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New bent-shaped azomethine monomers for optical applications

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ABSTRACT

It was convenient preparative method of new methacrylic monomers with banana-shaped structure and photoactive azomethine fragments synthesis. To determine the effect of large azomethine fragment on the process of homopolymerization, symmetrical model compounds with simpler structure were synthesized. The kinetic of its thermally initiated radical polymerization in DMF solution was studied and compared with the kinetics of model compounds does not containing bulky photochromic fragment. Peculiarities of photo initiated processes of E,Zisomerization were studied. **KEYWORDS**

azomethines; banana-shaped; methacrylate polyazomethines; photoisomerization

1. Introduction

Numerous investigations in recent years devoted to the development of polymers with a range of characteristics that cannot be implemented in one polymer. Polymers with predetermined properties that can be used in various industrial sectors for the development of devices with photosensitive elements are one of the most promising for practical application. These polymers can be created on the basis of polymethylmethacrylates with photoactive azomethine fragments.

Azomethines are of great importance in many areas of application, both in medicine [1–4] and in branches of industry related to information technologies [5–6]. They are used as a pigments and dyes, catalysts [17], intermediates in organic synthesis [7], in analytical chemistry [8], as polymer stabilizers [9]. Also examples of their use for the extraction of metals [10–11] and to obtain heat-resistant polymers with chelate type of structure [12–14] are well known.

Azomethines-based polymers have many useful properties such as thermal stability [15–17], liquid-crystalline (LC) properties [18–21], ability to fiber formation, nonlinear optical (NLO) [22–23] and luminescent properties [24–25], conductivity [26–28] and the ability to chelate formation [29]. Polyazomethines synthesized from aromatic amines and aldehydes, can be used as semiconductors [29–31].

Prospects for future research are to study polyazomethines photochromic behaviour for creating new materials with predictable properties. It is known that the large number of scientific papers devoted to azomethine complexes with metal ions or azomethine based polymers with only one photochromic fragment in monomer unit. Synthesis and properties investigation of polymers, where each monomer unit contains two equivalent photochromic

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azomethine fragments is a perspective direction in creation of NLO, LC, and other photoactive materials.

It should be noted that the photoinduced transformation of one isomeric form to another studied for many organic compounds. In literature much attention paid to photo-optical processes that are characteristic for dichroic dyes structurally similar to azomethines such as azobenzene dyes [32–33] and stilbenes [34–35].

Due to the development and improvement of photonic technologies as the most progressive for the optical information processing, interest for plastic materials which properties can be controlled by light is rapidly growing. Photochromic transformations, go along with a changing of the molecular geometry and dipole moment, affect the optical properties of photoactive compounds. This is particularly evident when each molecule contains the number of photoisomerizable fragments more than one.

Considering to the growing interest in the development of new materials with a range of specified properties the purpose of this work was a synthesis of symmetric bis-azomethines and its methacrylate derivatives, study of their photochemical properties and polymerization ability. Also, it is important to investigate the impact of a large lateral fragment on the polymerization ability and rate of polymerization with further comparing of the experimental data obtained for model compounds.

2. Experimental

2.1. Instrumentation

NMR experiments in solutions have been carried out on a Varian Mercury 400 (399.88 MHz for ¹H) spectrometer. The measurements were performed in DMSO-d6 solution and tetramethylsilane (TMS) was used as internal standard. Infrared spectra were recorded on Perkin Elmer Spectrum BX in the frequency range of 4000–400 cm⁻¹ using KBr pellets. Optical absorption spectra have been recorded at room temperature in quartz cuvettes using Varian Cary 50 UV-Vis-NIR spectrophotometer. Contractions during the process of thermal initiated free-radical polymerization were measured by KM-8 cathetometer.

2.2. Materials

All manipulations were performed in air atmosphere using commercial grade solvents. 4-Hydroxybenzaldehyde, potassium hydroxide (KOH) and all 4-substituted anilines were of reagent grade quality and used as received. Triethylamine and methacrylic anhydride were purchased from Sigma-Aldrich and used as received.

2.3. Synthesis

1,3-diphenoxypropan-2-ol DPP

In 250 ml flask, equipped with reflux, 40.42 g (0,44 mol) of phenol was dissolved in 45 ml of dioxane. The mixture was stirred at 95°C with 12.32 g (0.22 mol) of finely grind KOH for 30 minutes. After heating to 100–105°C, epichlorohydrin (ECH) was dropwisely added over 1 h. Then solution was intensively stirred at the same temperature for 2 hours. The precipitate of KCl was filtered out, and solvent was removed by evaporation in vacuum. The crude product washed with hot 15% KOH solution and extracted using ethyl acetate. **DPP** was purified by recrystallization from hexane and obtained as white vitreous substance. Yield 51%. M.p.:

80–81°C. ¹H-NMR (400 MHz, DMSO-d₆) δ /ppm: 7.23 (s, 4H, Ar), 6.90 (s, 6H, Ar), 5.28 (s, 1H, -OH), 4.17 (t, 1H, CH), 4.03 (m, 4H, CH₂). Selected IR bands (cm⁻¹): ν = 2944 (-CH₂- ν _{as}), 2874 (>CH- ν), 1322 (>CH- \cdot δ), 1118 (Ar, C-H δ).

1,3-Bis(4-formylphenoxy)propan-2-ol **FPP** was synthesized according to the modified procedure [36]

To 300 ml of water the 9.32 g (0.16 mol) of pre-grind in a mortar KOH and 20 g (0.16 mol) of 4hydroxybenzaldehyde were added. The mixture was warmed to 70°C and kept under vigorous stirring for 40 minutes. Then 5.8 ml (0.08 mol) of epichlorohydrin was added over 1 h. The reaction mixture was stirred at 70°C for an additional 4 h. After cooling, the precipitate was filtered off, washed with water and dried. The crude product was purified by recrystallization from ethanol-water (1:1, v/v). 1,3-Bis(formyl-phenoxy)-4-propanol was finally obtained as beige powder. Yield 64%. M.p.: 142–143°C.¹H-NMR (400 MHz, DMSO-d₆) δ /ppm: 9.89 (s, 2H, COH), 7.85–7.83 (d, 4H, Ar), 7.13–7.11 (d, 4H, Ar), 5.44 (d, 1H, -OH), 4.23 (s, 1H, CH), 4.19 (m, 4H, CH₂). Selected IR bands (cm-1): ν = 2936 (-CH₂- ν .as), 2844 (>CH- ν), 2760 (-<u>CHO</u> ν), 1680 (C = O), 1316 (>CH- δ), 1134 (1,4-subs Ar, C-H δ).

1,3-bis(4-((p-tolylimino)methyl)phenoxy)propan-2-ol FPP-CH₃

FPP (2 g, 0,0067 mol), p-toluidine (1.52 g, 0,0138 mol) and formic acid as catalyst in benzene (30 mL) were placed in a an oven-dried two-necked flask fitted with a Dean-Stark trap. After heating at reflux for 2 h, the crude product was filtered off and washed with hot ethanol. Yield 85%. M.p.: 208–209°C.¹H-NMR (400 MHz, DMSO-d₆) δ /ppm: 8.42 (s, 2H, CM = N), 7.84–7.82 (d, 4H, Ar), 7.16–7.14 (d, 4H, Ar), 7.07 (t, 8H, Ar), 5.36 (s, 1H, OH), 4.23–4.13 (m, 5H, 2CH₂ + CH), 2.36 (s, 6H, CH₃). Selected IR bands (cm-1): ν = 2936 (-CH₂-, ν _{as}), 2914 (Ar-CH₃, C-H ν _{as}), 2876 (>CH- ν), 1606 (CH = N ν), 1308 (>CH- δ).

4-Formylphenyl methacrylate M-F

To the solution of 2.4 g (0.02 mol) of 4-hydroxybenzaldehyde in 20 ml of THF and the 3.05 ml (0.022 mol) of triethylamine were added. The mixture was cooled to about 0°C and 2.3 g (0.022 mol) of methacryloyl chloride were added dropwisely to the stirred mixture. Afterwards, the system was stirred at room temperature for 6 hours. The precipitate of triethylamine hydrochloride was filtered out, the solvent was removed in vacuum. The crude product was washed with ethanol and obtained as yellow oil. Yield 88 %. ¹H-NMR (400 MHz, DMSO-d₆) δ /ppm: 9.98 (s, 1H, -CHO), 7.98 (d, 2H, Ar), 7.35 (d, 2H, Ar), 6.34 (s, 1H, = CH2), 5.86 (s, 1H, = CH2), 2.05 (s, 3H, -CH3).

1,3-diphenoxypropan-2-yl methacrylate M-DPP

DPP (1,5 g, 0,006 mol) with phenothiazine (as polymerization inhibitor) and sulfuric acid (as a catalyst in acylation process) were dissolved in dioxane (5 ml). The solution was heated to a temperature 65°C and after methacrylic anhydride (1.84 ml, 0.012 mol) was added. Then, solution was heated at 70–75°C for additional 4 hours. After finishing of the reaction (according to TLC) product was poured into water (70 ml), washed 3 times with 10% sodium carbonate solution, recrystallized from benzene and dried. Yield 86%. M.p.: 14–15°C.¹H-NMR (400 MHz, DMSO-d₆) δ /ppm: 7.35 (d, 4H, Ar), 7.01 (m, 6H, Ar), 6,26 (s, 1H, = CH₂), 5,71 (s, 1H, = CH₂), 5,58 (s, 1H, CH), 4,41(s, 4H, CH₂), 2,1 (s, 3H, CH₃).

1,3-bis(4-formylphenoxy)propan-2-yl methacrylate M-FPP

M-FPP was synthesized according to previously described methods for M-**DPP**. Yield 57%. M.p.: 18–19°C.¹H-NMR (400 MHz, DMSO-d₆) δ /ppm: 9.85 (s, 2H, COH), 7.85–7.83 (d, 4H, Ar), 7.14–7.12 (d, 4H, Ar), 6,09 (s, 1H, C = CH₂), 5,65 (s, 1H, C = CH₂), 5,54 (s, 1H, CH), 4,43(s, 4H, CH₂), 1,93 (s, 3H, CH₃). Selected IR bands (cm⁻¹): ν = 2930 (-CH₂- ν .as), 2832 (>CH- ν), 2740 (-<u>CH</u>O ν), 1722 (C = O ν), 1690 (C = O), 1428 (CR₁R₂ = CH₂, CH₂ δ).

1,3-bis(4-((p-tolylimino)methyl)phenoxy)propan-2-yl methacrylate M-FPP-CH₃

The synthesis of 1,3-bis(4-((p-tolylimino)methyl)phenoxy)propan-2-yl methacrylate is described as a representative case. **FPP-CH**³ (1 g, 0.0021 mol) solution in 20 ml of dichloroethane was added dropwisely during 30 minutes to a solution containing methacrylic acid (0.3 g, 0.0035 mol), dicyclohexylcarbodiimide (DCC, 0.43 g, 0.0021 mol), and dimethylaminopyridine (DMAP, 0.19 g, 0.0016 mol) in 10 ml of dichloroethane at about 0°C. The reaction mixture was stirred for 36 h at room temperature. Then solvent was evaporated until about 5 ml of solutionremained, the product was filtered and purified by recrystallization from ethanol to provide M-FPP-CH₃. Final products were obtained as bright yellow powder. Yield 56%. M.p.: 139–140°C.¹H-NMR (400 MHz, DMSO-d₆) δ /ppm: 8.41 (s, 2H, CH = N), 7.84–7.82 (d, 4H, Ar), 7.14–7.12 (d, 4H, Ar), 7.05–7.07 (t, 8H, Ar), 6,12 (s, 1H, = CH₂), 5,65 (s, 1H, = CH₂), 5,54 (s, 1H, CH), 4.40–4.41 (d, 2H, CH₂), 4.17–4.15 (m, 2H, CH₂), 2.36 (s, 6H, CH₃), 1,95 (s, 3H, CH₃). Selected IR bands (cm-1): ν = 2874 (>CH- ν), 2856 (Ar-CH₃, C-H ν _{as}), 1718 (C = O ν), 1598 (CH = N ν), 1420 (CR₁R₂ = CH₂, CH₂ δ)

2.1.4. Polymerization

Polymerization of monomers was carried out in dry dimethylformamide (DMF) solution under argon atmosphere at 80°C in the presence of 1wt % 2,2′-azobisisobutyronitrile (AIBN) as an initiator in dilatometer. Contractions were determined by KM-8 cathetometer, and conversions - by gravimetric method. The resulting polymer solution was cooled and poured into ethanol to precipitate the polymer. The polymer was purified by reprecipitation. This procedure was repeated until the polymer contained no trace of monomer.

2.1.5. Calculations

Geometry optimization of the compounds was performed in semi-empirical PM6 approximation [36] (program package MOPAC 2012). The correctness of the optimized structure in the minimum on the potential energy surface was confirmed by the absence of imaginary frequencies in the vibration spectrum. The wavelengths of 20 electronic transitions and the corresponding oscillator strength in the absorption spectra were calculated by INDO/S-CI [37] in the ArgusLab 4.0.1 program [38] using the geometry of the ground state. Thus in CI calculations were applied 20 orbitals (HOMO - 9 - HOMO i LUMO - LUMO +9). Simulated absorption spectra obtained through expanding of every transition using Gaussian function.

3. Results and discussion

The synthesis of methacrylate derivatives of 4,4'-substituted 1,3-bis(4(4-phenylimino) methyl)phenoxy)propan-2-ol was carried out by a multi-step synthetic route as shown in Scheme 1.

Initial hydroxyl azomethines obtained by condensation of 1,3-bis(4-formylphenoxy) propan-2-ol with 4-substituted aniline in benzene in the presence of a catalytic amount of formic acid. Four hours is usually enough to finish this reaction, but the end of the



Scheme 1. Synthesis of the 4,4'-substituted 1,3-bis(4-((4-phenylimino)methyl)phenoxy)propan-2-ol methacrylate derivative.

reaction can be determined by the amount of water in the Dean-Stark trap. Azomethine methacrylates obtained by acylation reaction of hydroxy derivatives by methacrylic acid in the presence of N,N'-Dicyclohexylcarbodiimide (DCC) and 4-Dimethylaminopyridine (DMAP) at 0°C in dichloroethane. **DPP** and **FPP** methacrylic derivatives obtained by the action of methacrylic anhydride in DMF solution in the presence of a catalytic amount of concentrated sulfuric acid. The structure of all obtained compounds was proved by NMR spectroscopy.

In order to study the polymerization ability of new methacrylates in radical thermoinitiated polymerization process the kinetics of its polymerization were investigated. For determination of contraction in definite moment of time dilatometric method was used. All monomers were studied in 10% dimethylformamide solution in the presence of 1wt% 2,2'azobisisobutyronitrile (AIBN) as an initiator in argon atmosphere.

Figure 1 shows the polymerization kinetic curves for methacrylates M-FPP, M-F, M-FPP-CH₃, M-DPP (curves 1, 2, 3 and 4, respectively) and methyl methacrylate (MMA) (curve 5).

According to kinetic curves rate of propagation V_p , reduced rate of propagation V_{re} and total rate polymerization constant K_{Σ} were calculated (Table 1).

As seen from the data in Table 1, in case of all new methacrylates polymerization rate a little bit higher than in the case of methyl methacrylate and 1.5–2 times slower than phenyl



Figure 1. Polymerization kinetic curves for 10% solution of new monomers in DMF at 80°C in the presence of 1% AIBN (argon): 1 - m-FPP, 2 - m-F, 3 - m-FPP-CH₃, 4 - m-DPP and 5 - MMA.

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Compound	Mr	Conversion, %, (225 min)	$V_p \times 10^5$, mol/l×s ⁻¹	$V_{re} \times 10^4$, s ⁻¹	$K_{\Sigma} imes 10^4$, mol/l $ imes$ s $^{-1}$
MMA	100	33	10.8	1,08	5.1
PhMA	162	_	6.1	0,37	11.1
M-F	190	49	7,96	1,51	7.13
M-DPP	312	34	4.34	1,35	6.38
M-FPP	368	55	3.25	1.20	5.64
M-FPP-CH ₃	547	35	2.06	1,13	5,32

Table 1 Kinetic parameters of thermoinitiated radical polymerization, 10% solution of methacrylic monomers and phenylmethacrylate [37] in DMF (80°C, 1% AIBN, argon).

methacrylate polymerization. It should be mentioned, that all kinetic parameters were calculated for steady state.

Among the new monomers methacrylate derivative with one aldehyde group (**M**-**F**) can be polymerized fastest. Bis-phenyl (M-**DPP**) polymerization proceeds with a slightly lower speed, than M-F. Dialdehyde containing derivative (**M**-**FPP**) demonstrates least low polymerization ability than M-**DPP**, but only during first 9 minutes, then polymerization rate of M-**DPP** decreases, whereas the **M**-**FPP** polymerization rate remains constant for another 10 minutes. Though for **M**-**FPP** polymerization continuing to a larger conversion value than for M-**DPP**, but total rate polymerization constant during steady state is larger for M-**DPP**. In case of The bis-azomethine (**M**-**FPP**-**CH**₃) lowest rate of polymerization possibly observed due to highest molecular weight of monomer unit. The obtained data are in agreement with the regularities of radical polymerization of such alkyl methacrylates.

Therefore, it was found that new symmetrical monomers containing bis-azomethine fragment are capable to thermoinitiated radical polymerization and it provides the possibility to obtain polymers with predetermined structure.

Photo-induced isomerization of azomethines and their complexes were have been investigated for a long time [39–40]. But the process of isomerization of symmetrical bisazomethines not yet described in the literature, so requires accurate study.

Figure 2 and 3 shows the changes in absorbance spectra of azomethine solutions in acetonitrile under irradiation by 254 nm light and reversing process of Z,E-isomerization after turning off the light, respectively. The process of reverse Z-E isomerization more than in 3



Figure 2. Changes in the absorption spectrum of FPP-CH₃ in acetonitrile (C = $5*10^{-4}$ mol/l) solution under irradiation.



Figure 3. Changes in the absorption spectrum of previously irradiated FPP-CH₃ in acetonitrile (C = $5*10^{-4}$ mol/l) solution after the end of irradiation.

orders slower than the process of photo-induced trans-cis isomerization (half-reaction time are 2180 minutes (36 hours) and 2 minutes, respectively). For that reason to increase the resolution for reverse process spectrum shown in Figure 3 only in absorption maximum region.

Theoretical absorption spectra of E,E-, E,Z- and Z,Z- isomers of original azomethines in a vacuum were calculated by INDO/S method after geometry optimization with semi-empirical PM6 approximation. In INDO/S approximation wavelengths and corresponding oscillator strengths for 20 first transitions in absorption spectra in a vacuum were calculated. Figure 4 shows calculated absorption spectra of **FPP-CH**₃ in vacuum:

After irradiation of **FPP-CH**₃ solutions by UV light decreasing of a long-wave adsorption band (corresponding to E,E–isomer) and increasing of a short-wavelength adsorption band (corresponding to E,Z– and Z,Z–isomer) can be observed. As a result appearance of isobestic point takes place. Theoretically calculated spectra excluding the effect of solvent are in good agreement with the experimental absorption spectra and confirmed experimentally obtained photo-conversion direction.



Figure 4. Calculated absorption spectra of FPP-CH₃ in vacuum: 1 - E, E- isomer, 2 - E, Z- isomer, 3 - Z, Z- isomer.

Conclusions

A convenient method of synthesis of new methacrylic monomers containing bis-azomethine photoactive fragment have been developed. The processes of photoinduced E,Z-isomerization for original azomethine was investigated. It has been shown that the process is reversible. It should be noted, that unlike the already known azomethines, bis-azomethines inclined to continue the process of isomerization even after the termination of irradiation. The kinetics of thermally initiated radical homopolymerization of azomethine monomer and model methacrylates in solution was studied. Kinetic investigation of radical polymerization process for new methacrylic monomers show their high polymerization activity that allows getting different special function copolymers for the photophysical application.

Ultimately, it has been proven that vinyl polymers for special purpose and for use in photophysics based on synthesized monomers may be obtained.

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