

Synthesis of Azobenzene-Containing Polymers Based on Polymethacrylic Acid and Their Photooptical Properties Studies

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Preparative method of synthesis of new photochromic polymers based on polymethacrylic acid by post-coupling reaction was found. Azobenzene side-chains of obtained polymers contain derivatives of different nature. Photooptical properties of polymer films, in particular the orientation under polarized light influence and the ability to orient the liquid crystal covered on them were studied.

Introduction

Amorphous polymer materials with side-chain azochromophore groups are attractive for researcher's attention due to some their properties. Firstly, azobenzene groups are able to involve the photoinduced dipole orientation in polymeric matrices, which can be used for creation reversible optical storage materials [1]. Secondly, azobenzene derivatives are dipole nonlinear optical chromophores, which are used for electro optical polymer materials synthesis indispensable for wide-band light modulator and integral optoelectronic systems based on it [1-3].

Among such materials the creation of light-controlled high-sensitivity polymeric systems is most topical question to date. Control of optical properties of polymeric materials using of light exposure has significant advantages over electrical and magnetic fields using due to their simpler and handier applications for recording-reading machines,

easier polymer processing and thin polymer films preparation.

Efficiency and stability of photoinduced processes in polymers depend on both chemical nature of chromophore and polymer and on the way of including of the chromophore in polymer. Azochromophores possess high thermal and chemical stability and these ones can be included in polymeric matrices by the polycondensation or radical (co)polymerization ways as well as by post-coupling reaction.

Radical (co)polymerization of photosensitive methacrylates is promising and widely applicable method of chromophore group incorporating in side chain of macromolecule. Radical (co)polymerization of azobenzenemethacrylates [4-8] as the most accessible chromophores is thoroughly investigated at present.

Methacrylic azomonomers were synthesized by reaction of methacrylchloride with corresponding phenol in organic solvent

medium. This method has some essential disadvantages due to the necessity of utilizing of hydrogen chloride and difficulties of chromophore purification from ionic impurities, which lead to film conductivity and dipole polarization efficiency reduction in electric field.

Next problem deals with presence of only one polymerizable groups in such monomers. So, it is necessary to add another monomer, containing hydroxyl [5, 9-10] or other functional groups for obtaining reticulate matrices.

At last, polymerization of methacrylic azomonomers doesn't lead to the high-molecular products as a result of low monomer activity, where azogroups play the role of free radical «traps» during polymerization.

To overcome these difficulties, we obtained light-sensitive polymers based on polymethacrylic acid, containing azofragments and carboxylic functional side-chain groups. By means of post-coupling reaction, in particular by the condensation of carboxylic groups with hydroxyazobenzenes, polymethacrylic acid, where part of the carboxylic functional groups was transformed into photochromic moieties, was synthesized.

Amorphous photosensitive polymers containing photochromic fragments and functional groups are materials of special interest due to their dual properties. The presence of the azofragments, which are responsible for ordered structure forming, in combination with functional charged groups

allows to enhance substantially the ability of new photosensitive materials creation. Functional groups presence allows to use them not only for carrying out chemical reaction but also for noncovalent binding with different low-molecular dopants such as chiral substances, dyes, biological active fragments and even liquid crystals molecules. Such «binding» may be realized due to ionic interaction of corresponding complementary pairs as well as due to formation of hydrogen bonds between interacted groups.

Results and discussion

The attempts to copolymerize methacrylic acid with methacrylic azomonomers leads to polymethacrylic acid (PMMA) formation with isolated azobenzene moieties. Apparently, at high temperature, required for radical copolymerization carrying out, and at presence of active functional carboxylic groups in reaction mixture the acidolysis of ester groups occurs. As results, the blend of polymethacrylic acid and separate covalent unbound azodye molecules were obtained. Therefore, we tried to synthesize structural dyed polymers by post-coupling reaction of polymethacrylic acid with corresponding hydroxyazobenzenes of different structures.

Synthesis of azopolymers by post-coupling reaction of methacrylic acid with azobenzene derivatives was carried out in two steps.

On the first stage of synthesis model 4-hydroxyazobenzenes containing electrodonor

substituents were obtained. Azo compounds were synthesized accordingly to the classical scheme of diazotation of aniline derivatives (4-methylaniline, 4-methoxyaniline, 4-bromoaniline) and their further azocoupling with phenol [6]. Purity of corresponding Azo1, Azo2 and Azo3 (fig.1.) was controlled by thin-layer chromatography and these substances were identified accordingly to NMR-spectroscopy data. Synthesized materials are well-solved in majority of organic solvents, possess yellow (Azo1), orange (Azo2) and pink (Azo3) colors as well as stability to light and air.

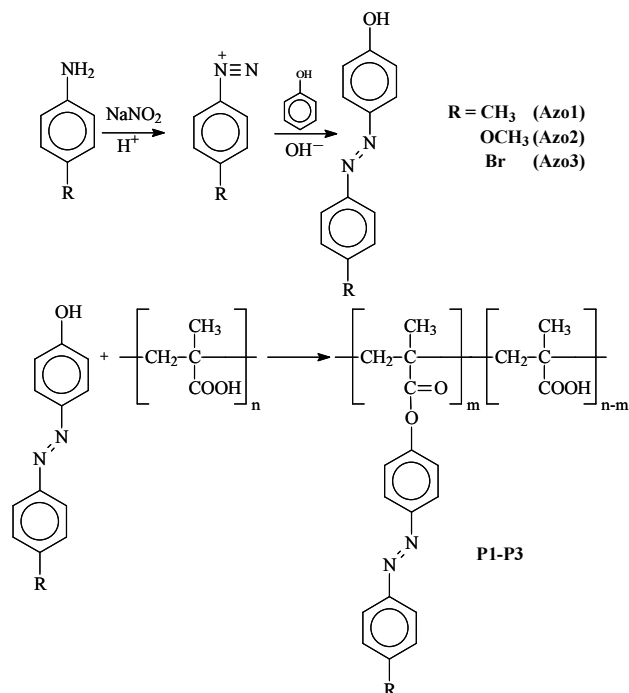


FIGURE 1. Polymer synthesis scheme.

On the second stage the condensation of hydroxyazocompounds with polymethacrylic acid was carried out. This reaction occurred at dicyclohexylcarbodiimide as catalyst and 4-dimethylaminopyridine as cocatalyst in dry DMF at room temperature. Scheme of synthesis is represented on figure 1.

Concentration of azofragments covalently bonded to PMA was determined by NMR-spectroscopy data, it was approximately 30% (Tab. 1).

Table 1. Azopolymers and their properties

polymer	R	azo fragment % mol.	λ_{\max} , nm	photo orientation quality
P1	CH ₃	30	360	good
P2	OCH ₃	31	380	good
P3	Br	32	410	good/satisfactory

Investigation of photo orientation ability of azopolymer obtained on PMA base was fulfilled as follows. Previously, polymer films were prepared and after irradiated with UV-light. Irradiated films were used for cells preparation which were filled with LC and LC orientation was observed through crossed polarizers and polarization microscope. It was investigated that all obtained polymer films can be orientated under polarized light influence and subsequently can orientate liquid crystal, covered film surface. (fig. 2).

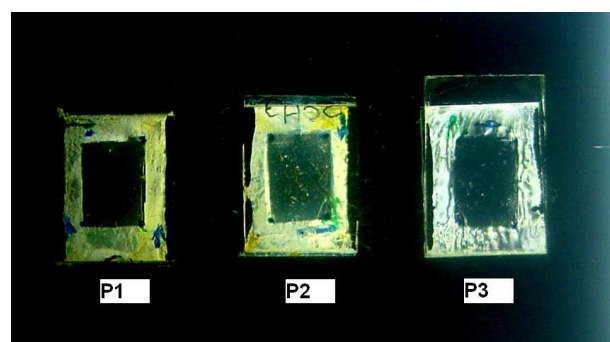


Figure 2. Cells with oriented LC on polymer films (view in crossed polarizers).

By qualitative criterion polymer P1, having azo fragment with methyl group as substitute is the best for this purpose.

Conclusions

Polymethacrylates with side-chain azobenzene fragments, containing substituents of different nature, and carboxyl functional groups were synthesized by post-coupling reaction based on polymethacrylic acid. It was shown, that their films has ability for orientation under polarized light influence. Oriented films have important property to orient liquid crystal (LC), covered them. This peculiarity can be used for creation of photosensitive layers for LC displays and other devices.

Experimental part

Materials

All starting chemicals were purchased from commercial sources and used without further purification unless otherwise noted. The structures of all the precursors and final products were confirmed by ^1H NMR spectroscopy. The ^1H NMR spectra were measured on samples dissolved in CDCl_3 . Obtained results are in a good agreement with supposed structure.

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 nitrate 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 cool water and dried. Substance purification was made by recrystallization from isopropanol.

Yield 87 %. $T_g = 155^\circ\text{C}$. $R_f = 0.7$ (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).

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%. $T_g 142^\circ\text{C}$. $R_f = 0.73$ (eluent – ethyl acetate, toluene = 1:1). NMR ^1H (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%. $T_g 158^\circ\text{C}$. $R_f = 0.72$ (eluent – ethyl acetate, toluene = 1:1). NMR ^1H (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

0,3 g (0,0034 mol) PMA and equimolar amount of corresponding hydroxyazobene were dissolved in 2 ml DMF. To obtained solution 0,72 g (0,0034 mol) dicyclohexylcarbodiimide as catalyst and 0,144 g 4-dimethylaminopyridine (20 wt. % from catalyst) were added. Reaction mixture was mixed during 5 hours and left overnight at room temperature. Next it was filtered, oxalic acid trace was added for catalyst

remainder remove and it 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.

Methods

Films preparation and samples irradiation were carried out by next manner. Polymers were dissolved in dichloroethane (3 wt. %) and the solution were spin-coated on quartz substrates. Polymer films were annealed at 90°C for an hour and left overnight at room temperature for solvent residue remove. Film thickness (d) was measured by profilometer. It varied from 300 to 1000 nm. Absorption spectra in films were measured at 250-600 nm of spectral range by spectrometer of Ocean Optics (USA).

Anisotropy in films was induced by UV-light with $\lambda_{\text{exp}} = 365$ nm and $I = 4,5$ mV/cm². A light was linearly polarized by Glan-Thompson prism. Thus, obtained polarized monochromatic light beam was directed normally to polymer film, the polarization of exciting light was parallel to the film axis x .

For testing and estimation of LC orientation the symmetric cells were made. Cell thickness was defined by spacer and was 20 μm . The cells were filled with nematic liquid crystal

E7. LC orientation quality in cells was observed with the naked eye as well as with the polarization microscope help. It was estimated by the five-point scale: 'excellent', 'good' (singular orientation defects), 'satisfactory' (traces of defects), 'bad' (a lot of defects) and «there are no orientation».

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