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THE INFLUENCE OF CHEMICAL STRUCTURE OF CHROMOPHORE ON POLYMERIZATION OF METHACRYLIC AZOMONOMERS

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Abstract. Methacrylic azomonomers based on para-aminoacetanilide suitable for preparation of liquid crystal (LC) photoaligning functionalized polymers were synthesized. Azofragments include various aromatic rings: benzene, naphthalene, 8-oxyquinoline, and thiazole derivatives. The kinetics of polymerization of synthesized azomonomers was studied. Efficient polymerization constants K_Σ of thermo-induced radical polymerization are presented. The relative activities r_1 and r_2 were calculated by the Fineman-Ross method. It was shown that the nature of the aromatic ring in azochromofore influences polymerization rate by two ways: steric effect and chemical structure. Thus, structurally coloured (co)polymers based on synthesized monomers were obtained and the absorption spectra of polymer films were recorded. We have used different electron donor and electron-acceptor groups (push–pull effect creation) in rings to enhance absorption and charge transfer properties. The structure–property relationship has been studied, which allowed us to conclude that push-pull effect influences absorption maximum shift of synthesized polymers.

Keywords: azomonomer, polymerization, monomers reactivity, UV-spectra.

1. Introduction

Among scientific trends concerning the photochromic materials, investigations aimed at creation and study of photoactive polymers and their blends with low-molecular photochromic dopant prevail [1-3]. The concept of such system generation is based on incorporation of photoactive fragments (chromophores) in macromolecular structures. Light initiates chemical reactions in photoactive groups that serve as molecular switches and launch further structural and chemical transformations. These photoinduced chemical processes and structural transformations may be used for manipulation of optical properties of polymers.

Different derivatives of azobenzene show the best advantage as photoactive fragments [4]. It is known that azochromophores are subject to reversible and irreversible chemical transformation from the action of light [5]. That is why these polymers are promising materials as new photoactive media for reversible (or irreversible) black-and-white and color data recording and storage for various optical memory-based systems, display technology, opto-electronics, holography, and telecommunication systems.

In our paper we present synthesis and investigation of polymerizable properties of methacrylic azomonomers based on p-amino acetanilide. In this case azofragments, which contain different aromatic rings, including heterocyclic ones, in their structure, were attached to methacrylate chain. It was interesting to study photooptical properties of azopolymers with various chromophores depending on different chemical structures too. Acetanilide was chosen as starting material due to the presence of *Fries photo-rearrangeable* acetamide group as additional photoactive center [6], which also can be the source of orientation of the side-chain fragments. The influence of azocomponent chemical structure on copolymerization rate of synthesized methacrylic monomers was studied. The main polymer linking agent is polymethacrylate due to its ability to form qualitative thin films and to transmit light in the range from 300 nm, which makes it suitable for spectrometric investigations.

2. Experimental

Azomonomers synthesis is presented in Scheme 1.
Azocomounds (Azo1–Azo5) were synthesized *via* diazotization reaction and followed by coupling with
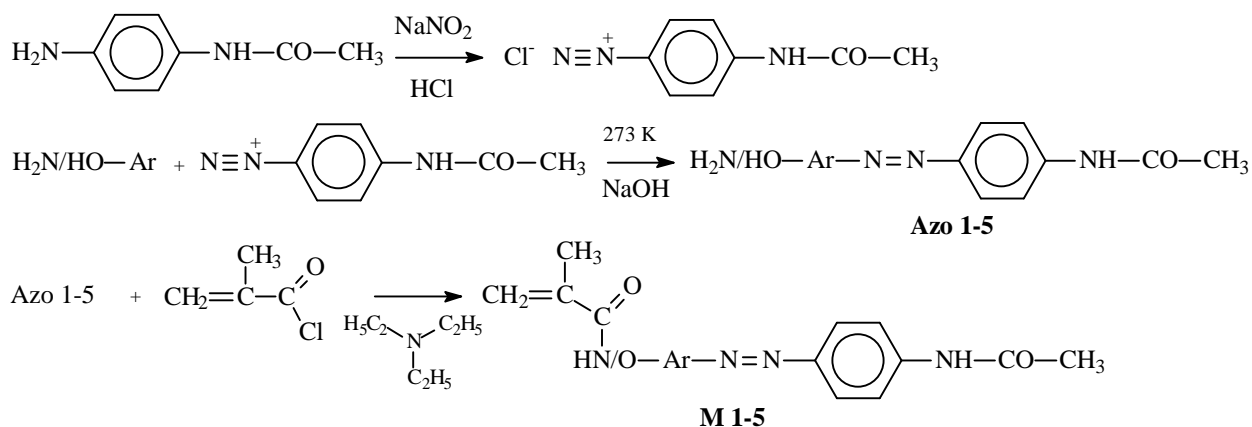
Fig. 1. Scheme of azomonomer synthesis

phenol (1-naphthol, 8-hydroxyquinoline, 2-amino-4-(4-chlorphenyl)-thiazole, 2-amino-4-(4-methoxyphenyl)-thiazole, correspondingly). 4-Aminoacetanilide (6 g, 40 mmol) was dissolved in 50 ml of hydrochloric acid HCl (1:1). The temperature was maintained at 273–278 K. Sodium nitrite (3.1 g, 44.9 mmol) dissolved in a small amount of water was added dropwise to the stirred solution. The reaction was carried out at 278 K for 2 h. The corresponding hydroxycompound (40 mmol) was dissolved in sodium hydroxide solution (or *N*-methylpyrrolidone for Azo4 and Azo5) and were added slowly. The resulted brown solution was stirred for 4 h at 273–278 K and for additional 16 h at room temperature. Sodium acetate solution was slowly added to neutralize the reaction mixture. The precipitate formed was collected by filtration, washed with a large amount of water, and dried. The crude products were purified by recrystallization from ethanol or dioxane. The pure azocompounds of different colors were obtained.

4-(4-hydroxy-1-phenylazo)-acetanilide (Azo1): Light brown crystals. Yield: 60 %. Mp: 476–478 K.

4-(4-hydroxy-1-naphthylazo)-acetanilide (Azo2): Brown crystals. Yield: 56 %. Mp: 377–378 K.

4-(8-hydroxy-1-quinolinazo)-acetanilide (Azo3): Blue-green crystals. Yield: 64 %. Mp: 376–378 K.

4-(2-amino-4-(4-chlorphenyl)-5-thiazolylazo)-acetanilide (Azo4): Bright red crystals. Yield: 39 %. Mp: 451–453 K.

4-(2-amino-4-(4-methoxyphenyl)-5-thiazolylazo)-acetanilide (Azo5): Yellow crystals. Yield: 33 %. Mp: 440–442 K.

Azomonomers (M1–M5). In a three-necked flask, freshly purified azocompound (Azo1–Azo5) (20 mmol) was dissolved in 50 ml of freshly distilled THF. Freshly distilled triethylamine (2.02 g, 20 mmol) was added to the three-necked flask by syringe through the rubber septum,

and methacryloyl chloride (2.09 g, 20 mmol) was dissolved in 10 ml of freshly distilled THF. The reaction mixture was cooled to 273 K, and methacryloyl chloride solution was added to the reaction mixture dropwise while stirring over a period of 2 h. The reaction mixture was kept overnight and then poured into water (1 l). The solid was filtered and purified by recrystallization in ethanol. Methacrylic azomonomers (M1–M5) of different structures were obtained:

4-(4-methacryloxy-1-phenylazo)-acetanilide (M1). Yield: 78 %. Mp: 525 K. ^{1}H NMR (CDCl$_3$), *d* (ppm): 9.9 (s, NH), 7.8 (d, 2H, Ar), 7.74 (d, 2H, Ar), 7.7 (d, 2H, Ar), 6.9 (d, 2H, Ar), 6.5 (s, 1H, CH$_2$=), 5.9 (s, 1H, CH$_2$=), 2.07 (s, 3H, CH$_3$), 1.8 (s, 3H, CH$_3$).

4-(4-methacryloxy-1-naphthylazo)-acetanilide (M2). Yield: 64 %. Mp: 388 K. ^{1}H NMR (CDCl$_3$), *d* (ppm): 10.1 (s, NH), 8.97 (d, 2H, Ar), 7.7 (d, 4H, Ar), 7.7 (t, 2H, Ar), 7.4 (d, 2H, Ar), 6.45 (s, 1H, CH$_2$=), 5.97 (s, 1H, CH$_2$=), 2.15 (s, 3H, CH$_3$), 1.73 (s, 3H, CH$_3$).

4-(8-methacryloxy-1-quinolinazo)-acetanilide (M3). Yield: 60 %. Mp: 503 K. ^{1}H NMR (CDCl$_3$), *d* (ppm): 10.2 (s, NH), 9.3 (d, H, Ar), 8.96 (d, H, Ar), 7.98 (d, 2H, Ar), 7.93 (t, H, Ar), 7.84 (d, 2H, Ar), 7.7 (d, H, Ar), 7.6 (d, H, Ar), 6.45 (s, 1H, CH$_2$=), 5.92 (s, 1H, CH$_2$=), 2.13 (s, 3H, CH$_3$), 2.1 (s, 3H, CH$_3$).

4-(2-methacrylamino-4-(4-chlorphenyl)-5-thiazolylazo)-acetanilide (M4). Yield: 56 %. Mp: 520 K. ^{1}H NMR (CDCl$_3$), *d* (ppm): 10.98 (s, NH), 8.24 (d, 2H, Ar), 8.1 (s, NH), 7.7 (d, 2H, Ar), 7.58 (d, 2H, Ar), 7.49 (d, 2H, Ar), 6.45 (s, 1H, CH$_2$=), 5.92 (s, 1H, CH$_2$=), 3.6 (s, 3H, CH$_3$), 2.07 (s, 3H, CH$_3$).

4-(2-methacrylamino-4-(4-methoxyphenyl)-5-thiazolylazo)-acetanilide (M5). Yield: 62 %. Mp: 520 K. ^{1}H NMR (CDCl$_3$), *d* (ppm): 10.06 (s, NH), 8.22 (d, 2H, Ar), 7.9 (s, NH), 7.7 (d, 2H, Ar), 7.58 (d, 2H, Ar), 7.02 (d, 2H, Ar), 6.45 (s, 1H, CH$_2$=), 5.92 (s, 1H, CH$_2$=), 3.26 (s, 3H, CH$_3$), 2.07 (s, 3H, CH$_3$), 1.27 (s, 3H, CH$_3$).

<u>Azomonomers polymerization</u> was carried out by radical mechanism using azo-bis-isobutyrolnitrile (AIBN) as initiator. Copolymerization MMA (M_1) with azomonomers (M_2) was carried out in DMF medium at different ratios of the comonomers (1:0, 3:1, 2:1, 1:1, 1:2, 1:3, 0:1). The total concentration of comonomers was 1 mol·l^{-1}, initiator concentration was $0.95 \cdot 10^{-2}$ mol·l^{-1}, $T = 343$ K, and the duration of the reaction was 6 h for experiments on determination of the yields of copolymers formed and 1.5 h for experiments on determination of copolymer compositions. Sealed ampules (or dilatometer) were placed in thermostat and after the end of reaction the contents of the ampules were transferred into cooled methanol, and (co)polymers were isolated as a precipitate. The product was dried to a constant weight in a vacuum drying oven.

The yields of the polymers were determined by gravimetry.

The copolymers compositions were determined from elemental analysis data for nitrogen at the comonomers conversion of at most 5 %.

The relative activities r_1 and r_2 were calculated by the Fineman-Ross method [7], r_1 and r_2 were obtained as graphical solution of Eq. (1):

$$\frac{F}{f}(f-1) = r_1\frac{F^2}{f} - r_2 \qquad (1)$$

where $F = [M_1]/[M_2]$ – molar ratio of comonomers in the initial mixture; $f = [m_1]/[m_2]$ – molar ratio of comonomers in (co)polymer.

The reactivity ratios were used for calculation of polar effects e_2 and intrinsic reactivity Q_2 for azomonomers based on Alfrey-Price equations (2a, 2b):

$$r_1 = (Q_1/Q_2)\exp[-e_1(e_1-e_2)] \qquad (2a)$$
$$r_2 = (Q_2/Q_1)\exp[-e_2(e_2-e_1)] \qquad (2b)$$

where $Q_1 = 0.74$, $e_1 = 0.40$ for MMA from [8].

3. Results and Discussion

Methacrylic azomonomers (M1–M5) containing azofragments with different aromatic rings and acetamide substituent were synthesized according to the Scheme (Fig. 1).

4-Aminoacetanilide was used as starting substance because acetamide group contained in it may play a role of the additional photoactive center in final azopolymer product.

The polymerizable properties of synthesized methacrylic azomonomers were studied on the basis of their polymerization kinetics data, obtained by dilatometry method.

Calculated from experimental kinetic curves parameter of total polymerization rate V_t was employed

for further evaluation of effective constant K_Σ for thermo-induced polymerization. The constant was evaluated from Eq. (3):

$$V_t = K_\Sigma \cdot [I]^{0.5} \cdot [M] \qquad (3)$$

where $[I]$ – molar concentration of initiator, $[M]$ – molar concentration of monomer [8].

Kinetics curves of homopolymerization for monomers M1–M5 as well as their data of copolymerization with MMA are represented in Figs. 2 and 3.

Following a comparison of kinetics curves of homopolymerization of azomonomers and methyl methacrylate it is obvious that polymerization rate of azomethacrylates is lower than for methylmethacrylate. This azomonomers peculiarity is quite consistent with the ability of azogroup to play the role of "traps" for free radicals at polymerization [9-11]. Nevertheless in our studies supplementary regularity in behaviour of azo-containing monomers at their polymerization were found. As we can see from Fig. 2, in the series of monomers M1, M3 and M2 increase of azochromophore system, in which greater delocalization of conjugated electrons takes place, leads to an essential decrease of their activity.
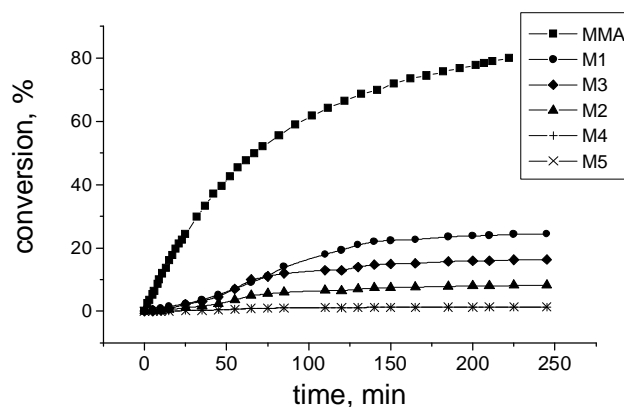

Fig. 2. Kinetics curves of homopolymerization for MMA and azomonomers

The obtained values of *effective polymerization constant K_S* for thermo-induced radical polymerization are presented in Table 1. From these data we should especially stress on increasing monomer activity after introduction in naphthalene ring of nitrogen heteroatom (M3 is quinoline derivative, and M2 is naphthalene derivative). It should be noted that azomonomers containing thiazole fragment in their structure and having such heteroatoms as sulphur and nitrogen practically do not homopolymerize. As a result of copolymerization with methylmethacrylate corresponding azopolymers are obtained only at high initiator concentration (Table 1).

Table 1

Polymerization data of methacrylic azomonomers

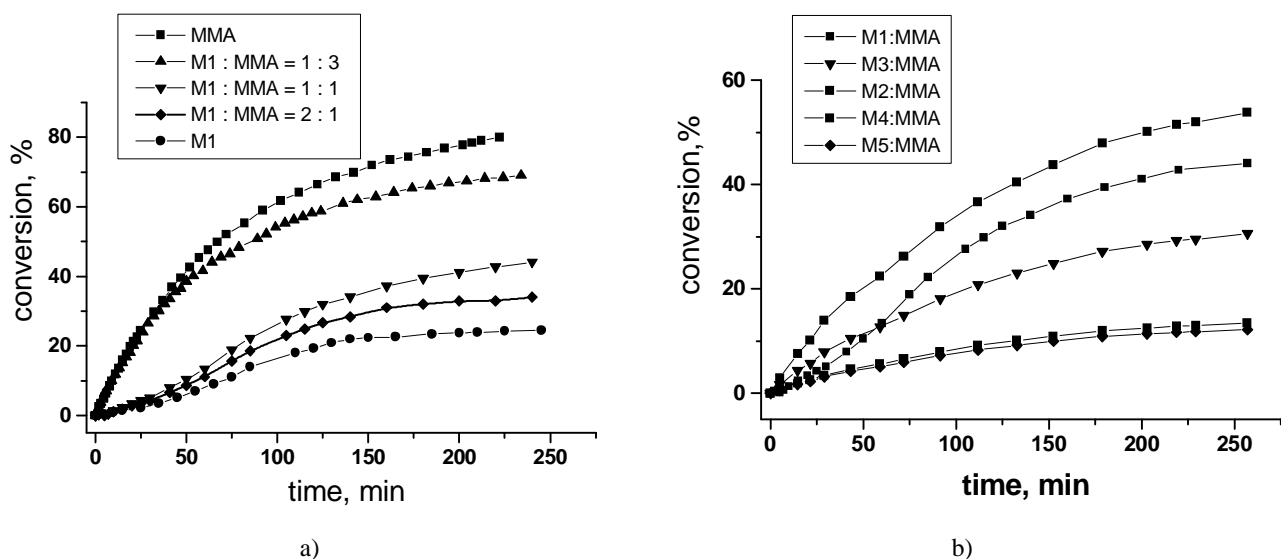| Monomers composition	Monomers ratio	Initiator concentration, %	$K_\Sigma \cdot 10^{-6}$, $1^{0.5}/(mol^{0.5} \cdot s)$	Yield, %	Content of units with azofragments in polymer, %	l_{max}, nm
M1		1	2,1	23	100	362
M2		1	0,8	7	100	340
M3		1	1,5	16	100	380
M1:MMA	1:3	1	7,2	72	20	362
M1:MMA	1:1	1	3,0	46	45	362
M1:MMA	2:1	1	1,5	33	55	362
M2:MMA	1:1	1	7,6	22	43	340
M3:MMA	1:1	1	8	59	55	380
M4:MMA	1:1	1	5,3	25	32	420
M5:MMA	1:1	1	5	22	28	410

Fig. 3. Kinetics curves of copolymerization with MMA: monomer M1 at different monomers ratios (a) and monomers M1–M5 at 1:1 comonomers ratio (b)

Table 2

Calculated reactivity ratios (r_1, r_2) for reaction of copolymerization of monomers M1–M3 and MMA

Azomonomer M_2	Q_2	e_2	r_1	r_2	$r_1 \cdot r_2$	$1/r_1$
M1	2.000	1.440	0.560	0.600	0.336	1.790
M2	1.650	1.720	0.760	0.230	0.175	1.310
M3	1.920	1.590	0.600	0.420	0.252	1.670

In Figs. 3a and 3b diagrams of conversion-time dependence for copolymerization of azomonomer M1 with MMA at different mole ratios as well as comparative characteristics of copolymerization velocities for azomonomers M1–M5 with MMA are shown.

As it was expected, the copolymerization velocity is in direct proportion to the azomonomer concentration in the reaction mixture and it decreases at increasing of the number of radical "azotraps". It should be noted that regularities obtained during homopolymerization for azomonomers M1–M3, are reproduced at their copolymerization with MMA. Copolymerization of monomers M4 and M5 under these selected conditions is very low and can be explained not only by low polymerization activity of azomonomers, where azogroups play the role of free radical "traps", but also by steric factors.

Thus, by (co)polymerization of synthesized new azomonomers based on 4-aminoacetanilide, containing different aromatic rings, structural dyed polymers were obtained (P1–P5):
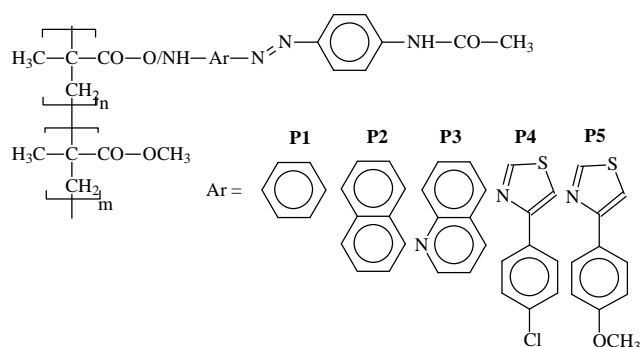
The reactivity of monomers was assessed by the means of copolymerization data. *Q-e* scheme takes into account the intrinsic thermodynamic stability and polar effects in the transition state. M1–M3 monomers are considered to have an intrinsic reactivity of Q_2. The polar effects in the transition state, 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 apparent copolymerization constants r_1 (MMA) and r_2 (Azomonomer) determined by the Feynman–Ross method indicate that this interaction results in the formation of a copolymer with predominantly alternating units, $r_1 \cdot r_2 < 1$ (Table 2).

In a series of azomethacrylates from monomers with benzene aromatic ring in azofragment (M1) to monomers containing naphthalene or 8-oxyquinoline aromatic rings (M2 and M3), which are characterized by wider conjugated system of bonds and delocalized electrons, the electron-seeking effect of substitute on methacrylic double bond is increased, which leads to increasing of polar factor *e*. Calculated values e_2 for methacrylic azomonomers, as for other previously investigated methacrylic monomers [12, 13], indicate significant electropositive effect on double bonds conditioned by electrophilic carbonyl groups influence. It causes the same polarity activation effects for the participation of groups in the copolymerization. According to [14] large positive e_2 values for azomonomers can be explained by strong interaction of azomethacrylates with solvent.

Values of intrinsic reactivity *Q* of methacryloyl double bond depend of spatial volume of azofragments. It was estimated by $Q_2 = 2.00$ of monomer M1 with benzene ring in azofragment and monomers M2 and M3 with bulky cromophores display lower intrinsic reactivity: $Q_2 = 1.65$ and 1.92, respectively.

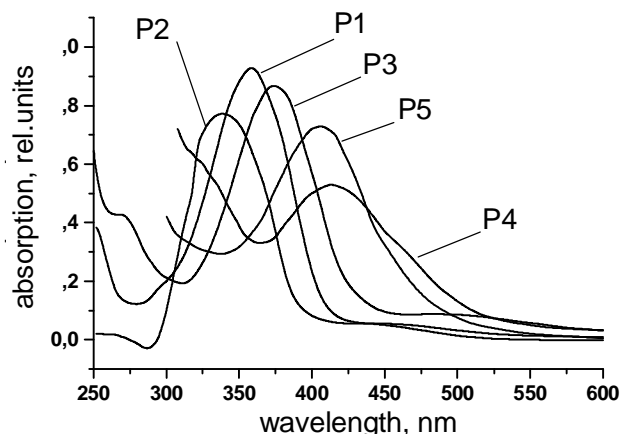It was interesting to study absorption spectra for these polymers (Fig. 4).

Fig. 4. Absorption spectra of azopolymers in films

All polymers absorb in the range from 340 to 420 nm (Table 1). Maximum absorption positions of azopolymers depend on energy of donor-acceptor interaction, which occurs as a result of electron delocalization in azochromophor. Since acetanilide group possess strong donor nature, appearing of electron-acceptor atoms in aromatic rings (nitrogen in P3, sulphur and nitrogen in P4 and P5) leads to increasing of electron deficiency and produces push-pull effect. Such heteroatom incorporation leads to absorption maximum shift to long-wave spectrum range [9, 15]. This rule is true for polymers P5 ($\lambda_{max} = 410$ nm) and P4 ($\lambda_{max} = 420$ nm), which have similar aromatic fragments and differ by the nature of substituents in benzene ring.

Such structural chromophore variation allows to select optimal object for investigation of physicochemical transformations in polymers under illumination by definite light waves.

4. Conclusions

New methacrylic azomonomers based on 4-aminoacetanilide with different aromatic ring nature in azochromophore structure were synthesized. The investigation of kinetics of polymerization for these monomers was carried out and it was shown that the presence of heteroatom in aromatic ring, which is bonded with methacrylic group, can improve polymerizable properties of azomonomers. Nevertheless, this effect is not reproduced for azomonomers with bulky azofragments, which create steric difficulties. It is also shown that absorption maxima of corresponding azopolymer films span from 340 to 420 nm and shift to

long-wave region in case heteroatom appears in aromatic ring of azochromophor. On the basis of synthesized monomers structural-dyed polymers were obtained. They are promising materials for development of polymer composite as well as for physical investigations in the field of nonlinear optic and reversible optical storage.

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ВПЛИВ ХІМІЧНОЇ ПРИРОДИ ХРОМОФОРА НА ПОЛІМЕРИЗАЦІЙНІ ВЛАСТИВОСТІ МЕТАКРИЛОВИХ АЗОМОНОМЕРІВ

Анотація. *Синтезовано метакрилові азомономери на основі пара-аміноацетаніліду, що використовуються для отримання функціоналізованих полімерів для орієнтації рідких кристалів. Азофрагменти містять у своїй структурі різноманітні ароматичні ядра: бензольне, нафталінове, 8-оксихінолінове та похідні тіазолу. Вивчено кінетику полімеризації синтезованих азомономерів. Представлено сумарні константи ефективності термоінфційованої полімеризації K_S. Методом Файнмена-Росса визначено константи кополімеризації та розраховано параметри Q та e. Показано, що природа ароматичного ядра впливає на швидкість полімеризації двома шляхами: через стеричний чинник та безпосередньо хімічну будову. Отримано структурно-забарвлені (ко)полімери на основі синтезованих мономерів, а також записано їх спектри поглинання. Показано, що при використанні електоноакцепторних та електронодонорних замісників (створення пуш-пульного ефекту) можливе посилення як поглинання, так і здатність до перенесення заряду в системі. Вивчено взаємовплив структура-властивості і показний вплив пуш-пульного ефекту на зміну максимуму поглинання синтезованих полімерів.*

Ключові слова: *азомономер, полімеризація, активність мономерів, УФ-спектри.*