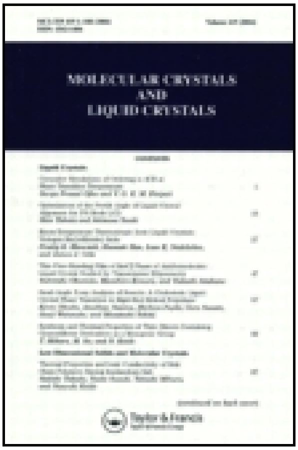

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New Methacrylic Oxazolone and Thiazolidinone Containing Polymers for Nonlinear OpticalApplications

Vitaliy Smokal [a] , Aleksey Kolendo [a] , Oksana Krupka [a] , Beata Derkowska [b] , Robert Czaplicki [c] & Bouchta Sahraoui [c]

[a] Kyiv Taras Shevchenko National University, Volodymyrska, Kiev, Ukraine

[b] Institute of Physics, N. Copernicus University, Grudziądzka, Toruń, Poland

[c] Laboratory POMA, UMR CNRS, University of Angers, Angers, France

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New Methacrylic Oxazolone and Thiazolidinone Containing Polymers for Nonlinear Optical Applications

Vitaliy Smokal[1], Aleksey Kolendo[1], Oksana Krupka[1], Beata Derkowska[2], Robert Czaplicki[3], and Bouchta Sahraoui[3]
[1]Kyiv Taras Shevchenko National University, Volodymyrska, Kiev, Ukraine
[2]Institute of Physics, N. Copernicus University, Grudziądzka, Toruń, Poland
[3]Laboratory POMA, UMR CNRS, University of Angers, Angers, France

Oxazalone and thiazolidinone derivatives were synthesized and their physicochemical properties are determined by absorption, HNMR spectroscopies. The third order nonlinear optical properties of oxazolone and thiazolidinone containing compounds were investigated in solutions using degenerate four wave mixing (DFWM) method at 532 nm.

Keywords: aryl(meth)acrylates; NLO properties; oxazolone; radical polymerization; thiazolidinone

INTRODUCTION

Thiazolidinone derivatives and benzene oxazolones and their analogs are known for their biological properties [1–3]. Compounds with oxazolones ring have exhibited antibacterial[4] as well as antifungal activities. However, thiazolidinones have shown a wide range of pharmaceutical properties [5]. These molecules are promising due to their photophysical properties [6,7].

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Address correspondence to Vitaliy Smokal, Kyiv Taras Shevchenko National University, Volodymyrska 60, 01033 Kiev, Ukraine. E-mail: smokal@mail.univ.kiev.ua

In the present work, we chose oxazolone and thiazolidinone derivatives, synthesized the methacrylic monomers containing the model fragments, polymers, co-polymers with methyl methacrylate investigated their spectral characteristics. The third order nonlinear optical properties of oxazolone and thiazolidinone derivatives have been investigated in solutions using degenerate four wave mixing (DFWM) method at 532 nm.

EXPERIMENT

Materials and Characterization Methods

N,N-dimethylformamide (DMF) were vacuum-distilled off from calcium hydride just prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from absolute methanol. Methacrylic anhydride and methacryloyl chloride were vacuum-distilled, immediately before use. Methylmethacrylate (MMA) was dried by distillation under argon. All other reagents and solvents were commercially available and used as received.

^{1}H NMR (400 MHz) spectra were recorded on a "Mercury-400" spectrometer using DMSO-d_6 as solvent. Chemical shifts are in ppm from the internal standard tetramethylsilane (TMS).

UV-VIS measurements in the 210–600 nm spectral regions were performed at room temperature in ethanol in quartz cuve ($C = 10^{-5}$ mol/L) with a Perkin-Elmer UV/VIS/NIR Lambda 19 spectrometer.

Synthesis

Oxazolone derivatives were prepared by condensation of different arylaldehydes with hippuric acid in acetic anhydride, in the presence of anhydrous sodium acetate as a homogeneous basic catalyst as was describe previously (Fig. 1) [9].

2-phenyl-4-[[4-acetyloxyphenyl]methylene]-5(4H)-oxazolone (**p-1b**): m.p. 168°C, yield: 80%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.36 (s, 1H, $-C\mathbf{H}=$), 2.44 (s, 3H, $C\mathbf{H}_3$), 8.26–8.18 (m, 4H, Ph$-$**H**), 7.3–7.65 (m, 5H, Ph$-$**H**). UV-VIS (ethanol) λ_{max}: 225, 261, 366 nm.

2-phenyl-4-[[3-acetyloxyphenyl]methylene]-5(4H)-oxazolone (**m-1b**): m.p. 140°C (lemon coloured crystals from AcOH), yield 75%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.32 (s, 1H, $-C\mathbf{H}=$), 2.3 (s, 3H, $C\mathbf{H}_3$), 7.21–8.04 (m, 4H, Ph$-$**H**), 7.70–8.15 (m, 5H, Ph$-$**H**). UV-VIS (ethanol) λ_{max}: 223, 260, 361 nm.

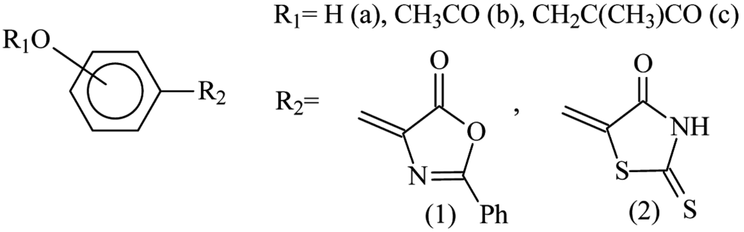


FIGURE 1 Chemical structures of oxazolone and thiazolidine derivatives.

2-phenyl-4-[(4-hydroxyphenyl)methylene]-5(4H)-oxazolone (**p-1a**): m.p. 218°C, yield: 35%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.22 (s, 1H, –C**H**=), 10.27 (s, 1H, –O**H**), 6.88–8.14 (m, 4H, Ph–**H**), 7.60–8.13 (m, 5H, Ph–**H**). UV-VIS (ethanol) λ_{max}: 258, 383 nm.

2-phenyl-4-[(4-methacryloyloxyphenyl)methylene]-5(4H)-oxazolone (**p-1c**): m.p. 170°C, yield 55%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 5.89 (s, 1H, C$\mathbf{H_2}$=), 6.34 (s, 1H, C$\mathbf{H_2}$=), 2.06 (s, 3H, –C$\mathbf{H}_3$), 7.28–8.18 (m, 4H, Ph–**H**), 7.70–8.35 (m, 5H, Ph–**H**).

2-phenyl-4-[(3-methacryloyloxyphenyl)methylene]-5(4H)-oxazolone (**m-1c**): m.p.: 138°C, yield 76%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 5.90 (s, 1H, C$\mathbf{H_2}$=), 6.37 (s, 1H, C$\mathbf{H_2}$=), 2.08 (s, 3H, –C$\mathbf{H}_3$), 7.25–8.16 (m, 4H, Ph–**H**), 7.67–8.15 (m, 5H, Ph–**H**).

(4-hydroxyphenyl)methylene-2-thioxo-4-thiazolidinone (**p-2a**): 2-thioxo-4-thiazolidinone (1 g, 0.0075 mol.) in isopropyl alcohol was added to 4-hydroxybenzaldehyde (0.91 g). The reaction mixture was heated for 2 h on a steam bath 80–90°C and then poured into water. The resultant solid product was collected, washed with cold ethanol, hot water, ethanol and then small amount of hexane and then dried to afford compound **p-2a** as yellow solid m.p. 283–285°C, yield 80%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.49 (s, 1H, –C**H**=), 10.26 (s, 1H, –O**H**), 13.52 (s, 1H, –N**H**), 6.87–7.70 (m, 4H, Ph–**H**). UV-VIS (ethanol) λ_{max}: 242, 292, 395 nm.

(3-hydroxyphenyl)methylene-2-thioxo-4-thiazolidinone (**m-2a**) was obtained as described for **p-2a**, m.p. 250–252°C, yield 75%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.47 (s, 1H, –C**H**=), 9.68 (s, 1H, –N**H**), 6.85–7.27 (m, 4H, Ph–**H**). UV-VIS (ethanol) λ_{max}: 252, 276, 380 nm.

(4-acetyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (**p-2b**): **(p-2a)** (1 g) in acetic anhydride (3 ml) was heated on a steam bath 80–90°C. After 2 h, the mixture was cooled and then poured into water. The resultant solid product that formed were filtered off, washed with water and dried. Recrystallization from ethanol alcohol gave yellow

crystals m.p. 238–240°C, yield 70%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.61 (s, 1H, –C**H**=), 2.29 (s, 3H, –C**H**$_3$), 13.75 (s, 1H, –N**H**), 7.25–7.50 (m, 4H, Ph–**H**). UV-VIS (ethanol) λ_{max}: 240, 266, 377 nm.

(3-acetyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (**m-2b**) was obtained as described for (**p-2b**), m.p. 175–177°C, yield 60%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 7.58 (s, 1H, –C**H**=), 2.30 (s, 3H, C**H**$_3$), 13.73 (s, 1H, –N**H**), 7.22–7.53 (m, 4H, Ph–**H**). UV-VIS (ethanol) λ_{max}: 239, 264, 374 nm.

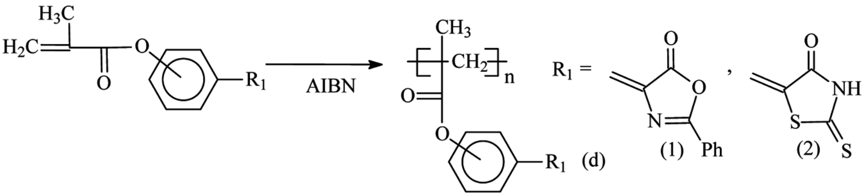
4-(methacryloyloxy)benzaldehyde: 4.9 g (0.04 mol) 4-hydroxybenzaldehyde and 11.4 ml (0.08 mol) triethylamine in 150 ml of diethyl ether was cooled to 0°C. To the solution 8.4 g (0.08 mol) of methacryloyl chloride in 8 ml of diethyl ether was added dropwise in 40 min while stirring. The precipitated triethylammonium chloride was filtered off and the filtrate was allowed to stand for 12 h at 4°C. The suspended matter formed in the solution was separated by filtration. Then the solvent was evaporated and the residue was dried to give 7.0 g (90%) of a pale yellow solid.

4-(methacryloyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (**p-2c**): (2 g) 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 m.p. 195°C, 65%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 5.86 (s, 1H, C**H$_2$**=), 6.31 (s, 1H, C**H$_2$**=), 2.03 (s, 3H, –C**H**$_3$), 7.28–7.66 (m, 4H, Ph–**H**), 7.62 (s, 1H, –C**H**=), 13.69 (s, 1H, –N**H**).

3-(methacryloyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (**m-2c**) was obtained as described for (**p-2c**), m.p. 155°C, yield 60%. ^{1}H NMR (400 MHz, DMSO-d_6), % (ppm): 5.87 (s, 1H, C**H$_2$**=), 6.33 (s, 1H, C**H$_2$**=), 2.05 (s, 3H, –C**H**$_3$), 7.28–7.54 (m, 4H, Ph–**H**), 7.6 (s, 1H, –C**H**=), 13.75 (s, 1H, –N**H**).

Polymerization

The synthesis of homo- and copolymers based on methacrylic monomers and methylmethacrylates (MMA), as a typical polymerization procedure [8], is discussed below. The polymerization ability of the new monomer was investigated kinetically for radical homo- and copolymerization using the dilatometric method. The process was conducted in 10% DMF solution at 80°C (argon atmosphere, initiator – AIBN 1%); contractions were measured by KM-6 cathetometer.



SCHEME 1 Synthesis of oxazolone and thiazolidinone derivatives.

The resulting viscous solution was added dropwise into ethanol to precipitate polymeric materials. Polymers were repeatedly purified by centrifugal separation from ethanol. The conversion rate was controlled gravimetrically. Monomers conversion during the homopolymerization process of (**m-1c**) was 37% in 260 minutes with resulting homopolymer (**m-1d**); (**m-2c**) was 63% in 240 minutes with homopolymer (**m-2d**); (**p-2c**) was 67% in 261 minutes with homopolymer (**p-2d**). The conversion rate during the copolymerization process of (**m-1c**) with methylmethacrylates was 67% in 390 minutes. The structure of oxazolone containing copolymer (**m-1e**) calculated from ^{1}H NMR data is approximately the same as the structure of the initial mixture 1:3. (cf. Scheme 1).

RESULTS AND DISCUSSION

Nonlinear optical properties of studied compounds were investigated using nonlinear transmission and degenerate four wave mixing (DFWM) measurements at 532 nm in solutions [10,11]. In this experiment, three optical pulses (two pump beams and a probe beam), each of 30 ps duration produced by Nd:YAG laser and 1 Hz repetition rate, were obtained by using two beam splitters. The pulses were aligned so as to coincide within the sample, both temporally and spatially. The angle between the pump beams and weak-probe beam was about 12°. Two of these beams interfere inside the sample to form a grating from which the third beam diffracts to form a phase-conjugate signal that retraces the probe path. The photodetector and photomultiplier tube, which were fed to a digital storage oscilloscope and linked to the computer, recorded the incident and phase-conjugate energies, respectively.

The studied compounds were dissolved in DMF. The solvent produced signals under the experimental conditions. Third order nonlinear optical susceptibility of DMF was estimated to be $\chi^{<3>} = 1.28 \cdot 10^{-12}$ [esu]. Carbon disulfide (CS_2) was used as reference to calibrate the measurement system in DFWM ($\chi_{CS_2}^{<3>} = 1.26 \times 10^{-12}$ [esu]). The thiazolidinone and oxazolone derivatives were contained in 1 mm and 2 mm thick quartz cuvettes, respectively.

We used the nonlinear transmission measurement to check if studied compounds possess the two-photon absorption. The coefficient (β) that corresponds to the imaginary parts of the third order nonlinear optical susceptibility at 532 nm. For studied compounds we obtained the transmission curves constant with the incident intensity, the transmission value being lower than unity, which favors a one-photon contribution to the absorption. This means that the molecules exhibited only linear absorption at the excitation wavelength, showing that the third order nonlinear optical susceptibility of these materials has a real number at 532 nm, so the imaginary parts of the third order nonlinear optical susceptibility equal zero.

The third order nonlinear optical susceptibilities of studied compounds dissolved in DMF were obtained from the degenerate four wave mixing measurements. The experimental and theoretical results of DFWM reflectivity (*R*) of studied compounds dissolved in DMF are presented in Figure 2. The DFWM reflectivity (*R*) was calculated from the propagation equation of the four beams in interaction taking into account linear absorption (α) coefficient. The intensity of generated beam is proportional to the product of intensities of interacting beams.

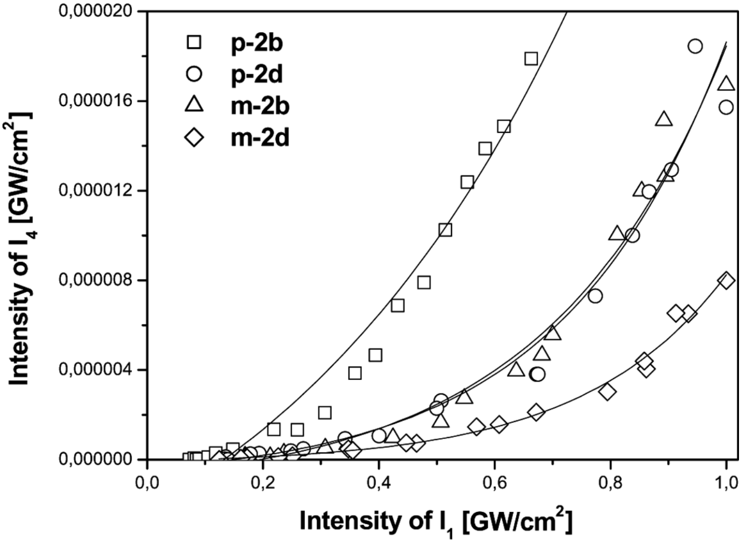


FIGURE 2 DFWM reflectivity (*R*) of studied compounds as a function of input pump intensity.

TABLE 1 The Values of the Linear Absorption Coefficient (α) and the Absolute Values of the Third Order Nonlinear Optical Susceptibility ($\chi^{<3>}$) of Studied Compounds Dissolved in DMF

Compounds	α [cm^{-1}]	$\chi^{<3>}$ [esu]
m-1e	1.70	1.11×10^{-12}
m-1d	1.70	0.75×10^{-12}
p-2d	2.23	2.16×10^{-13}
m-2d	2.11	1.28×10^{-13}
p-2b	2.61	2.24×10^{-13}
m-2b	2.48	1.92×10^{-13}

The DFWM reflectivity (R) can be expressed as follows [10,11]:

$$R = \frac{I_4(0)}{I_3(0)} = \left(\frac{48\pi^3}{n^2 c\lambda}\chi^{<3>}\right)^2 \frac{I_1(0)I_2(0)\exp(-\alpha L)}{\left[p\coth(pL) + \frac{\alpha}{2}\right]^2} \tag{1}$$

where $p^2 = \frac{\alpha^2}{4} - \left(\frac{48\pi^3}{n^2 c\lambda}\chi^{<3>}\right)^2 I_1(0)I_2(0)$ and α, L, λ, and n are the linear absorption coefficient, the thickness of the sample, wavelength of the used laser beam and the linear refractive index of the considered material, respectively.

The best fit of experimental variations of R given by Eq. (1) versus I, represented by solid lines in Figure 2, led to the estimation of the absolute value of $\chi^{<3>}$ (see Table 1).

We can see that the value of third order nonlinear optical susceptibilities for copolymer **m-1e** is bigger than for homopolymer **m-1d** (see Table 1) due to steric factor. We notice that the values of the third order nonlinear optical susceptibility ($\chi^{<3>}$) of **p-2b** and **p-2d** are almost the same. We can also see that the third order nonlinear optical susceptibility ($\chi^{<3>}$) values of the para thiazolidine derivatives **p-2b** and **p-2d** are larger than m- substituent compounds **m-2b** and **m-2d**. We supposed that the behaviour come from different photoisomerization processes of investigated compounds.

CONCLUSIONS

We synthesized the novel NLO polymer containing oxazalone and thiazolidinone moiety. The polymerization ability of the new monomers were investigated kinetically for radical homopolymerization and copolymerization using the dilatometric method. The NLO effect of copolymer is higher than the corresponding homopolymer, and for modeling compounds of methacrilic monomers higher than for polymers due to steric factor. New polymers are great promise for practical device applications.

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