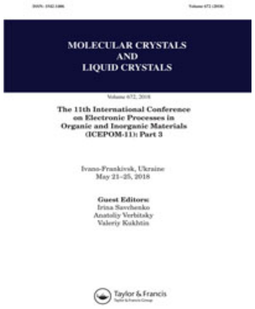

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Photochemical activities of polymers with aurone fragment

Vitaliy Smokal, Oksana Kharchenko, Yuriy Karabets, Nataliia Iukhymenko, Andrii Kysil, Oksana Krupka, and Aleksiy Kolendo

Kyiv Taras Shevchenko National University, Volodymyrska 60, 01033 Kyiv, Ukraine

ABSTRACT

In this work we report preliminary results obtained for methacrylic polymers incorporating aurone side-group as photochemical active molecule. The aurone polymers were obtained by a three-step synthetic approach: (2Z)-6-hydroxy-2-(4-R-benzyliden)-1-benzofuran-3(2H)-ones were synthesized by using condensation reation of 6-hydroxybenzofuran-3-one with benzaldehydes; then methacrylate monomers were synthesized by reaction the alcohols with methacryloyl chloride; and the polymers were synthesized by free radical polymerization. Polymers were characterized by ^{1}HNMR spectroscopy and DSC techniques. Their physicochemical properties are determined by absorption, fluorescence excitation and emission spectroscopies.

KEYWORDS

Radical polymerization; aryl(meth)acrylates; luminescent properties; photochemical properties; aurone containing polymers

1. Introduction

Aurones are well known group of natural dyes that are contained in vegetables, especially fruits, and flowers [1]. Aurones contained in the sunflower family, or asteraceae, were the first to be discovered in the early 1940s [2]. It's belonging to the flavonoid class of natural products [3]. Recent investigations have shown that these compounds have good biological activities and much better than flavones and chalcones [4]. Investigations in vitro have established that natural aurones and their synthetic analogies exhibit antibacterial, antiviral, antiparasitic, antioxydant, anticancer activity [5–7]. 4-Hydroxy aurones have been developed as receptors, which allow for ″naked-eye″ detection of cyanide anions with high selectivity and sensitivity. These compounds exhibit remarkable response to cyanide anions. The addition of CN^- to acetonitrile solutions induced obvious colour, UV–vis and fluorescence change [8].

A number of naturally occurring aurones which possess various hydroxylation patterns have numerous biological activities [4]. Therefore, formidable efforts have been made on the synthesis of (*Z*)-aurone and its derivatives.

In particular, researches have reported that synthetic derivatives of aurone exsist in thermodynamically more stable *Z*-isomer. They are able to photoinduced *Z*-*E*-isomerization and in some cases to reversible photoisomerization [9]. Photochromism attract attention of researcher as striking phenomena in photochemistry, which involves light induced reversible transformation of a molecule between two states with different absorption spectra [10–15]. In this respect, aurones show unique photochemical and

CONTACT Vitaliy Smokal vitaliismokal@gmail.com; Nataliia Iukhymenko yukhimenko.n@gmail.com Kyiv Taras Shevchenko National University, Volodymyrska 60, 01033, Kyiv, Ukraine

photophysical properties as fluorescent photochromic materials, which could be useful in a variety of applications such as fluorescent labels and probes in biology and medicine, as photoswitches in optics in optical memory applications because the stored information is accessed from written form by fluorescence property [16, 17].

The present work deals with the photochemical properties of functionalized methacrylic polymers with aurone fragments. It has been shown that irradiation of aurone derivatives in various solutions gives a rise to a product the *trans* isomerisation. The changes in the absorption under UV irradiation of these compounds were investigated in solution.

2. Experimental

Methods

^{1}H NMR (400 MHz) spectra were recorded on a Mercury (Varian) 400 spectrometer. Chemical shift are in ppm from the internal standard tetramethylsilane.

UV-VIS spectra were recorded on a Shimadzu UV-1800 spectrometer (Shimadzu, Kyoto, Japan) at room temperature in solution in a quartz liquid cell.

Infrared spectra were recorded on Perkin Elmer BX with KBr. EL-TEMP melting point apparatus was used for melting points measurements.

Differential Scanning Calorimetry (DSC): A Q20 model DSC (TA Instruments) with a continuous N_2 purge was used to determine the glass and phase transition temperatures (T_g) of all polymers. Two scans were run at a heating rate of 10 °C/min up to 200 °C, followed by a cooling to 20 °C, giving the values of T_g.

The absorption and steady-state fluorescence spectra were recorded on a Shimadzu UV-1800 spectrophotometer and Shimadzu RF-6000 spectrofluorometer, respectively. The emission spectra were measured by adjusting the excitation wavelengths to the wavelength maximum in the absorption spectra, while fluorescence excitation spectra were recorded at wavelengths corresponding to the maximum in the emission spectra. An intensity scale of fluorescence excitation and fluorescence spectra is given in arbitrary units. Spectral grade tetrahydrofuran (THF) and ethanol from Fluka were used as solvents in all spectroscopic measurements.

Materials

Standard distillation procedures were performed for triethylamine and THF just prior to use. All other reagents and solvents were commercially available and used as received.

General procedure for synthesis of 6-hydroxyaurones. Aromatic aldehyde (10 mmol) and 50% aqueous potassium hydroxide solution (2.3 ml) were added to the solution of 6-hydroxybenzofuran-3-on (1.5 g, 10 mmol) in the mixture of ethanol (10 ml) and dimethylformamide (DMF) (10 ml) the mixture was stirred 4-6 hours (monitoring by TLC). Reaction mixture was precipitated in 50 ml hot water with stirring and was neutralized by concentrated hydrochloric acid to getting pH 6-7. The precipitate was formed, and then it was filtered and washed with water. After crystallization from methanol/DMF the yellow or red crystalline 6-hydroxyaurones were obtained.

(2Z)-2-Benzylidene-6-hydroxy-1-benzofuran-3(2H)-one. The yellow crystals were obtained, m.p. 259-260 °C, yield: 83%.

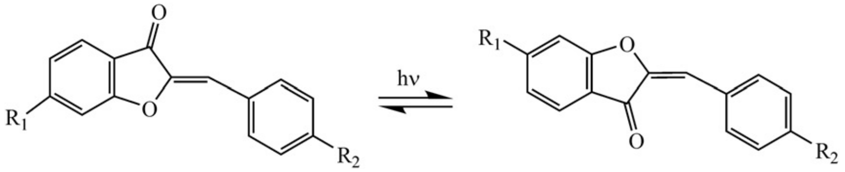

Figure 1. *Z-E*-isomerization of the aurone fragment.

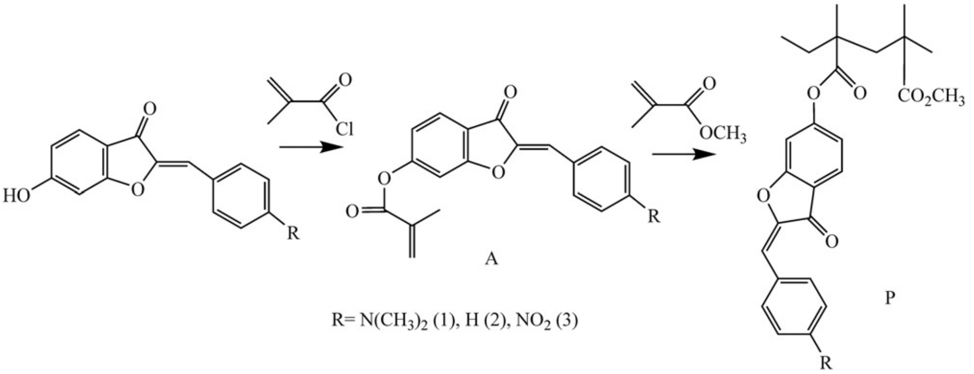

Figure 2. Synthesis of aurones methacrylate monomers and copolymers.

^{1}H NMR (400 MHz, DMSO-d$_6$), δ, ppm: 6.61-6.68 (3H, m, –C = CH, 2a, 7-H), 7.44 (3H, m, 3´, 4´, 5´-H), 7.55 (1H, d, ^3J = 8.4 Hz, 4-H), 7.89 (2H, d, ^3J = 7.5 Hz, 2´, 6´-H), 10.98 (1H, s, 6-OH).

(2Z)-2-[4-(Dimethylamino)benzylidene]-6-hydroxy-1-benzofuran-3(2H)-one. The red crystals were obtained, m.p. 242-244°C, yield: 84%.

^{1}H NMR (400 MHz, DMSO-d$_6$), δ, ppm: 3.20 (6H, s, NMe$_2$), 6.61 (1H, s, –C = CH), 6.61 (1H, d, J = 2.0 Hz, H-7), 6.65 (1H, dd, J = 8.4, 2.0 Hz, H-5), 6.72 (2H, d, ^3J = 8.5 Hz, H-3′, 5′), 7.50 (1H, d, ^3J = 8.5 Hz, H-4), 7.73 (2H, d, ^3J = 8.5 Hz, H-2′, 6′), 10.74 (1H, s, 6-OH).

IR (KBr, cm^{-1}): 3072, 2960, 1674, 1644, 1580, 1455, 1376, 1315, 1285, 1249, 1207, 1154, 1131, 1109, 770, 684.

(2Z)-6-Hydroxy-2-(4-nitrobenzylidene)-1-benzofuran-3(2H)-one. The yellow crystals were obtained, m.p. 249-251°C, yield: 80%.

^{1}H NMR (400 MHz, DMSO-d$_6$), δ, ppm: 6.695 (1H, dd, J = 8.4, 2.0 Hz, H-5), 6.725 (1H, d, J = 2.0 Hz, H-7), 6.82 (1H, s, –C = CH), 7.57 (1H, d, J = 8.4 Hz, H-4), 8.14 (2H, d, J = 8.9 Hz, H-2′, 6′), 8.26 (2H, d, J = 8.9 Hz, H-3′, 5′), 11.15 (1H, s, 6-OH).

General procedure for synthesis of 6-methacryloxyaurones. (2Z)-6-Hydroxyaurone (1 mol) was dissolved in 10 ml DMF and triethylamine (1 mol) was added to the solution. The reaction mixture was kept in an ice-water bath at 0°C with stirring. Methacryloyl chloride (1.5 mol) was added drop wise. The reaction mixture was stirred for 4 h at 0°C. After stirring the reaction mixture was precipitated in ice. Precipitate was filtered, washed with water and dried. Solid precipitate was crystallized from mixture toluene:hexane (1:2). Yellow-orange solid of 6-methacryloxyaurones were obtained with yields 60-80%.

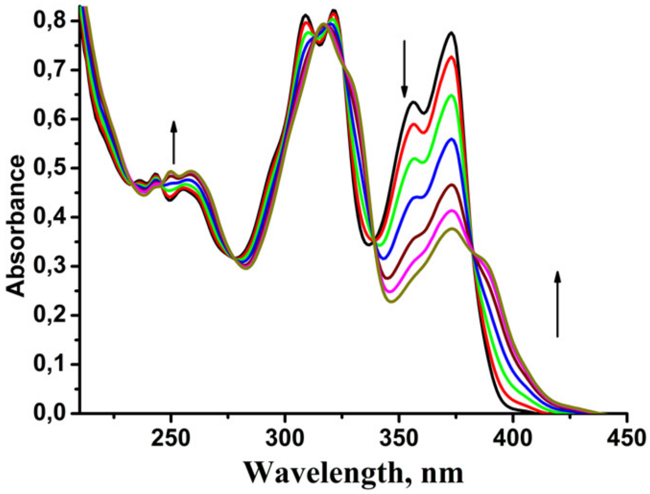

Figure 3. Changes in the absorption spectra of **P2** in THF before (1) and after 1 s period (2) after 3 s (3), 4 s (4), 5 s (5), 5 s (6), 5 s (7) upon irradiation at λ= 366 nm revealing the trans-cis isomerization.

***(2Z)-2-Benzylidene-6-methacryloxy-1-benzofuran-3(2H)-one* (A2).** The light yellow crystals were obtained, m.p. 129°C, yield: 60%.

^{1}H NMR (400 MHz, DMSO-d$_6$), δ, ppm: 2.07 (3H, s, CH$_3$), 5,90 (s, -C = CH (cis)), 6.36 (s, -C = CH (trans)), 7.07 (1H, dd, *J* = 8.5, 2.0 Hz, H-5), 6.87 (1H, d, *J* = 2.0 Hz, H-7), 7.33 (1H, s, -C = CH), 7.83 (1H, d, *J* = 8.5 Hz, H-4), 7.39-7.48 (2H, m, H-2′, 6′), 7.94 (2H, d, *J* = 8.8 Hz, H-3′, 5′).

IR (KBr, cm^{-1}): 3072, 3041, 2960, 1734, 1714, 1660, 1606, 1452, 1436, 1316,1272, 1250, 1188, 1144, 1127, 1098, 966, 942, 770, 684.

***(2Z)-2-[4-(Dimethylamino)benzylidene]-6-methacryloxy-1-benzofuran-3(2H)-one* (A1)**. The orange crystalline compound was obtained, m.p. 153°C, yield: 68%.

^{1}H NMR (400 MHz, DMSO-d$_6$), δ, ppm: 2.06 (3H, s, CH$_3$), 3.05 (6H, s, NMe$_2$), 5,88 (s, -C = CH (cis)), 6.35 (s, -C = CH (trans)), 7.05 (1H, dd, *J* = 8, 2.0 Hz, H-5), 7.00 (1H, d, *J* = 2.0 Hz, H-7), 7.38 (1H, s, -C = CH), 7.85 (1H, d, *J* = 8 Hz, H-4), 8.18 (2H, d, *J* = 8.9 Hz, H-2′, 6′), 8.28 (2H, d, *J* = 8.9 Hz, H-3′, 5′).

***(2Z)-6-Methacryloxy-2-(4-nitrobenzylidene)-1-benzofuran-3(2H)-one* (A3)**. The yellow crystalline compound was obtained, m.p. 220°C, yield: 82%.

^{1}H NMR (400 MHz, DMSO-d$_6$), δ, ppm: 2.07 (3H, s, CH$_3$), 5,91 (s, -C = CH (cis)), 5,91(s, -C = CH$_2$ (trans)), 7.05 (1H, dd, *J* = 8, 2.0 Hz, H-5), 7.00 (1H, d, *J* = 2.0 Hz, H-7), 7.38 (1H, s, -C = CH), 7.85 (1H, d, *J* = 8 Hz, H-4), 8.18 (2H, d, *J* = 8.9 Hz, H-2′, 6′), 8.28 (2H, d, *J* = 8.9 Hz, H-3′, 5′).

Polymerization

The aurone polymers were synthesized by free-radical polymerization. The polymerization was carried out in 10 wt% DMF solution of monomers and was conducted using azobis(isobutyronitrile) (AIBN) as a free-radical initiator (1 wt% of monomer) at 80°C 24 h in argon atmosphere. The reaction mixture was precipitate in absolute methanol,

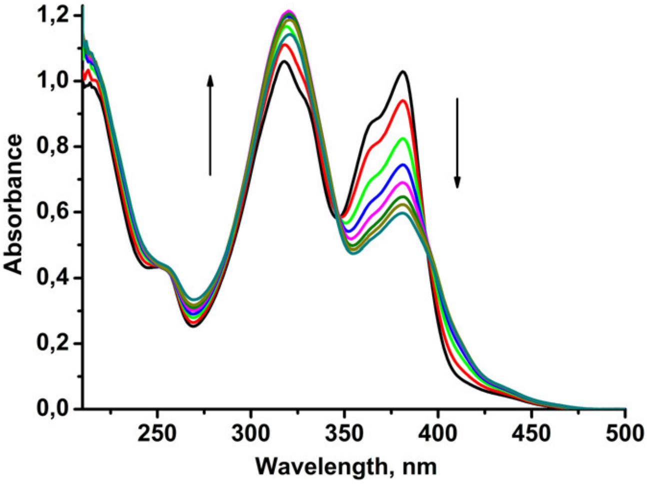

Figure 4. Changes in the absorption spectra of **P3** in THF before (1) and after 2 s period (2) after 4 s (3), 4 s (4), 4 s (5), 4 s (6), 10 s (7), 20 s (8) upon irradiation at $\lambda = 366\,\text{nm}$ revealing the trans-cis isomerization.

and then the polymer was redissolved in THF, and then precipitated in methanol. This procedure was repeated several times to ensure removal of unreacted methacrylic monomer and finally the copolymer was dried under reduced pressure at 60°C for constant weight. The synthesis of copolymers based on aurones methacrylic monomers and methylmethacrylate (MMA) was as a typical polymerization procedure [18,19,20].

3. Results and discussion

The 6-hydroxyaurone derivatives with different substituents have been obtained by the condensation of 6-hydroxybenzofuran-3-ones with benzaldehydes in solution of ethanol and DMF. The aurone methacrylate monomers were synthesized by reacting the aurone alcohols with methacryloyl chloride in the presence of triethylamine as nucleophilic catalyst and hydrochloric acid acceptor. The polymers were synthesized by free radical polymerization using AIBN as radical initiator.

Polar substituents in aurone compounds such as $-N(CH_3)_2$ and $-NO_2$ can act as retarding agents of free radical polymerization reaction. Therefore, long reaction time is needed to synthesize polymers with high yield. The structures of obtained polymers were confirmed by 1H NMR spectra. The compositions of the copolymers were well-controlled as the initial ratio of the aurone monomers and MMA (n:m = 1:3). The Tg are 106°C, 95°C, 106°C for P1, P2, P3 . As expected, the glass transition temperatures (Tg) are typical for methacrylate copolymers without conformationally flexible alkyl chains and rigid moieties. Also the introduction of polar substituents in aurone compounds such as $-N(CH_3)_2$ and $-NO_2$ in the methacrylate monomers tend to slightly increase Tg (P1 and P3 vs P2).

Investigation of photochemical properties of aurones were conducted taking into account the spectral characteristic which we can study after measurement absorption

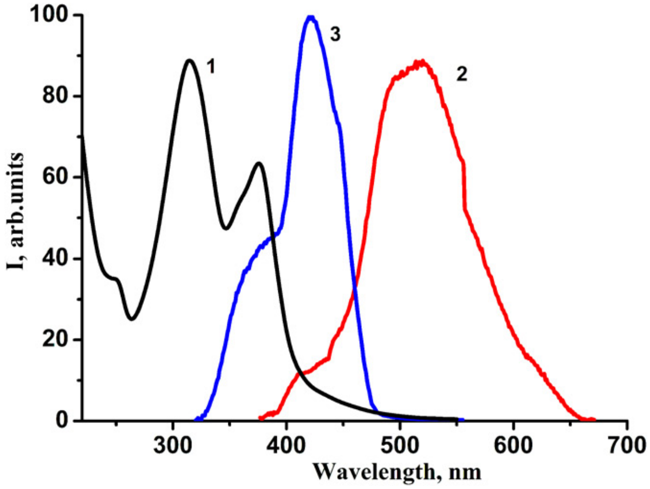

Figure 5. The absorption -1, emission (λ_{ex}=366:375-700 nm) -2, fluorescence of excitation (220-515:515, $\lambda = 420$ nm) -3 of A3 in ethanol at room temperature.

and fluorescence emission spectra. Absorption and fluorescence emission spectra of aurones were measured in quartz cells, which were filled with THF or ethanol .

The absorption spectra compounds P2 and P3 during UV irradiation are represented in Fig.3, 4.

In the spectrum of absorption the THF solutions of P2 (Fig. 3) and P3 (Fig. 4) have three bands with vibrational structure, i.e. the intensive long-wave bands with approximate maximum of 370 nm and 316 nm for P2, of 380 nm and 317 nm for P3 and a medium-intensity absorption band with its maximum about 250 nm for both P2 and P3 copolymers.

During the P2 and P3 solutions irradiation process the decolouration is observed accompanied with a drop of the long-wave maximum intensity, as well as an decrease of absorption intensity at 370 nm with isosbestic point at 346, 396 nm for P2 and the decrease of the absorption intensity at 380 nm with isosbestic point at 345, 396 nm for P3. The presence of isosbestics points at 396 can be also prompting the running processes of photo-Fries rearrangement typical of o- oxyketones structures.

The stable state of the aurone molecule is the *cis* isomeric configuration [9]. 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*-isomerization. From the *trans* form, molecules come back to the *cis* form by two mechanisms – spontaneous thermal reactions and *trans-cis* photoisomerization. The normalised absorption, fluorescence of excitation and fluorescence spectra of A3 in ethanol are shown in Fig.5.

The emission was observed between 400 and 650 nm with λ_F at 514 nm for A3 and corresponding to S1→S0 transition. The methacrylic polymers based on aurone derivatives offer great promise for practical device applications due to their photochemical properties particularly for the optical data storage.

4. Conclusion

The present work reflects the experimental investigations of the photochemical properties of the aurone derivatives. The idea of the photo-Fries reaction possibility by UV-irradiation has been obtained. The total understanding of the relationship between the structure and photochemical properties of aurone derivatives reveals the possibility for their potential applications in the field of photonics and optoelectronics. Polymers based on them are very promising for optical data storage as well as the orientation of photochromic polymers, the photoalignment of liquid crystals and all-optical processing.

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