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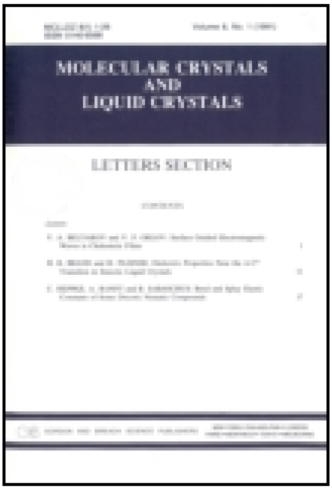

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Some Multifunctional Methacrylic Polymers with Azobenzene Fragments and Free Double Bonds in Side Chains as Liquid Crystal Alignment Agents

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Some Multifunctional Methacrylic Polymers with Azobenzene Fragments and Free Double Bonds in Side Chains as Liquid Crystal Alignment Agents

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Two series of polymers based on the polymethacrylic acid were obtained and investigation of their orientation ability was carried out: "azobenzene-containing" polymers; "azobenzene-oxyethylmethacrylate-containing" polymers. Under the action of actinic UV light photosensitive fragments of these materials are undergone the orientation and crosslinking due to trans-cis *isomerization of azofragments and photopolymerization of free C═C bonds. Liquid crystal photoalignment ability of these materials is investigated.*

Keywords Azopolymers; photoinduced anisotropy; liquid crystal; photoalignment.

1. Introduction

Nowadays the rapid development is observed for studies aimed at the creation of nanostructured materials with external-stimuli-controlled physicochemical properties [1,2]. In this respect, the multifunctional thermocontrolled, photocontrolled, and electrically controlled nanostructured polymer materials show promise for various applications: optics, optoelectronics, photonics, display technology, optical memory devices, telecommunications systems, etc.

Among the materials of this kind, the design of light-controllable high-sensitive materials is currently the most urgent problem. Diverse derivatives of azobenzene are used as photoactive fragments. At present, studies of the photoactive properties of azocontaining polymers are intensively pursued in creation of command surfaces for low-molecular liquid crystals (LC) [3] and desired LC photoalignment [4].

One of the most common classes of photoalignment materials consists of azopolymers. The design of such photoaligning systems is based on the incorporation of photoactive azochromophore into side or main polymer chain. Illumination of these materials with exciting light stimulates reversible or irreversible *trans-cis* isomerization of azochromophores. When the exciting light is polarized, initially isotropic orientation distribution of photosensitive fragments transforms into anisotropic one characterized by some degree

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*Corresponding author, Oksana Nadtoka. Tel.: +38(044)2393300. E-mail: oksananadtoka@ukr.net of orientational order [5,6]. The LC molecules, adjacent to the orientationally ordered photoaligning film, reproduce to certain extend this order due to anisotropic interaction with the molecules or anisotropic fragments from the surface of this film [7].

Nevertheless this type of photoalignment materials has its advantages and disadvantages. The azocompounds usually give excellent LC alignment at low exposure dose. However, this alignment is not sufficiently stable against heat and light because of reversible photochemistry and orientational disordering of azofragments. It is known, the photo-crosslinking materials demonstrate the best promise in this case due to irreversible photochemistry and strongly restricted molecular motions [8].

In our work we make an attempt to improve photoalignment stability of methacrylic azopolymers by including of crosslinkable unsaturated hydrocarbon groups in side chain of polymer along with azobenzene fragments. So the photoinduced orientation of azofragments was fixed with accompanying crosslinking reaction to enhance thermal stability of the induced order.

Most of photochromic azopolymers are usually synthesized via the copolymerization (meth)acrylic monomers with photochromic azomonomers. [9–15]. This method has some disadvantages: the azochromophore concentration is, as a rule, varied from 10 to 60 mol%, the low-molecular mass polymers as a result of reactionlessness of azomonomers and, at last, azomonomers usually have only one polymerizable group. So for obtaining of cross-linked matrix structure need the complementary monomer, containing functional groups - hydroxylic, for example [16].

In our work we have synthesized photosensitive side-chain azopolymers by polymer analogues reaction based on polymethacrylic acid. Polymer analogues reaction provides a convenient way to synthesize functionalized polymers with different degrees of functionalization on the same backbone structure [8, 15–19]. It is often the simplest way to prepare azo functionalized polymers. In addition, versatile functional groups were incorporated in the azobenzene moiety.

2. Experimental Section

Materials

We have synthesized multifunctional methacrylic polymers with azobenzene fragments and methacrylic groups in side chains differing by the substitutes of the azochromophore. Figure 1 shows polymer synthesis scheme and the general formula of these compounds.

Hydroxy-azobenzenes Synthesis

4-*methyl-4'-hydroxyazobenzene (Azo1)*. 6,8 g (0.05 mol) as hydrochloride was dissolved in 100 mL hydrochloric acid (2M). Solution was cooled by ice bath up to 0°C and solution of 3,3 g (0.05 mol) sodium nitrite in minimal volume of water was added slowly. To the cooled solution of phenol 4,4 g (0.05 mol) in water the diazonium salt was added under stirring. Yellow azodye precipitate was filtered, washed by cooled water and dried. Substance purification was made by recrystallization from isopropanol.

Yield 87%. $T_g = 155°C$. Rf = 0.7 (eluent – ethyl acetate, toluene = 1:1). NMR ^1H (400 MHz, DMSO-d_6), ppm: 9.92 (s, 1H, OH), 7.71 (m, 4H, Ar), 7.27 (d, 2H, Ar), 6.86 (d, 2H,Ar), 2.42 (s, 3H,CH_3).

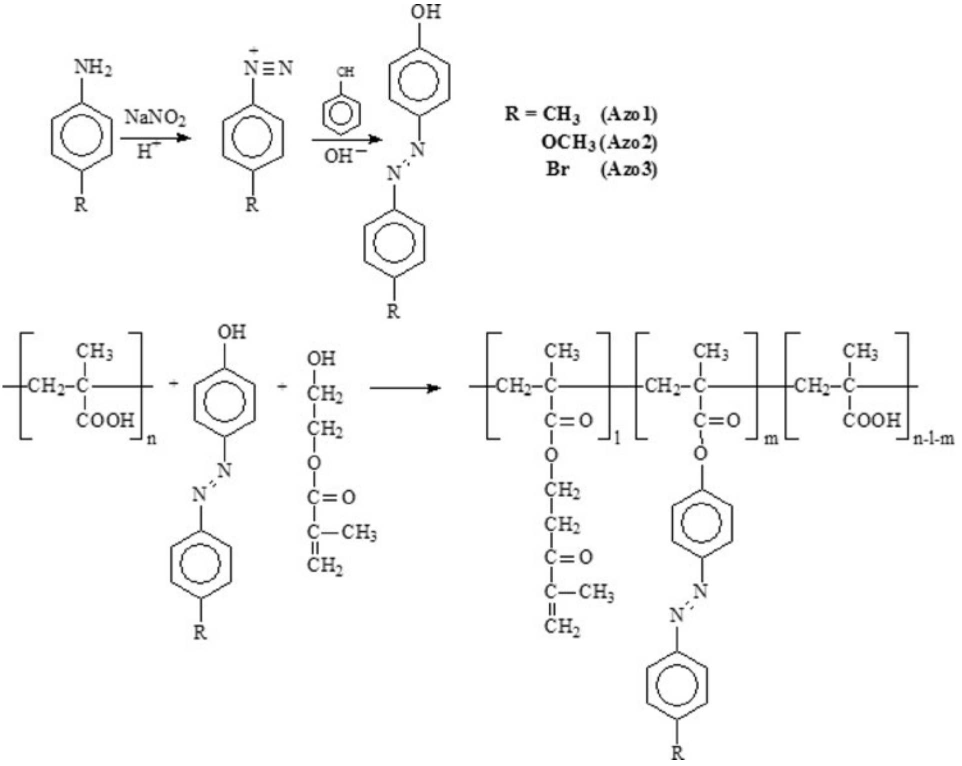

Figure 1. Chemical structure of investigated polymers.

4-methoxy-4'-hydroxyazobenzene (Azo2) and *4-bromo-4'-hydroxyazobenzene (Azo3)* were synthesized by the same method but as aniline derivatives were used 4-methoxyaniline hydrochloride and 4-bromoaniline hydrochloride correspondently.

For *Azo 2*: Yield 83%. T_g 142°C. Rf = 0.73 (eluent – ethyl acetate, toluene = 1:1). NMR ^{1}H (400 MHz, DMSO-d_6), ppm.: 9.9 (s, 1H, OH), 7.79 (d, 2H, Ar), 7.69 (d, 2H, Ar), 7.03 (d, 2H, Ar), 6,85 (d, 2H,Ar), 3.86 (s, 3H,OCH_3).

For *Azo 3*: Yield 85%. T_g 158°C. Rf = 0.72 (eluent – ethyl acetate, toluene = 1:1). NMR ^{1}H (400 MHz, DMSO-d_6), ppm: 10.09 (s, 1H, OH), 7.49 (m, 4H, Ar), 7.65 (d, 2H, Ar), 6.87 (d, 2H, Ar).

Azopolymers Synthesis

a) 0,3 g (0,0034 mol) PMA and equimolar amount of corresponding hydroxyazobene were disolved in 2 ml DMF. To obtained solution 0,72 g (0,0034 mol) dicyclohexylcarbodimide as catalyst and 0,144 g 4-dimethylaminopyridine (20 wt.% from catalyst) were added. Reaction mixture was stirred during 5 hours and left overnight at room temperature. Next it was filtered, oxalic acid trace was added for catalyst remainder removal and it was left overnight once more. Solution was iteratively filtered and the filtrate was precipitated in alcohol. Polymers were purified by reprecipitation from DMF in alcohol. So polymers based on PMA containing 4-methyl-4'-oxyazobenzene **(P1)**, 4-methoxy-4'-oxyazobenzene **(P2)** and 4-bromo-4'-oxyazobenzene **(P3)** fragments were obtained. All of them are dissolved in acetone, dioxane, toluene, dichloroethane.

b) The mixtures of PMA (0,3 g (0,0034 mol), hydroxyazobene derivative and hydroxyethylmethacrylate in the molar ratios: 1:1:1; 1:2:1; 1:1:2 and 1:2:2 were disolved in 2 ml DMF. To each of obtained solutions 0,72 g (0,0034 mol) dicyclohexylcarbodimide as catalyst and 0,144 g 4-dimethylaminopyridine (20 wt.% from catalyst) were added. These reaction mixtures were stirred during 5 hours and left overnight at room temperature. Next they were filtered, oxalic acid trace was added for catalyst remainder removal and it was left overnight once more. Solutions were iteratively filtered and the filtrate was precipitated in alcohol. Polymers were purified by reprecipitation from DMF in alcohol. So series of polymers of different functional groups concentrations based on PMA containing side-chain oxyethylmethacrylate and 4-methyl-4'-oxyazobenzene groups **(P4)**, oxyethylmethacrylate and 4-methoxy-4'-oxyazobenzene groups **(P5)** and oxyethylmethacrylate and 4-bromo-4'-oxyazobenzene groups **(P6)** were obtained. All of them are dissolved in acetone, dioxane, toluene, dichloroethane.

For photooptical investigations the polymers of approximately equal composition were chosen (Table 1).

Methods

The synthesized azocompounds and polymethacrylates were characterized by elemental analysis and ^{1}H NMR spectroscopy. *Films preparation* and samples irradiation were carried out in the following way. Selected polymers were dissolved in dichloroethane (3 wt.%) and the solution were spin-coated on quartz substrates. Polymer films were annealed at 50°C for an hour and left overnight at room temperature for solvent residue removing. Film thickness (d) was measured by profilometer. They varied from 300 to 500 nm. Absorption spectra in the films were measured in the spectral range of 250-600 nm by the spectrometer from Ocean Optics (USA).

The anisotropy in the polymer films was induced by UV light with $\lambda_{\text{exp}} = 365$ nm and $I = 4.5$ mW/cm^2. The light was linearly polarized by Glan-Thompson prism. Thus-obtained polarized monochromatic light beam was directed normally to polymer film so that the polarization of exciting light was parallel to the film axis x (Fig. 2).

Table 1. Azopolymers and their photoaligning properties

polymer	R	azo fragment % mol.	oxyethyl methacrylate fragments,% mol.	λ_{max}, nm	LC alignment quality: before heating	LC alignment quality: after heating to 80°C	Pretilt angle, θ
P1	CH_3	30		340	g	n/a	9.0°–10.0°
P2	OCH_3	31		345	g	n/a	1.0°–1.5°
P3	Br	32		360	g - s	n/a	0°–2.0°
P4	CH_3	30	11	340	g	s	1.0°–1.3°
P5	OCH_3	29	10	345	s	s	1.0°–1.1°
P6	Br	27	10	360	s	n/a	—

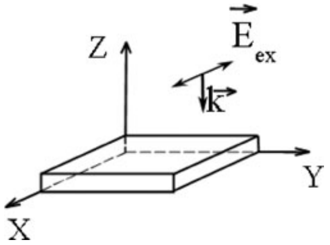

Figure 2. Sample irradiation geometry.

For testing of LC alignment we used symmetric LC cells made of two equally treated photoaligning layers with parallel easy axis. The cell thickness was defined by spacers of 20 μm in diameter. The cells were filled with nematic LC E7 purchased from Merck. LC alignment quality in the cells was observed with the naked eye and polarizing microscope. It was evaluated by the five-point scale: "excellent" (e), "good" (g) (singular orientation defects), "satisfactory" (s) (traces of defects), "bad" (b) (a lot of defects) and "no alignment" (n/a).

For unambiguous setting of pretilt angle, the substrates with covered aligning films were irradiated in two steps. At the beginning, linearly polarized light ($I_{exp} = 4.5$ mW/cm^2) was directed normally to polymer film for 15 minutes and anisotropy in film was detected as result. Thereafter these films were exposed for 1 min to a nonpolarized exciting light at the angle of 45° to with a film surface. The obtained in this manner two equally treated photoaligning layers were used for assembling of LC cells in antiparallel configuration.

The pretilt angle of a liquid crystal in the cell was measured by the commonly used crystal rotation method [20].

Alignment thermostability was investigated by keeping cells with LC at high temperature (80°C) for 30 min and subsequent cooling and testing with a polarizing microscope.

3. Results

The attempts to copolymerize methacrylic acid with methacrylic azomonomers leads to polymethacrylic acid (PMA) formation with isolated azobenzene moieties. Apparently, at high temperatures required for radical copolymerization and at presence of active functional carboxylic groups in reaction mixture the acidolysis of ester groups occurs. As result, the blends of polymethacrylic acid and separate covalent unbound azodye molecules were obtained.

The other problem of radical copolymerization method is disability of obtaining of linear polymer having free double bonds in side-chains due to crosslinkable free methacrylic groups. Therefore we tried to use polymer analogues reaction method for synthesis of structural dyed polymers based on polymethacrylic acid and hydroxyazobenzenes of different structures. For the purpose of stabilization the photoinduced orientational order of azochromophores, groups capable of photocrosslinking were incorporated in the azopolymer structure. Polymer analogues reaction of PMA with hydroxyethylmethacrylate was used in this case too.

Thus, polymers of two structure types based on polymethacrylic acid were obtained for investigation of their orientational ability: a) "azobenzene-containing" polymers (P1-P3); b) "azobenzene-oxyethylmethacrylate-containing" polymers (P4-P6).

Synthesis of azopolymers by polymer analogues reaction of methacrylic acid with azobenzene derivatives as well as 2-hydroxyethylmethacrylate was carried out in two steps (Fig. 1).

On the first stage of synthesis model, 4-hydroxyazobenzenes containing electron-donor (CH_3 and OCH_3) as well as electron-acceptor (Br) substituents were obtained. Azocompounds were synthesized accordingly to the classical scheme of diazotation of aniline derivatives (4-methylaniline, 4-methoxylaniline, 4-bromoaniline) and their further azocoupling with phenol [12]. The synthesized materials were well-solved in majority of organic solvents, possessing yellow (Azo1), orange (Azo2) and pink (Azo3) colors stable to light and air.

On the second stage, the condensation of hydroxyderivatives with polymethacrylic acid was carried out. This reaction was occurred at dicyclohexylcarbodimide as catalyst and 4-dimethylaminopyridine as cocatalyst in dry DMF at room temperature.

In case of "azobenzene-containing" polymers (P1-P3) hydroxyazocompounds/PMA blends of different concentrations were used for functional groups condensation. For obtaining of "azobenzene-hydroxyethylmethacrylate-containing" polymers (P4-P6), hydroxyazocompounds/2-hydroxyethylmethacrylate/PMA mixtures of different concentrations were prepared and polymer analogues reaction was carried out at above mentioned conditions.

Concentration of the fragments covalently bonded to PMA was determined by ^1H NMR-spectroscopy data. Concentration of azofragments was approximately 30 mol%; whereas the concentration of hydroxyethylmethacrylate was 10-20 mol%.

For LC alignment tests, the polymers with approximately the same concentration of azofragments and hydroxyethylmethacrylate fragments were chosen (Table 1).

In our study, first of all, we measured the UV/Vis absorption spectra of azopolypolymers containing azobenzene groups with electron-donor (P1, P2, P4 and P5) and electron-acceptor (P3 and P6) substituents. Some of these spectra are represented in Fig. 3. All investigated polymers strongly absorb light in the visible region. These UV/Vis spectra display high-intensity $\pi\pi^*$ bands in the UV (at about 350 nm) and low-intensity $n\pi^*$-bands in the visible region (at about 450 nm) [13]. The exact positions of the maximum of the $\pi\pi^*$ absorption bands, λmax, are presented in Table 1.

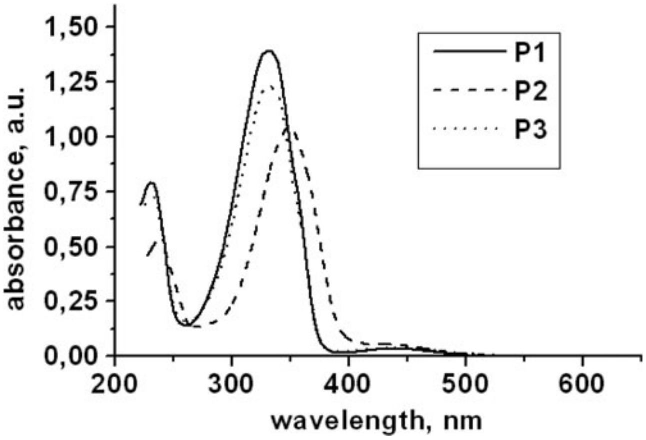

Figure 3. The absorption spectra of **P1**-**P3** polymer films.

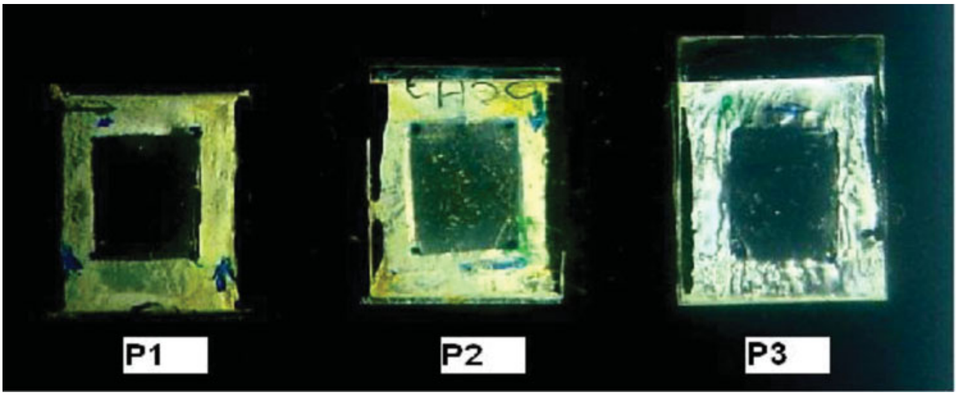

Figure 4. Photoalignment of nematic liquid crystal E7 in the cells based on azopolymers **P1-P3,** tilted alignment. Cells are in crossed polarizers.

A red shift of P3 spectrum is explained by stretching of π-electronic system of azochromophore due to the presence of electron-acceptor Br group.

It should be noted, that polymers P4-P6 have identical to P1-P3 spectra depending on substituents in azobenzene groups. Presence of additional methacrylic side-chain groups in corresponding azopolymers practically do not influence maximum of the $\pi\pi^*$ absorption bands.

The anisotropy in the polymer films was obtained under UV polarized light due to reversible or irreversible *trans-cis* isomerization of azochromophores. It was detected in crossed polarizers.

According to LC alignment tests, all obtained polymers show photoalignment effect (Fig. 4). The polymer P1, having azofragment with methyl terminal group, demonstrates the best alignment capability. Alignment characteristics of P4-P6, having three functional groups are worse that can be explained by steric effect (Table 1). The data of LC pretilt angle presented in this table were obtained before testing thermal stability of corresponding cells.

Table 1 also shows that the synthesized polymer show insufficient alignment stability of liquid crystals. Polymers P4 and P5 with good photoalignment quality demonstrate satisfactory alignment result after heating and following cooling of the LC cells. At this stage, we did not improve stability in the homologues with photocrosslinking methacrylic groups. It is probably due to the fact that such substituents as bromine in P6 plays the role of free radical traps, obstructing photopolymerization of methacrylic group.

Conclusions

Polymethacrylates with side-chain azobenzene fragments, containing substituents of an electron-donor and electron-acceptor nature, carboxyl functional groups and methacrylic side-chain groups were synthesized by polymer analogues reaction based on polymethacrylic acid. It was shown that the films of these polymers have the ability to photoorientation under polarized light. Due to this fact, they show clear photoalignment effect for nematic LCs. We obtained polymers showing good LC alignment with controllable pretilt angle. Insertion of methacrylic groups with free double bonds to the studied polymer structure leads to slight deterioration of LC alignment. In the future, we plan to modify the studied polymer structures to combine stabilization function of photocrosslinking groups with a good alignment quality achieved in the present research.

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