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Synthesis and Investigation of Polymerization Properties of Methacrylic Monomers with Chiral Fragments

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Methacrylic monomers containing chiral moieties and azobenzene derivatives were synthesized. As the chiral component a menthol was used. The polymerization properties of monomer (5-methyl-2-(1-methyl)cyclohexanol with azomonomers were studied and the reactivity ratios as well as parameters *Q* and *e* characterizing the activity of the obtained monomers have been calculated. On the basis of the monomers synthesized a chiral-photochromic copolymers were prepared and their absorption spectra were studied. It was shown that in the absorption spectra of copolymers the absorption maxima are located in the wavelength region of 340-360 nm, corresponding to trans-form of azo fragments.

Introduction

Among the scientific directions in the field of photochromic materials developing, very special place is occupied by research aimed at the creation and study of photoactive polymers and polymer blends with photochromic and chiral dopants [1-3]. Due to photoregulation of optical properties of these polymers it is possible to create the photoactive materials for black-and-white recording and optical data storage. Thus, as is known, the combination of such systems and liquid crystal polymers opens much more opportunities in this area. The chiroptical property of a chiral molecule can be remarkably magnified as a result of molecular alignment because of molecular interactions in a liquid crystal or because of the conformation of a polymer chain. In this case it is possible to create the new photoactive light- and electro-controlled media and obtain polymer films for color data recording.

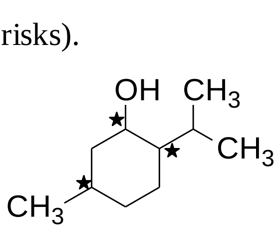
The main methods of creation of these materials are the synthesis of chiral photochromic copolymers or obtaining polymer blends containing a low molecular weight chiral and photochromic dopants.

The principle of regulation of the helical structure of the cholesteric polymer containing a combination of chiral and photochromic groups is irradiation of the polymer film. Light initiates chemical reactions in photoactive groups that leads to further structural and chemical transformations. These photoinduced chemical processes and structural transformations influence on the side-chain chiral groups conformation. This effect in turn causes a decline in twisting power of the chiral additive owing to a decrease in its anisometry. As result, a decline in twisting power leads to untwisting of the cholesteric helix, which is accompanied by a shift in the peak of the selective reflection of light tothe longwave spectral region.

The various azobenzene derivatives are the ones of the most effective photosensitive moieties. It is known that, azochromophores undergone reversible and irreversible chemical transformations under the actinic light. In addition, they possess a rigid structure and high anisotropy [4].

We synthesized a series of the methacrylic polymers containing chiral derivatives as optically active groups and azobenzene derivatives as photochromic fragments of a wide moieties concentration range.

For the synthesis of methacryl derivatives with chiral substituent was used menthol (5-methyl-2-(1-methyl)cyclohexanol) with three chiral centers (chiral groups are marked with asterisks).



Synthesized methacrylic azopolymers with chiral substituents in the side chain are perspective materials for the study of the influence of steric effects of the chiral groups on the induction of cholesteric liquid crystals. Photo isomerizable conformationally rigid chromophoric groups in the side chain of the polymer molecule are structured and changed it when irradiated with light of a certain frequency. The photosensitive films based on these polymers can be used as a material for nonlinear optics and photo alignment layers in the production of liquid crystal displays.

Results and discussion

Figure 1 shows the main stages of the synthesis of methacrylic monomers with azobenzene fragments (M1-M2) as well as chiral substituent (M3). In particular, the synthesis of monomers with azobenzene fragments involves the obtaining a precursory azobenzene derivatives (Azo).

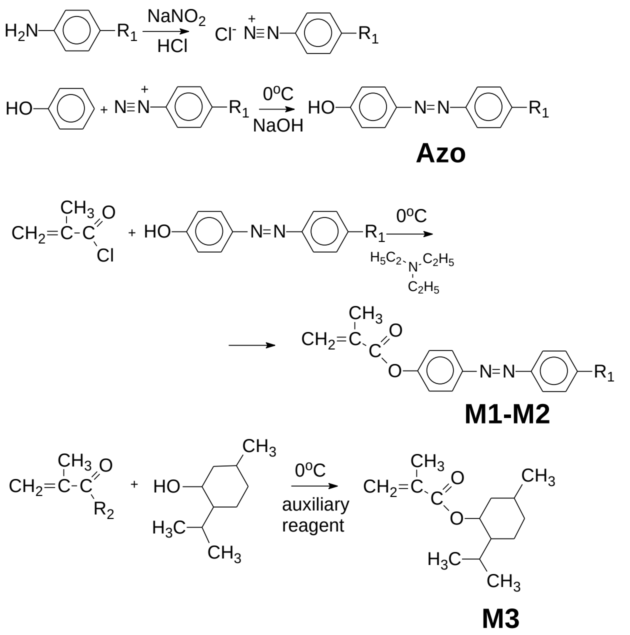


Figure 1. Scheme of the synthesis of methacrylic monomers.

It is known [5-6] various options of synthesis of methacrylic acid esters. In our case, synthesis techniques were reproduced by using menthol as the alcohol. Synthesis of menthol derivatives is complicated by the fact that the hydroxyl group which takes part in the esterification reaction is related to the volumetric cyclic moiety. Results of the testing of the synthesis procedure are shown in Table 1.

Table 1. The synthesis techniques of 5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane at synthesis time of 18 hours

R_2	Auxiliary reagent, 1 g-eq.	Solvent	Condi-tions	Yield, %
-OH	Benzene-sulfonic acid	Benzene	by boiling	27
-OH	Benzene-sulfonic acid	Benzene-dioxane	by boiling	42
-Cl	Pyridine	Pyridine	0-20 C^o	45
-Cl	Triethyl-amine	methyl tert-butyl ether	0 C^o	90

The experimental data analysis has allowed us to find the optimal conditions for the synthesis of methacrylic monomer with a chiral fragment based on menthol. The best monomer yield was obtained by the reaction of the menthol acylation with methacrylic acid chloride in the presence of triethylamine as an additional reagent. Triethylamine reacts with escaped hydrogen chloride and as result the reaction shifts toward the formation of menthol containing methacrylate (Fig. 1).

The characteristic spectrum of 5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane (M3) confirms the presence of double bonds in the chemical structure of compounds (Fig. 2) that makes it suitable for subsequent polymerization:

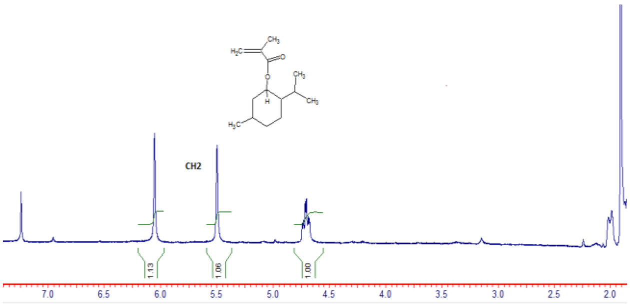


Figure 2. ^{1}H-NMR spectrum of 5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane (M3).

The polymerization of methacrylic monomers was carried out by a radical mechanism using the azo-bis-isobutyronitrile as initiator [7].

The ratio of monomers links in copolymers was determined by the ratio of characteristic peaks of different substituents in the ^{1}H-NMR at a conversion of the comonomers not more than 10% by the weight.

First of all it should be noted from the spectral data that methacrylate with chiral menthol moiety M3 is able to homopolymerization. The characteristic spectrum of poly-5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane has not any peaks corresponding to the double bonds of monomer M3 but has characteristic peak of cyclohexane fragment. The homopolymer yield after polymerization of 1.5 hours was 24%.

Figure 3 shows as an example the spectrum of the copolymer of M1 (4'-methacryloiloxy-4-nitroazobenzene) and M3.

The characteristic peak of M3 chain relating to cyclohexane fragment is determined at 4.7 ppm, and azobenzene fragments of M1 is characterized by peaks at 7.3, 7.8, and 8.3 ppm, corresponding to the absorption of aromatic rings.

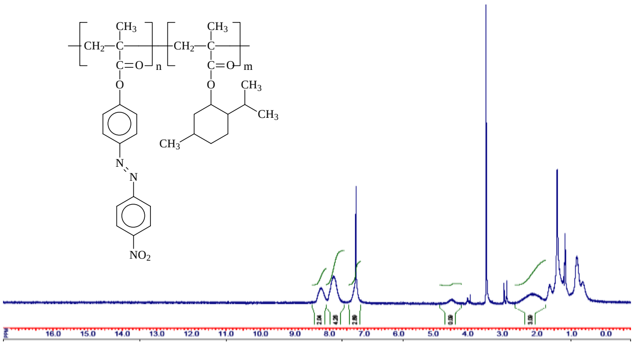


Figure 3. ^{1}H-NMR spectrum of M1-co-M3.

The ratio of these peaks corresponds to the ratio of the monomers, which were included in the copolymers. These and other data are given in Table 2.

Table 2. Copolymerization data of M3.

monomer mixture	initial monomers ratio, mole		content of M3 in copolymer, %	Yield*, %
M3:M1	1,5	1	67	6.2
M3:M1	1	1,5	50	6.3
M3:M1	1	3	32	7.6
M3:M2	1,5	1	70	5.5
M3:M2	1	1,5	57	6.2
M3:M2	1	3	40	5.7

* The reaction time is 1.5 hours.

As shown in Table 2, in the polymer chain higher concentrations of chiral fragments were achieved by copolymerization of M3 with azo monomer containing strong acceptor nitro group. Acceptor substituent in the benzene ring is involved in π-E-system of the azo groups and enhances there ability to act as a "trap" for free radicals during polymerization. Also, the influence of steric effects of bulk azo fragments with substituents is enhanced.

The reactivity of monomers was assessed by the means of copolymerization data. The Fineman Ross [8] graphical method was used to determine the reactivity ratios r_1, r_2 for M3/M1 copolymerization system.

Reactivity ratios $r_1 = 0{,}560$ (M3) and $r_2 = 0{,}620$ (M1) indicate that this interaction results in the formation of a copolymer with predominantly alternating units, $r_1 \cdot r_2 < 1$.

Q-e scheme takes into account the intrinsic thermodynamic stability and polar effects in the transition state. M3 monomer is considered to have an intrinsic reactivity of Q_1. The polar effects in the transition state, the supposed permanent electric charge carried by that entity, is quantified by the factor *e*, which is a constant for a given monomer, and has the same value for the radical derived from that specific monomer.

The reactivity ratios were calculated based on Alfrey-Price equations:

$$r_1=(Q_1/Q_2)\exp[-e_1(e_1-e_2)] \qquad (1a)$$

$$r_2=(Q_2/Q_1)\exp[-e_2(e_2-e_1)] \qquad (1b)$$

Using the values of the reactivity ratios and taking for the M1 $e_2 = 1.65$; $Q_2 = 1{,}72$ [9], e_1 and Q_1 were calculated for monomer M3.

Among the investigated earlier methacrylate [10, 11] the monomers that do not contain a broad system of conjugated bonds with delocalized electrons, as well as polar groups, is characterized by low polarity factor *e*. The weak interaction of investigated monomer containing chiral substituents with a polar solvent causes a low positive parameter $e_1 = 0.4$.

Values of the intrinsic reactivity (Q) of methacryloyl double bonds depend on the spatial volume of the fragments. It was found that $Q_1 = 0{,}84$ for the monomer M3 for a given monomers pair, i.e, 5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane is more active in comparison with azobenzene containing methacrylate and thus it can be expected predominating chiral groups in chiral-photochromic copolymer.

One of the important features of the polymer materials used in photochemical studies are the spectral characteristics of the substances, allowing to estimate the spectral region of the light effects on the investigated material. Obtained UV-Vis absorption spectra of polymer films are on the Figure 4.

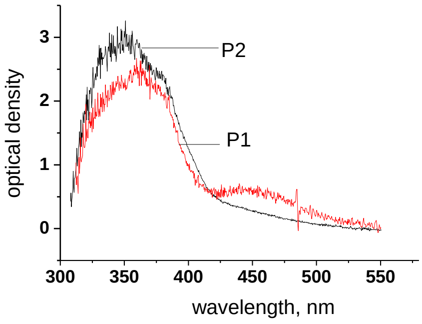


Figure 4. Absorption spectra of copolymers: P1 (M1-co-M3), P2 (M2-co-M3).

The two samples of polymers containing both chiral and azobenzene moieties absorb in the range of 340 to 400 nm. The wavelength of the absorption maxima of chiral-photochromic copolymer depends on the strength of the donor-acceptor interaction as a result of delocalization of electrons in azo chromophore. When strong donor nitro group presents in the azobenzene fragment (P1), the maximum absorption of the trans-form is shifted to longer wavelengths, while clearly expressed by the presence of a low-intensity absorption bands responsible for the absorption of the cis-form azo fragment in the field of 460 nm.

Conclusions

The methacrylic monomer containing the chiral fragment based on menthol was synthesized and its polymerization properties were investigated. Investigation of the polymers structure showed that the methacrylate containing menthol is capable of homopolymerization and copolymerization with methacrylates containing azobenzene derivatives.

Based on the copolymerization data the reactivity ratios as well as parameters *Q* and *e* characterizing the activity of the obtained methacrylic monomer have been calculated. According to the study, menthol containing methacrylate is much more active monomer compared with azobenzene containing methacrylates, therefore the synthesized functionalized copolymers contain comparatively higher concentration of side chiral fragments.

In the absorption spectra of the copolymers there are two absorption maxima. The maximum in the wavelength region of 340-360 nm corresponds to the trans-form of azo fragments and the maximum at ≈460 nm corresponds to their cis-form.

The obtained polymethacrylates containing in the side chains as photochromic azobenzene moieties and chiral menthyl fragments could be considered as photo aligning materials in modern devices for recording and data storage.

Experimental part

The azo compounds were synthesized by diazotization of aniline derivatives followed by coupling with the phenol.

4-nitroaniline / aniline (6.8/5 g, 50 mmol) was dissolved in 50 ml of hydrochloric acid (1 M). Concentrated aqueous solution of sodium nitrite (3.1 g, 44.9 mmol) was added dropwise to the amine solution with constant stirring. The temperature of the reaction mixture should not exceed 5°C. The resulting diazonium salt was added to the alkaline solution of phenol (4.7 g, 40 mmol) at 0-5°C. As a result of azo coupling the solution becomes intense red/orange color owing to the resulting dye. After the reaction, dilute acetic acid was added to neutralize the reaction mixture and a precipitates of the corresponding azobenzene derivatives were obtained. The precipitate was filtered, washed with distilled water and dried. The azo compound was purified by recrystallization from ethanol. Azocompounds 4'-hydroxy-4-nitroazobenzene and 4-hydroxyazobenzene were obtained. The chemical structure of azodyes was proved by NMR spectroscopy.

The monomers were synthesized by acylation of hydroxy derivatives with methacryloyl chloride.

4'-methacryloyloxy-4-nitroazobenzene (M1) and 4-methacryloyloxyazobenzene (M2). In the conical flask azo compound (20 mmol) and triethylamine (2.8 mL, 20 mmol) were dissolved in THF (50 mL). 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. Characteristics of the resulting azo monomers are following:

M1: Tm. = 96-99 ^{0}C, R_f = 0.81 (eluent - methanol: chloroform: hexane = 0,15:1:1). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.10 (d, 2H, Ar), 7.89 (d, 2H, Ar), 7.56 (m, 3H, Ar), 7.36 (d, 2H, Ar), 6.36 (s, 1H, =CH_2), 5.90 (s, 1H, =CH_2), 2.08 (s, 3H, CH_3).

M2: Tm . = 145 ^{0}C, R_f = 0.72 (eluent - methanol: chloroform: hexane = 0,15:1:1). ^{1}H-NMR ($CDCl_3$), δ (ppm): 8.43 (d, 2H, Ar), 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, $-CH_3$).

5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane (M3). In a three-necked flask, menthol (20 mmol) was dissolved in 50 mL of freshly distilled methyl tert-butyl ether. Freshly distilled triethylamine (2.8 mL, 20 mmol) was added to the solution via a syringe through the latex septum. Methacryloyl chloride (2.09 mL, 20 mmol) was dissolved in 10 ml of methyl tert-butyl ether and added to the reaction mixture dropwise with stirring for 2 hours at 0°C. Then the solution was poured into distilled water (1 L) and the emulsion of methacrylic acid ester was obtained, pooled and separated by separatory funnel. The substance was dried and purified by reprecipitation from ethanol.

M3: Tm.= 0-5^{0}C, ^{1}H-NMR ($CDCl_3$), δ (ppm): 6.34 (s, 1H, $=CH_2$), 5.5 (s, 1H, $=CH_2$), 4.6 (m, 3H, -CH-), 1.95 (s, 9H, $-CH_3$), 1.9 (s, 6H, $-CH_2-$).

Copolymerization of 5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane (M3) and azomonomers M1, M2 was carried out in DMF with different comonomers ratios at 70°C (Table 2.). The total comonomer concentration was 1 mol×l^{-1} and the concentration of azo-bis-isobutyronitrile as initiator was 0,95×10^{-2} mol×l^{-1}. The reaction time for experiments to determine the composition of the copolymers was 1.5 hours. After reaction, the copolymers precipitated into methanol, the precipitate was filtered out and dried to constant weight in a vacuum oven.

Homopolymerization of 5-methyl-2-(1-methyl)-1-methacryloyloxy-cyclohexane was carried out in the same way.

Polymer yields were determined gravimetrically.

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^{0}C for an hour and left overnight at room temperature for solvent residue removing. Film thickness (d) was measured by profilometer. It 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).

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