H, $=CH_2$), 2.05 (s, 3H, $-CH_3$). UV-vis (Ethanol) λ_{max}: 360, 485 nm. Elem. Anal. Calcd for $C_{16}H_{13}O_4N_3$: C, 61.74%, H, 4.18%; N, 13.50%. Found: C, 61.70%, H, 4.16%; N, 13.52%.

4′-Methacryloxyethyloxy-4-Nitroazobenzene (M2)

Orange crystals; yield 56%; mp 130°C (by DSC). ^{1}H NMR ($CDCl_3$), δ (ppm): 8,00 (d, 2H, Ar), 8,37 (d, 2H, Ar), 7,62 (d, 2H, Ar), 7,13(d, 2H, Ar), 6.4 (s, 1H, $=CH_2$), 5.8 (s, 1H, $=CH_2$), 2.15 (s, 3H, $-CH_3$), 4,10 (m, 2H, $ArOCH_2$), 1,72 (m, 2H, OCH_2). UV-vis (Ethanol) λ_{max}: 360, 490 nm. Elem. Anal. Calcd for $C_{18}H_{17}O_5N_3$: C, 60.85%, H, 4.79%; N, 11.83%. Found: C, 60.88%, H, 4.81%; N, 11.85%.

4′-Methacryloxyhexyloxy-4-Nitroazobenzene (M3)

Orange crystals; yield 50%; mp 72°C (by DSC). ^{1}H NMR ($CDCl_3$), δ (ppm): 8,02 (d, 2H, Ar), 8,34 (d, 2H, Ar), 7,68 (d, 2H, Ar), 7,10 (d, 2H, Ar), 6.30 (s, 1H, $= CH_2$), 5.95 (s, 1H, $=CH_2$), 2.20 (s, 3H, $-CH_3$),

TABLE 1 Properties of Azopolymers

Code	X, mol.%	T_g, °C	λ_{Max}, nm	M_n	M_w	M_w/M_n
AP1	20	111	350	6100	8240	1.35
AP2	20	109	355	7020	9760	1.39
AP3	20	102	362	8000	11120	1.39

4.10 (m, 2H, $ArOCH_2$), 3,9 (m, 2H, $HOCH_2$) 1, 72 (m, 4H, H_2) UV-vis (Ethanol) λ_{max}: 365, 490 nm. Elem. Anal. Calcd for $C_{22}H_{25}O_5N_3$: C, 61.74%, H, 4.18%; N, 13.50%. Found: C, 61.70%, H, 4.16%; N, 13.52%.

Polymerization

Copolymers were synthesized by free-radical polymerization of the corresponding azomonomers with MMA in toluene. The polymerization was carried out in a 10wt.% toluene solution of monomer with AIBN as a free radical initiator (1 wt.% of monomers) at 80°C for more than 30 h. Copolymers were isolated from the reaction solution by precipitation into the excess of methanol followed by reprecipitation from toluene into methanol and then dried at 20°C overnight. The synthetic work is described in more details in [12].

The synthesized azopolymers were characterized by ^1H NMR spectroscopy. The obtained results are in agreement with the proposed structures.

The phase transitions were studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-2 instrument equipped with a IFA GmbH processor at a scan rate of 20° K/min. The calorimetry calibration was carried out according to the well-known recent recommendations [13–15] using sapphire and quartz as standards.

Copolymers glass-transition temperatures (T_g) and chain-length characteristics are represented in Table 1. All polymers are characterized by high T_g (above 100°C). The insertion of the alkyl spacer leads to a decrease of T_g as a result of the appearance of unconfined space and due to an increase in the macromolecule mobility. As for the azopolymer chain, its length is moderate, as seen from Table 1. We explain it by the ability of azogroups to play a role of "traps" for radicals, and, as a result, the role of the chain termination and chain transfer reactions increases extremely.

2.2. Films

The samples for investigation were prepared as structures which have the free surface of a polymer film: glass substrate layer – electroconductive layer SnO_2: In_2O_3 – polymer film. The sample preparation method is described in [8]. The thickness of polymer films was 2–3 μm.

2.3. Methods

In the samples, we measured the optical density (D) spectra for $\lambda = 350$–$900\,\text{nm}$ and the quantity $\delta I_E = (I_E - I_0)/I_0$, where I_0 and I_E are the intensities of monochromatic light transmitted through the sample with system of two polarizers before and after switching on the external electric field, respectively. A sample was placed between two polarizers, with the angle between the planes of polarization being equal to 90°. Values of δI_E were measured after the prolonged (60 min) irradiation of the sample through a polarizer with UV-Vis light (440 nm, normal incidence). The electric field intensity $E = 1\ 10^8\,\text{V/m}$ in the film was generated using the corona electric discharge as

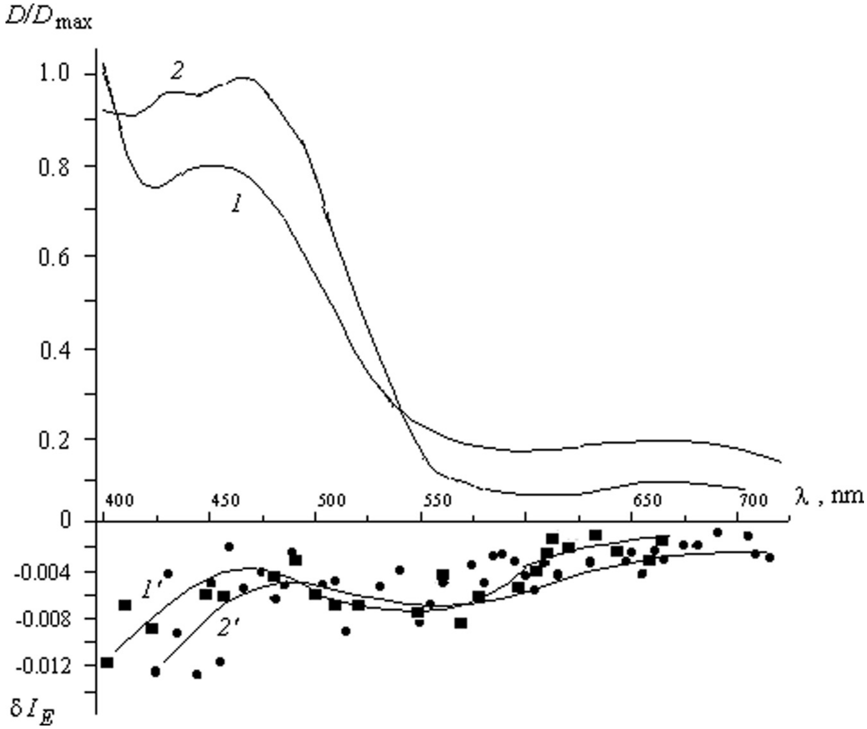


FIGURE 1 Curves of dependence $D/D_{\max}$ (*1,2*), and δI_E (1′,*2*′) on λ in samples with films AP1 (*1*, *1*′), AP3 (*2*, *2*′).

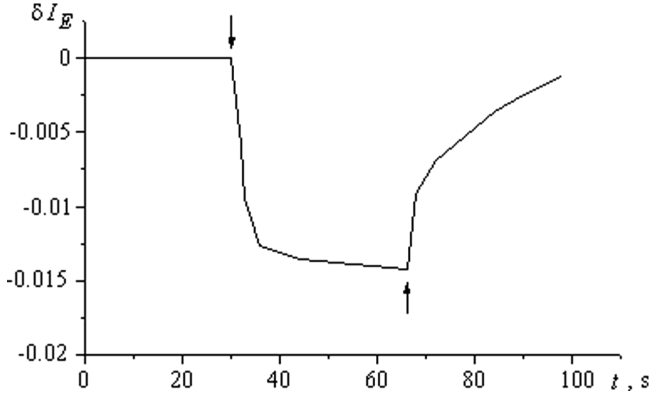


FIGURE 2 Dependence δI_E on t after the switching-on and switching-off of the external electric field E in a sample with film AP3, which previously was irradiated by a linearly polarized light with $\lambda =$ 440 nm. Curve was obtained for $\lambda =$ 650 nm. The time moments of switching off and on the electric field E are pointed by the vertical arrows.

described in [8]. The value of δI_E was determined as a function of λ. All measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

The absorption of AP1-AP3 films lies in the range $\lambda < 550$ nm (Fig. 1). It strongly depends on the optical excitation of azobenzene groups and is almost not sensitive to the presence of a "spacer" in the polymer structure. The influence of E on the light transmission becomes significant when the sample was previously irradiated with polarized light in the absorption range of azobenzene groups ($\lambda < 550$ nm). The largest change in I_0 under the switching-on of E was observed when the light passed throught a polarizer for a long time period ($t > 40$ min) (Fig. 1). After the long exposure by a linearly polarized light with $\lambda < 550$ nm, the influence of the external electric field on the light transmission intensifies in the long-wavelength range of absorption of the compound under study (in the wavelength range $\lambda = 400$–750 nm). The kinetics of the light intensity change from I_0 to I_E before and after the switching-off of the electric field (Fig. 2) can be described by the simple relations $I(t) = I_0 + (I_E - I_0)(1–\exp(-t/\tau_E))$ and $I(t) = I_0 + (I_E - I_0)(\exp(-t/\tau_E))$, where τ_E is the time constant. In series AP1-AP3, the value of $|\delta I_E|$ increases.

4. CONCLUSIONS

In the same way as in [8], we consider that, under the action of a linear polarized light from the range of azochromophore *trans*-isomer absorption in AP1-AP3, the *trans-cis*-isomerization of azofragmensts occurs, and the concentration ratio of fragments with different dipole moments changes. In the external electric field, the photoinduced dipole moments change their orientation relatively to the polarization direction, which leads to a change of the transmission of the polymer films. The "spacer" influence in azopolymer series at the transition from AP1 to AP3 is revealed in increasing the mobility of azofragments, and, at the same time, the electrooptic effect intensifies. The results of the present work could be used for the elaboration of new electrooptic modulators and media for the polarization holography with informational properties controlled by an external electric field.

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