Influence of Chemical Nature of Aromatic Rings in Methacrylic Azomonomers on Their Polymerization Properties

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Methacrylic azomonomers based on para-aminoacetanilide were synthesized. Azofragments include various aromatic rings: benzene, naphthalene, 8-oxyquinoline and thiazole derivatives. We studied the kinetics of their polymerization. It was shown that the polymerization rate depends on the nature of the aromatic ring in azohromofore. Structurally colored (co)polymers based on synthesized monomers were obtained and the absorption spectra of polymer films were recorded.

Introduction

Recently among topic developing in the field of photochromic materials, studies 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 molecule (chromophores) in macromolecular structure. They can undego to reversible and irreversible chemical transformation by the action of the light.

The light initiates chemical reactions in photoactive groups that work 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. In fact, the matter at hand is the development and design of light-controllable photoactive LC polymers with a phototunable supramolecular structure and phototunable optical properties. Such polymers are respective new photoactive media for reversible (or irreversible) black-and-white and color data recording and storage for various optical memory-based systems, display technology, optoelectronics, holography, telecommunication systems

Different derivatives of azobenzene show the best advantage as photoactive fragments [4]. The main polymer matrice is polymethacrylate which have abilities to form qualitative thin films and, as is known, to transmit light in range from 300 nm, that is suitable for spectrometric investigations.

In our paper we present synthesis and investigation of polymerizable properties of methacrylic azomonomers based on p-amino acetanilide. In this case azofragments contained different aromatic rings, including heterocyclic, in their structure attached to methacrylate. It was interesting to study photoinduced trans-cis isomerization processes in various chromophores depending on different chemical

structure. Acetanilide as basic compound was chosen because it contains *photo-rearrangeable* acetamide group as additional photoactive center [5], 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.

Results and discussion

Methacrylic azomonomers (M1-M5), containing azofragments with different aromatic rings and acetamide substitute were synthesized accordingly to scheme (figure 1.).

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

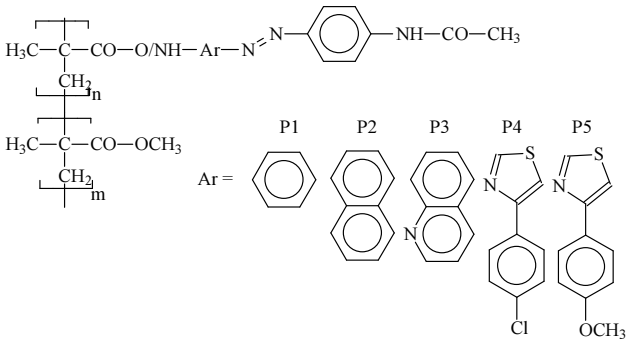
Polymerizable properties of synthesized methacrylic azomonomers were studied on the basis of their polymerization kinetics data, obtained by dilatometry method. Kinetics curves of homopolymerization for monomers M1, M2, M3, M4 and M5 as well as their copolymerization with MMA represented by figures 2 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 methylmethacrylate. This azomonomers peculiarity is quite consistent with ability of azogroup to play the role of "traps" for free radicals at polymerization [6-8]. Nevertheless, in our study it was found supplementary regularity in behavior of azo-containing monomers at their polymerization. As we can see from figure 2, in series of monomers M1, M3 and M2 increase azochromophore system, where delocalization of conjugate electrons takes place, leads to essential decrease of their activity. Efficient polymerization constant K_{Σ} of thermo-induced radical polymerization were presented in Table 1. From these data should make a special emphasis on increasing monomer activity when nitrogen heteroatom is introduced in naphthalene ring (M3 is quinolin derivative, and M2 is naphthalene derivative). It should be noted, that azomonomers, containing thiazole fragments in their structure and having such heteroatoms as sulphur and nitrogen, practically can't homopolymerize. As a result of copolymerization with methylmethacrylate only at high initiator concentration we obtain corresponding azopolymers. (Table. 1.).

(Co)polymerization conversion-time diagrams on figures 3a and 3b for azomonomer M1 with MMA at different mole ratios as well as comparative characteristic of copolymerization velocity for azomonomers M1-M5 with MMA are shown respectively. As it was expected copolymerization velocity was in direct dependence to the azomonomer concentration in reaction mixture and decreases at increasing of number of radical "azotraps". It should be noted that regularity obtained during homopolymerization for azomonomers M1-M3, reproduces at their copolymerization with MMA. Copolymerization 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 factor.

So by (co)polymerization of synthesized new azomonomers based on 4-aminoacetanilide, containing different aromatic rings, structural dyed polymers were obtained:



For this polymers absorption spectra in films were studied (fig. 4). All polymers can absorb within range from 340 to 420 nm. Notable, that incorporation of aromatic rings of complicated structure to azochromophores involves absorption maximum shift to long-wave spectrum range [6, 9]. Such structural chromophore variation allows to select optimal object for study physicochemical transformations in polymers under illumination with definite light wave.

Conclusions

New methacrylic azomonomers based on 4-aminoacetanilide with different aromatic ring nature in azochromophore structure were synthesized. The investigation of kinetic of polymerization for these monomers was carried out and it was shown, that presence of heteroatom in aromatic ring 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 shown also, that absorption maximums of corresponding azopolymer films span from 340 to 420 nm and shift to long-wave region, if heteroatom in aromatic ring of azochromophor appears. 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 nonlinear optic and reversible optical storage field.

Experimental part

Azomonomers synthesis is represented on Scheme 1.

Azocompounds (Azo 1-5) were synthesized by diazotization reaction and followed by coupling with 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 0-5°C. 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 allowed at 5 °C 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 0-5 °C and for an additional 16

h at room temperature. Sodium hydroxide 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 color were obtained.

4-(4-hydroxy-1-phenylazo)-acetanilide (Azo 1): Light brown crystals. Yield: 60%. Mp: 203-205°C.

4-(4-hydroxy-1-naphthylazo)-acetanilide (Azo 2): Brown crystals. Yield: 56%. Mp: 104-105°C.

4-(8-hydroxy-1-quinolinazo)-acetanilide (Azo 3): Blue-green crystals. Yield: 64%. Mp: 103-105°C.

4-(2-amino-4-(4-chlorphenyl)-5-thiazolylazo)-acetanilide (Azo 4): Bright red crystals. Yield: 39%. Mp: 178-180°C.

4-(2-amino-4-(4-methoxyphenyl)-5-thiazolylazo)-acetanilide (Azo 5): Yellow crystals. Yield: 33%. Mp: 167-169°C.

Azomonomers (M 1-5). In a three-necked flask, freshly distilled azocompound (Azo1-Azo5) (20mmol) were 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 0°C, and the methacryloyl chloride solution was added to the reaction mixture dropwise while stirring over a period of 2 h. The reaction mixture was stirred overnight and then poured into water (1l). The solid was filtered and purified by recrystallization in ethanol. Methacrylic azomonomers (M1-M5) of different structure were obtained:

4-(4-methacryloxy-1-phenylazo)-acetanilide (M1). Yield: 78%. Mp: 252°C. ^{1}H NMR ($CDCl_3$), δ (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: 115°C. ^{1}H NMR ($CDCl_3$), δ (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: 230°C. ^{1}H NMR ($CDCl_3$), δ (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: 250°C. ^{1}H NMR ($CDCl_3$), δ (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: 250°C. ^{1}H NMR

($CDCl_3$), δ (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).

Azomonomers polymerization was carried out by radical mechanism using azobisisobutyronitrile (AIBN) as initiator (0.95×10^{-2} mol/l) at 70°C. Monomers were dissolved in DMF, the total monomer concentration was 1 mol/l. For investigation of kinetics of polymerization quantities by mole of azomonomers and methylmethacrylate (MMA) (M:MMA) were taken at next ratio: 1:0; 1:3, 1:1; 2:1, 0:1. It was used the dilatometry method at 80°C throughout 4-7 hours for this purpose. The polymerization kinetic curves were obtained and the efficient polymerization constant K_Σ of thermo-induced radical polymerization were calculated.

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