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РЕАКЦИЯ МАННИХА В РЯДУ 3-(ГИДРОКСИФЕНИЛ)ИЗОКУМАРИНОВ

Разработан метод получения аминометильных производных 3-арилизокумаринов и 3-арил-3,4-дигидроизокумаринов действием аминалей формальдегида на 3-фенилизокумарины и 3-фенил-3,4-дигидроизокумарины, содержащие гидроксильные группы в фенильном заместителе.

Ключевые слова: изокумарины (1Н-изохромен-1-оны), аминаль, основания Манниха.

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MANNICH REACTION OF 3-(HYDROXYPHENYL)ISOCOUMARINS

This report is devoted to study the Mannich reaction applying to arylisocoumarines in which the aromatic substituent at the third position is active in electrophilic substitution reactions due to the presence of the hydroxyl group. 3-(4-Hydroxyphenyl)-, 3-(2-hydroxy-5-methylphenyl)-, 3-(2,5-dihydroxyphenyl)-, and 3-(2-methoxy-4-hydroxyphenyl)isocoumarin were selected as the objects of investigation. The starting materials can be easily obtained by acylation of the corresponding phenol with homophthalic acid in the presence of a Lewis acid.

It proved impossible to execute the reaction of 3-(hydroxyphenyl)isocoumarins aminomethylation in classical Mannich reaction conditions; so to produce the target aminomethyl derivatives we have used formaldehyde aminals – bis(dimethylamino)methane and bis(diethylamino)methane. A series of dialkylaminometyl derivatives of isocoumarine were obtained, in all cases the substitution took place in the third position of the phenyl substituent. The reaction occurs by refluxing equimolar amounts of the products in a polar inert solvent, in a short time and with high enough yield; the obtained products can be isolated in the form of bases as well as in the form of hydrochlorides.

Double aminomethylation of 3-(4-hydroxyphenyl)isocoumarin– at positions 3', 5' – can probably be explained by both the smaller size of aminomethyl agent and the steric accessibility of the phenyl ring respective positions to attack, since only monoaminomethyl derivative formation were recorded in other cases. When there are two possible positions to aminomethylation 3-(2,5-dihydroxyphenyl)isocoumarin, product structure unambiguously established by the of ^{1}H NMR spectra data.

Under the same conditions and with the same efficiency aminomethylation to a third position of the phenyl substituent of 3-(2-hydroxy-5-methylphenyl)-3,4-dihydroisocoumarin was carried out.

Key words: isocoumarins (1H-isochromen-1-ones), aminal, Mannich bases

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SYNTHESIS OF BENZYLIDENE AND AZOCONTAINING POLYMERS FOR PHOTOPHISICAL APPLICATION

In the present work, the polymers built with the use of the free radical polymerization of methacrylic monomers incorporating an azobenzene side-group and monomers with benzylidene fragments have been synthesized. The polymerization was carried out in DMF with AIBN as initiator. The results of photochemical and optical activities of the corresponding polymers are presented.

Key words: aryl(meth)acrylates; oxazolone; thiohydantoine; azopolymers

Introduction. The development of modern technologies enables us to create polymer materials with a number of properties, which would be impossible to realize in a single polymer. Designing the structure of modified polymer chain with various photoactivatable groups is one of the issues of current importance in present day polymer chemistry. In this work, our investigation concentrates on synthesis of new oxazolone, thiazolidenone, thiohydantoin, hydantoine and azo- derivatives (Fig. 1), radical thermoinitiated copolymerization of new methacrylic monomers with methylmetacrylate (MMA) and investigation of the resulting polymers. The spectral characteristics of similar compounds were investigated previously [1]. Also it should be noted, that in the last few years there has been a growing research interest in developing materials which exhibit nonlinear optical (NLO) properties for applications such as optical signal processing and information storage [2-8]. Therefore the polymers containing azobenzene chromophore molecules have been extensively studied by many research groups due to their promising features for all-optical devices [9-16].

Besides organic materials might provide the systems developed with unique possibilities and higher flexibilities in comparison with inorganic materials because of the relatively easy way to process organic polymeric materials into practical devices. The main objective of this work is to realize and characterize from optical and physical-chemical point of view new polymers with benzyliden and azobenzene fragments in the side chain in order to find the correlation between the chemical structure of the polymers and its properties (switching etc.).

The aims of our work were synthesized polymers with photochemical properties typical for single molecules. Polar substituents in azobenzene compounds and nature of heterocyclic fragments in benzyliden containing derivatives lead to the change of electronic density during the photoisomerisation. This fact opens the possibility of creation polymer materials with predicted properties.

Results and discussion. The chemical structure of synthesized benzylidene and azocontaining monomers and copolymers are represented below.

The polymers were synthesized by radical polymerization using AIBN as radical initiator. Polar substituents in azobenzene compounds as -CN and $-NO_2$ can act as retarding agents of free radical polymerization reaction. Therefore, long reaction time is needed to syntheses polymers with high yield. In consideration of this singularity, only for new monomers with benzylidene fragment were investigated the kinetic characteristics of polymerization process. The kinetics of the polymerization for **M1**, **M2**, **M3**, **M4** were investigated during radical copolymerization with MMA using the dilatometric method.

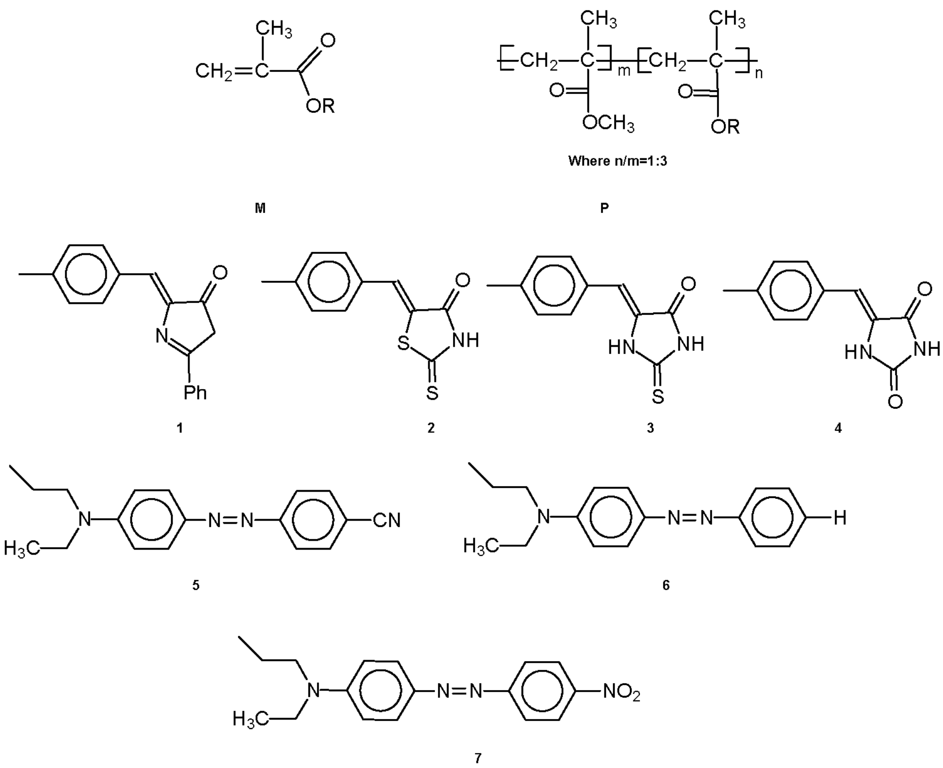

Fig. 1. The chemical structure of synthesized benzylidene and azo- containing monomers and copolymers

It should be note that azobenzenes can function as molecular switches by applying light of different wavelengths to obtain varying amounts of cis and trans isomers, where the excess of one of the two isomers may be detected by a change in UV absorption spectra.

In the previous work have been detailed describe the common photochemical properties of all azobenzene compounds. The possibility of these compounds for photoisomerization through rotation about N-N bond was retained in the synthesized polymers. As example, changes in the absorption spectra of **P5** due to optically induced transition to the *cis*- isomer and the reverse transition the *cis*- to the *trans*- state was described [17]. The results the investigation of photochemical and photophysical properties of benzylidene and azo compounds were described previously [1, 17]. It is well know that the stable state of the molecule with benzylidene fragment is the *cis*-isomeric configuration [18]. The absorption in the visible range of a photon induces the transition to the *trans*-isomer. This state is metastable with the reverse transition to the cis state taking place through photo activation. Therefore, a molecule absorbing of a photon undergoes a complete *cis–trans–cis* isomerization cycle [19]. We can suppose that these properties remaining in benzylidene containing polymers. Whereas previously for some of synthesized polymers were demonstrated NLO activity.

It should be noted that photoisomerisation by *trans-cis-trans* and *cis-trans-cis* mechanisms is typical for obtained polymers.

Experimental. Oxazolone containing monomer **M1** was prepared as describe previously [20].

2-phenyl-4-[(4-methacryloyloxyphenyl) methylene]-5(4H)-oxazolone (**M1**): yield 55%. ^{1}H NMR (400 MHz, DMSO-d_6), d (ppm): 5.89 (s, 1H, CH_2), 6.34 (s, 1H, CH_2), 2.06 (s, 3H, CH_3), 7.28-8.18 (m, 4H, Ar), 7.70-8.35 (m, 5H, Ar).

4-(methacryloyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (**M2**): (2g) 4-(methacryloyloxy)benzaldehyde, 2-thioxo-4-thiazolidinone (2.5 g), anhydrous sodium acetate (0.3 g; 0.2 mol) in 50 ml isopraponol was heated on a steam bath 80–90°C. After 2 h, the mixture was cooled and then was poured on ice. The resultant solid product that formed were filtered off, washed with water and dried. Recrystallization from ethanol alcohol gave yellow crystals, yield 65%. ^{1}H NMR (400 MHz, DMSO-d_6), d (ppm): 5.86 (s, 1H, CH_2), 6.31 (s, 1H, CH_2), 2.03 (s, 3H, CH_3), 7.28-7.66 (m, 4H, Ar), 7.62 (s, 1H, CH), 13.69 (s, 1H, NH).

Thiohydantoin containing monomers **M3** was synthesized analogously to thiazolidinone containing monomer **M2** as describe previously.

(4-methacryloyloxyphenyl)methylene-2,4-imidazolidine-dithione (**M3**): yield 64%. ^{1}H NMR (400 MHz, DMSO-d_6), d (ppm): 6.44 (s, 1H, CH), 2.04 (s, 3H, CH_3), 5.85 (s, 1H, CH_2), 6.3 (s, 1H, CH_2), 12.22 (s, 1H, NH), 12.04 (s, 1H, NH), 7.14-7.71 (m, 4H, Ar).

Hydantoin containing monomer **M4** synthesized analogously to thiazolidinone containing monomer **M2** as describe previously.

(4-methacryloyloxyphenyl)methylene-2,4-imidazolidine-dione (**M4**): yield 55%. ^{1}H NMR (400 MHz, DMSO-d_6), d (ppm): 7.56 (s, 1H, CH), 2.04 (s, 3H, CH_3), 5.8 (s, 1H, CH_2), 6.3 (s, 1H, CH_2), 8.98 (s, 1H, NH), 9.31 (s, 1H, NH), 7.2-7.6 (m, 4H, Ar).

4'-[(2-ethacryloyloxyethyl)ethylamino]-4-cyanoazobenzene (**M5**). A solution of 4′-[(2-hydroxyethyl)ethylamino]-4-cyanoazobenzene (3 g, 0.01 mol) and triethylamine (1.11 g, 0.011 mol) was dissolved in THF (35 ml). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (1.15 g, 0.011 mol) in THF (10 ml) was added slowly to the reaction mixture. After the addition of methacryloyl chloride, solution was stirred for 12 h at ambient temperature. The solvent was removed by rotary evaporation and the residue was washed with a solution of sodium carbonate (0.8 g) in water (40 ml). After removing the solvent, the resulting material was purified by column chromatography (silica gel, ethyl acetate/hexane 1/8). Red solid residue, yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$), d (ppm): 7.89, 7.87 (d, 4H, Ar), 7.75, 7.73 (d, 2H, Ar), 6.82, 6.8 (d, 2H, Ar), 6.1 (s, 1H,CH_2), 5.6 (s, 1H, CH_2), 4.36 (m, 2H, OCH_2), 3.7 (m, 2H, NCH_2), 3.55 (m, 2H, NCH_2), 1.94 (s, 3H, CH_3), 1.25 (m, 3H, NCH_2CH_3).

4'-[(2-Methacryloyloxyethyl)ethylamino]-azobenzene (**M6**). Azomonomer **M6** was synthesized using the above procedure for azomonomer **M5**. The product was purified by column chromatography (silica gel, ethyl acetate/hexane 1/8). Orange solid residue, yeld 75 %. ^{1}H NMR (400 MHz, $CDCl_3$), d (ppm): 7.83, 7.85 (d, 4H, Ar), 7.48 (t, 2H, Ar), 7.38 (t, 1H, Ar), 6.8 (d, 2H, Ar), 6.11 (s, 1H, CH_2), 5.6 (s, 1H, CH_2), 4.36 (m, 2H, OCH_2), 3.71 (m, 2H, NCH_2), 3.51 (m, 2H, NCH_2), 1.95 (s, 3H, CH_3), 1.24 (m, 3H, CH_3).

4'-[(2-methacryloyloxyethyl)ethylamino]-4-nitroazobenzene (**M7**). Azomonomer **M7** was synthesized in the same way as azomonomer **M5**. The solid was recrystallized from methanol. Dark red crystals yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$), d (ppm): 8.33, 8.31 (d, 2H, Ar), 7.92 (t, 4H, Ar), 6.83, 6.81 (d, 2H, Ar), 6.1 (s, 1H, CH_2), 5.6 (s, 1H, CH_2), 4.37 (m, 2H, OCH_2), 3.74 (m, 2H, NCH_2), 3.56 (m, 2H, NCH_2), 1.94 (s, 3H, CH_3), 1.24 (m, 3H, CH_3).

Polymers with azo fragments were synthesized by free-radical polymerization in toluene. The polymerization was carried out in 10 wt% toluene solution monomers and MMA with initial mole ratios 1:3. The polymerization was conducted using AIBN as a free radical initiator (1 wt% of monomer) at 80ºC 35 h in argon atmosphere. Previously initial mixture was degassed with repeated freeze-pump-taw cycles. The polymerization was stopped by pouring the reaction mixture into methanol. This procedure was repeated several times to ensure removal of unreacted methacrylic monomers and finally the polymers **P5, P6, P7** dried under vacuum at 50ºC overnight. The copolymerization ratios in the corresponding polymers were calculated on the basis of the integrated peak areas of ^{1}H NMR spectra in DMSO-d_6. The polymerization ability of the new benzylidene containing monomers was investigated kinetically for radical copolymerization using the dilatometric method. The process was conducted in 10% DMF solution at 80^{o}C (argon atmosphere, initiator - AIBN 1%); contractions were measured by KM-6 cathetometer. The resulting viscous solution was added dropwise into ethanol to precipitate polymeric materials. Polymers were purified from ethanol. The conversion rates were controlled gravimetrically. The conversion rate during the copolymerization processes of **M1** with MMA was 67% in 390 minutes, **M2** with MMA was 45% in 260 minutes, **M3** with MMA was 40% in 260 minutes, **M4** with MMA was 32% in 260 minutes. The structures of all copolymers calculated from ^{1}HNMR data are approximately the same in the all case as the structure of the initial mixture 1:3.

Conclusions. During the work new objects for NLO investigation were synthesized. The polymers with MMA with benzylidene and azo fragments were obtained. The polymerization ability of the new monomers was investigated kinetically for radical copolymerization using the dilatometric method. We suggest that the optical activity is determined by a steric delocalization of the active side chain of azoester and benzylidene and also based on different photoisomerization processes in investigated compounds. The azo polymers have been characterized as compound with repeatable *trans-cis-trans* isomerisation process, for the benzylidene containing polymers we can observe *cis–trans–cis* isomerization cycle. These polymers can prove to be important candidate for optical signal processing and information storage.

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СИНТЕЗ БЕНЗИЛІДЕН ТА АЗОВМІСНИХ ПОЛІМЕРІВ ДЛЯ ФОТОФІЗИЧНОГО ЗАСТОСУВАННЯ

В представленій роботі за механізмом вільно радикальної полімеризації отримано метакрильні полімери з синтезованих бензиліден та азовмісних мономерів. Полімеризацію проведено в ДМФ, як ініціатор полімеризації використано динітрил азо-біс-ізомасляної кислоти. Розглянуто фотохімічну активність відповідних полімерів.

Ключові слова: арилметакрилати; оксазолони; тіогідантоїни; азополімери.

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СИНТЕЗ БЕНЗИЛИДЕН И АЗОСОДЕРЖАЩИХ ПОЛИМЕРОВ ДЛЯ ФОТОФИЗИЧЕСКОГО ПРИМЕНЕНИЯ

В представленной работе термоинициированной радикальной полимеризацией получены метакрильные бензилиден и азо содержащие полимеры. Полимеризацию проводили в растворах ДМФА, как инициатор полимеризации исользовали динитрил азо-бис-изомасляной кислоты. Рассмотрена фотохимическая активность соответствующих полимеров.

Ключевые слова: арилметакрилаты; оксазолоны; тиогидантоины; азополимеры.