

Vitaliy Smokal¹, Oksana Krupka³, Aleksey Kolendo¹, Beata Derkowska²,
Robert Czaplicki³ and Bouchta Sahraoui³

SYNTHESIS, POLYMERIZATION ABILITY, NONLINEAR OPTICAL PROPERTIES OF METHACRYLIC MONOMERS AND POLYMERS WITH BENZYLIDENE MOIETY

¹ Kyiv Taras Shevchenko National University, 60 Volodymyrska str., 01033 Kyiv, Ukraine

² Institute of Physics, N. Copernicus University, Grudziądzka 5/7, 87-100 Toruń, Poland

³Laboratory POMA, UMR CNRS 6136, University of Angers, 2 Boulevard Lavoisier, 49045 Angers, France
oksana_krupka@yahoo.com

Received: October 4, 2007

Abstract. New methacrylic monomers and polymers with benzylidene fragment have been synthesized. Structures of all compounds have been determined by ¹H NMR and UV spectroscopy. The third order nonlinear optical properties of oxazolone, thiazolidinone and thiohydantoin containing derivatives have been investigated in solutions using degenerate four wave mixing method (DFWM) at 532 nm wavelength region. The dependence $\chi^{(3)}$ of copolymer is higher than that of the corresponding homopolymer, and for the modeling compounds of methacrylic monomers it is higher than for polymers due to the steric factor.

Keywords: oxazolone, thiazolidinone, thiohydantoin, aryl(meth)acrylates, radical polymerization, nonlinear optical properties.

1. Introduction

In the last few years nonlinear optical materials continue to attract attention because of their potential applications in optical signal processing and information storage [1–4]. Compounds with benzylidene fragment and their analogs are known for their biological properties [5–7]. Oxazolone derivatives have exhibited antibacterial [8] as well as antifungal activity. Thiazolidinones have shown a wide range of pharmaceutical properties [9]. These molecules are promising due to their photophysical properties [10, 11].

In our work we have examined spectral characteristics of oxazolone, thiazolidinone and thiohydantoin derivatives, synthesized methacrylic

monomers containing these fragments, polymers and copolymers with methylmethacrylate, butylmethacrylate. The third order nonlinear optical properties (NLO properties) of oxazolone, thiazolidinone and thiohydantoin derivatives have been investigated in solutions using the degenerate four wave mixing (DFWM) method at 532 nm.

2. Experimental

2.1. Materials

N,N-Dimethylformamide (DMF) was vacuum-distilled off from calcium hydride before its being used. 2,2'-Azo-bis(isobutyronitrile) (AIBN) was recrystallized twice from ethanol. Methacrylic anhydride and methacryloyl chloride were vacuum-distilled immediately before their use. Methylmethacrylate (MMA) and butylmethacrylate (BMA) were dried by distillation with argon. All other reagents and solvents were commercially available and were used as we received them.

¹H NMR (400 MHz) spectra were recorded by a "Mercury-400" spectrometer using DMSO-d₆ as solvent. Chemical shifts are in ppm from the tetramethylsilane internal standard (TMS).

UV measurements in the 210–600 nm spectral areas 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.

2.2. Synthesis

Oxazolone derivatives were prepared by condensation of *m*- and *p*- arylaldehydes with hippuric acid in acetic anhydride, in the presence of anhydrous sodium acetate as a homogeneous basic catalyst. The synthesis procedure was described previously [12].

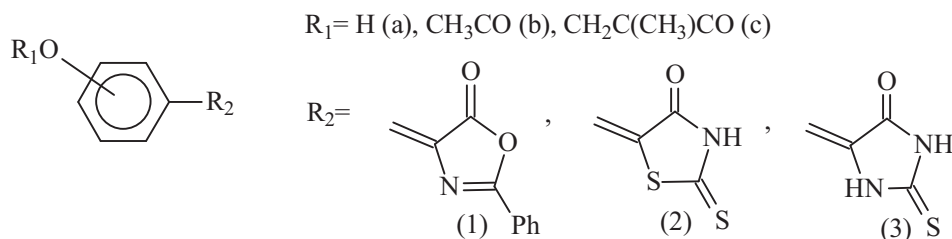


Fig. 1. Chemical structures of oxazolone, thiazolidinone and thiohydantoin derivatives

2-Phenyl-4-[[4-acetyloxyphenyl]methylene]-5(4H)-oxazolone (p-1b): melting point (mp) is 441 K, the yield is 80 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 7.36 (s, 1H, -CH=), 2.44 (s, 3H, CH₃), 8.26–8.18 (m, 4H, Ph-H), 7.3–7.65 (m, 5H, Ph-H). UV (ethanol) λ_{max}: 225, 261, 366 nm.

2-Phenyl-4-[[3-acetyloxyphenyl]methylene]-5(4H)-oxazolone (m-1b): mp is 413 K (lemon coloured crystals from AcOH), the yield is 75 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 7.32 (s, 1H, -CH=), 2.3 (s, 3H, CH₃), 7.21–8.04 (m, 4H, Ph-H), 7.70–8.15 (m, 5H, Ph-H). UV (ethanol) λ_{max}: 223, 260, 361 nm.

2-Phenyl-4-[(4-hydroxyphenyl)methylene]-5(4H)-oxazolone (p-1a): mp is 491 K, the yield is 35 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 7.22 (s, 1H, -CH=), 10.27 (s, 1H, -OH), 6.88–8.14 (m, 4H, Ph-H), 7.60–8.13 (m, 5H, Ph-H). UV (ethanol) λ_{max}: 258, 383 nm.

2-Phenyl-4-[(4-ethacryloyloxyphenyl)methylene]-5(4H)-oxazolone (p-1c): mp is 443 K, the yield is 55 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 5.89 (s, 1H, -CH₂=), 6.34 (s, 1H, CH₂=), 2.06 (s, 3H, -CH₃), 7.28–8.18 (m, 4H, Ph-H), 7.70–8.35 (m, 5H, Ph-H).

2-Phenyl-4-[(3-ethacryloyloxyphenyl)methylene]-5(4H)-oxazolone (m-1c): mp is 411 K, the yield is 76 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 5.90 (s, 1H, CH₂=), 6.37 (s, 1H, CH₂=), 2.08 (s, 3H, -CH₃), 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 (1g) dissolved in isopropyl alcohol was added to 4-hydroxybenzaldehyde (0.91 g). The reaction mixture was heated for 2 h on a steam bath (353–363 K) and then was poured into water. The obtained solid product was collected, washed with cold ethanol, hot water, ethanol and small amount of hexane and then dried to obtain **p-2a** compound as a yellow solid. Its mp is 556–558 K, the yield is 80 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 7.49 (s, 1H, -CH=), 10.26 (s, 1H, -OH), 13.52 (s, 1H, -NH) 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**. Its mp is 523–525 K, the yield is 75 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 7.47 (s, 1H, -CH=), 9.68

(s, 1H, -NH) 6.85–7.27 (m, 4H, Ph-H). UV (ethanol) λ_{max}: 252, 276, 380 nm.

(4-Acetyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (p-2b): 1 g of **p-2a** in acetic anhydride (3 ml) was heated on a steam bath (353–363 K). After 2 h the mixture was cooled and then poured into water. The obtained solid product was filtered off, washed with water and dried. Recrystallization from ethanol alcohol formed yellow crystals. Their mp is 511–513 K, the yield is 70 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 7.61 (s, 1H, -CH=), 2.29 (s, 3H, -CH₃), 13.75 (s, 1H, -NH), 7.25–7.50 (m, 4H, Ph-H). UV (ethanol) λ_{max}: 240, 266, 377 nm.

(3-Acetyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (m-2b) was obtained as described for **p-2b**, mp is 448–450 K, the yield is 60 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 7.58 (s, 1H, -CH=), 2.30 (s, 3H, CH₃), 13.73 (s, 1H, -NH) 7.22–7.53 (m, 4H, Ph-H). UV (ethanol) λ_{max}: 239, 264, 374 nm.

4-(Methacryloyloxy)benzaldehyde: 4.9 g (0.04 mol) of 4-hydroxybenzaldehyde and 11.4 ml (0.08 mol) of triethylamine dissolved in 150 ml of diethyl ether was cooled to 273 K. The solution consisting of 8.4 g (0.08 mol) of methacryloyl chloride and 8 ml of diethyl ether was added dropwise during 40 min while stirring. The precipitated triethylammonium chloride was filtered off and the filtrate was sustained for 12 h at 277 K. The suspended matter formed in the solution was separated by filtration. Then the solvent was evaporated and the residue was dried. 7.0 g (90 %) of a pale yellow solid was obtained.

4-(Methacryloyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (p-2c): 2g of 4-(methacryloyloxy)benzaldehyde, 2-thioxo-4-thiazolidinone (2.5 g), anhydrous sodium acetate (0.3 g; 0.2 mol) dissolved in 50 ml of isopropanol was heated on a steam bath (353–363 K). After 2 h the mixture was cooled and then was poured on ice. The obtained solid product was filtered off, washed with water and dried. Recrystallization from ethanol formed yellow crystals. Its mp is 468 K, the yield is 65 %. ¹H NMR (400 MHz, DMSO-d₆), (ppm): 5.86 (s, 1H, CH₂=), 6.31 (s, 1H, CH₂=), 2.03 (s, 3H, -CH₃), 7.28–7.66 (m, 4H, Ph-H), 7.62 (s, 1H, -CH=), 13.69 (s, 1H, -NH).

3-(Methacryloyloxyphenyl)methylene-2-thioxo-4-thiazolidinone (m-2c) was obtained as described for **p-2c**, mp is 428 K, the yield is 60 %. ¹H NMR (400 MHz,

DMSO- d_6), (ppm): 5.87 (s, 1H, CH₂=), 6.33 (s, 1H, CH₂=), 2.05 (s, 3H, -CH₃), 7.28–7.54 (m, 4H, Ph-H), 7.6 (s, 1H, -CH=), 13.75 (s, 1H, -NH).

Thiohydantoin derivatives were synthesized analogously to thiazolidinone derivatives.

(3-Hydroxyphenyl)methylene-2,4-imidazolidinedithione (**m-3a**): mp is 573-575 K, the yield is 80 %. ¹H NMR (400 MHz, DMSO- d_6), (ppm): 6.32 (s, 1H, -CH=), 11.94 (s, 1H, -NH), 12.15 (s, 1H, -NH), 9.31 (s, 1H, -OH), 6.74–7.16 (m, 4H, Ph-H). UV (ethanol) λ_{\max} : 246, 373 nm.

(4-Hydroxyphenyl)methylene-2,4-imidazolidinedithione (**p-3a**): mp is 588-590 K, the yield is 78 %. ¹H NMR (400 MHz, DMSO- d_6), (ppm): 6.37 (s, 1H, -CH=), 12.05 (s, 1H, -NH), 11.81 (s, 1H, -NH), 9.78 (s, 1H, -OH), 6.76–7.55 (m, 4H, Ph-H). UV (ethanol) λ_{\max} : 259, 389 nm.

(4-Acetyloxyphenyl)methylene-2,4-imidazolidinedithione (**p-3b**): mp is 523-525 K, the yield is 77 %. ¹H NMR (400 MHz, DMSO- d_6), (ppm): 6.43 (s, 1H, -CH=), 2.28 (s, 3H, CH₃), 12.02 (s, 1H, -NH), 12.21 (s, 1H, -NH), 7.11–7.74 (m, 4H, Ph-H).

(3-Acetyloxyphenyl)methylene-2,4-imidazolidinedithione (**m-3b**): mp is 551-553 K, the yield is 82 %. ¹H NMR (400 MHz, DMSO- d_6), (ppm): 6.41 (s, 1H, -CH=), 2.29 (s, 3H, CH₃), 12.26 (s, 1H, -NH), 12.07 (s, 1H, -NH), 7.06–7.54 (m, 4H, Ph-H).

(4-Methacryloyloxyphenyl)methylene-2,4-imidazolidinedithione (**p-3c**): mp is 508-510 K, the yield is 64 %. ¹H NMR (400 MHz, DMSO- d_6), (ppm): 6.44 (s, 1H, -CH=), 2.04 (s, 3H, CH₃), 5.85 (s, 1H, CH₂=), 6.3 (s, 1H, CH₂=), 12.22 (s, 1H, -NH), 12.04 (s, 1H, -NH), 7.14–7.71 (m, 4H, Ph-H).

2.3. Polymerization

The synthesis of homo- and copolymers based on methacrylic monomers and methylmethacrylates (MMA) or butylmethacrylate (BMA), as a typical polymerization procedure [13], is discussed below. The polymerization ability of the new monomers was investigated kinetically for radical homo- and copolymerization using the dilatometric method. The process was carried out in 10 % DMF solution at 353 K, in argon atmosphere, with AIBN as initiator (1 %); contractions were measured by KM-6 cathetometer. The obtained viscous solution was added dropwise into ethanol to precipitate polymeric materials. Polymers were purified of ethanol. The conversion rates were controlled gravimetrically. Monomers conversion during the homopolymerization process of **m-1c** was 37 % in 260 minutes with formation of **m-1d** homopolymer; conversion of **m-2c** was 57 % in 240 minutes with **m-2d** homopolymer formation; conversion of **p-2c** was 48 % in 261 minutes with **p-2d** homopolymer formation (Fig. 2). The conversion rate at the

copolymerization process of **m-1c** with methylmethacrylates was 65% in 259 minutes (copolymer **m-1e**), conversion of **p-3c** with butylmethacrylates was 40.8 % in 254 minutes (copolymer **p-3f**). The structures of copolymers **m-1e** and **p-3f** calculated from ¹H NMR data are approximately the same in all the cases as the structure of the initial mixture (1:3).

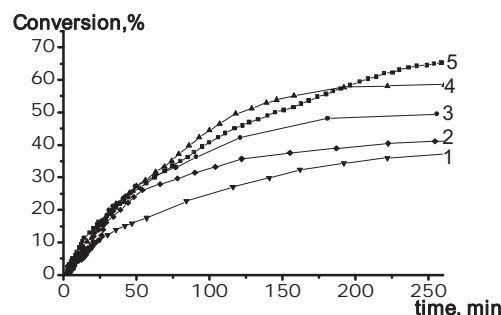


Fig. 2. The kinetic curves of the radical polymerization of 10 % methacrylic monomers in DMF at 353 K (argon atmosphere, 1 % of AIBN initiator). **m-1c**(1), **p-3c**: BMA = 1:3 (2), **p-2c** (3), **m-2c** (4), **m-1c**: MMA = 1:3 (5).

3. Results and Discussion

NLO properties of studied compounds were investigated using nonlinear transmission and DFWM measurements at 532 nm in solutions [14-16]. 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 and form a grating from which the third beam diffracts to form a phase-conjugate signal that retraces the probe path. The photodetector and photomultiplier tubes, 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 (CS₂) was used as a reference to calibrate the measurement system in DFWM ($\chi_{CS_2}^{(3)} = 1.26 \times 10^{-12}$ [esu]). The thiazolidinone, thiohydantoin 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 corresponds to the imaginary parts of the third order nonlinear optical

susceptibility at 532 nm. For studied compounds we obtained the transmission curve constant with the incident intensity, the transmission value being lower than that of the 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 part of the third order nonlinear optical susceptibility is equal to zero.

The third order nonlinear optical susceptibility of studied compounds dissolved in DMF was obtained from the degenerate four wave mixing measurements. The experimental and theoretical results of DFWM reflectivity R of the studied compounds dissolved in DMF are presented in Fig. 3. The DFWM reflectivity was calculated from the propagation equation of the four beams in interaction taking into account linear absorption coefficient α . The intensity of generated beam is proportional to the product of intensities of interacting beams. The DFWM reflectivity can be expressed as follows [14, 15, 17]:

$$R = \frac{2\alpha^2 L^2 \lambda^2 n^2}{\alpha^2 L^2 \lambda^2 n^2 + \chi^{(3)}} \quad (1)$$

where

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 versus I_1 obtained from the theoretical formula (1) and represented by solid lines in Fig. 3 estimated the absolute value of $\chi^{(3)}$ (see Table 1).

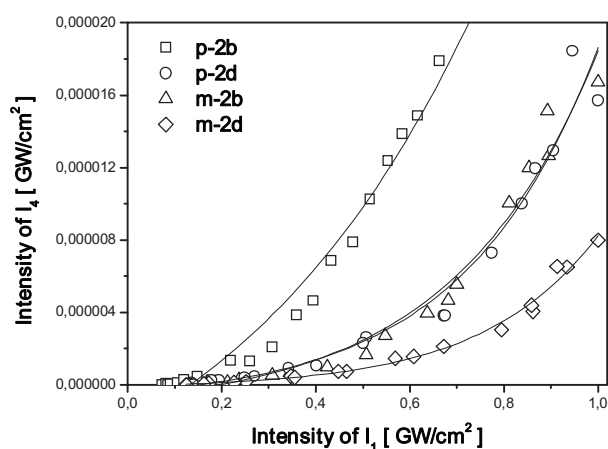


Fig. 3. DFWM reflectivity R of the studied compounds as a function of input pump intensity

Table

The values of the linear absorption coefficient α and the absolute values of the third order nonlinear optical susceptibility $\chi^{(3)}$ of the studied compounds dissolved in DMF

Compound	Linear absorption coefficient α [cm ⁻¹]	Third order nonlinear optical susceptibility $\chi^{(3)}$ [esu]
p-1b	0.00012	0.000018
p-2b	0.00012	0.000020
p-2d	0.00012	0.000018
m-2b	0.00012	0.000015
m-2d	0.00012	0.000010
m-1d	0.00012	0.000015
m-3b	0.00012	0.000018
m-3d	0.00012	0.000015

We can see that the values of the third order nonlinear optical susceptibility for copolymer **m-1e** are higher than those for homopolymer **m-1d** (see Table 1) due to steric factor. We noticed that the values of the third order nonlinear optical susceptibility of **p-2b** and **p-2d** are almost the same. It was also observed that $\chi^{(3)}$ values of the *para*-thiazolidinone derivatives **p-2b** and **p-2d** are higher than *m*-substituent compounds **m-2b** and **m-2d**. The same behavior was noticed in the case of thiohydantoin derivatives **p-3b** and **m-3b**. During our study we have found out the following dependence in the acetyl derivatives of oxazolone, thiohydantoin and thiazolidinone: **p-1b** > **p-3b** > **p-2b**. We suppose that such behaviour could be explained by different photoisomerization processes of investigated compounds.

4. Conclusions

We synthesized the novel NLO polymer containing benzylidene moiety. The polymerization ability of the new monomers was investigated kinetically for radical homopolymerization and copolymerization using the dilatometric method. The NLO effect of copolymer is higher than that of the corresponding homopolymer, and for the modeling compounds of methacrylic monomers it is higher than for polymers due to steric factor. New polymers are promising for practical device applications.

Acknowledgements

This work is financially supported by the Ukrainian Ministry of Research № 0101U002162.

References

- [1] Kajzar F. and Swalan J. (eds.): Organic thin films for waveguiding nonlinear optics. Gordon and Breach Publishers, 1996.
- [2] Kuzyk M. and Dirk C. (eds.): Characterization techniques and tabulations for organic nonlinear optical materials. Marcel Dekker, Inc., 1998.
- [3] Moloney J.V.: Nonlinear optical materials. Springer, New York 1998.
- [4] Kumar G.: J. Nonlinear Opt. Phys. Mat. 2003, **12**, 367.
- [5] Chen H., Fan Y.-H. et al.: Bioorg. Med. Chem. Lett., 2004, **14**, 5401.
- [6] Lohray B.B., Bhushan V. et al.: J. Med. Chem., 1999, **42**, 2569.
- [7] Roy K., Chakraborty S. and Sahab A.: Bioorg. Med. Chem. Lett. 2003, **13**, 3753.
- [8] Joshi H., Upadhyay P., Karia D. and Baxi A.: Eur. J. Med. Chem. 2003, **38**, 837.
- [9] Cetenko W., Connor D., Sorenson R., Unangst P. and Stabler S.: Preparation of (arylmethylenyl) thiazolidinones, -imidazolidinones and -oxazolidinones as antiinflammatory agents and antiallergy agents. Eur. Pat. Appl. Warner-Lambert Co., USA, 1989.
- [10] Koczan G., Csik G., Csampai A., Balog E., Bosze S., Sohar P. and Hudecz F.: Tetrahedron 2001, **57**, 4589.
- [11] Icli S., Icli H., Koc H. and McKillop A.: Spectrosc. Lett. 1994, **27**, 1115.
- [12] Smokal V., Czaplicki R., Derkowska B., Krupka O., Kolendo A. and Sahraoui B.: Synth. Met., (in press).
- [13] Krupka O., Kolendo A.Yu., Kushnir K. and Blazejowski J.: Mol. Cryst. Liq. Cryst. 2005, **427**, 233.
- [14] Derkowska B., Wojdyla M., Bala W., Jaworowicz K., Karpierz M., Grote J.G., Krupka O., Kajzar F. and Sahraoui B.: J. Appl. Phys., 2007, **101**, 083112.
- [15] Derkowska B., Mulatier J.C., Fuks I., Sahraoui B., Nguyen Phu X., and Andraud C.: J. Opt. Soc. Am. B – Opt. Phys. 2001, **18**, 610.
- [16] Sahraoui B. and Rivoire G.: Optics Comm. 1997, **138**, 109.
- [17] Xuan N.P., Ferrier J., Gazengel J. and Rivoire G.: Optics Comm. 1984, **51**, 433.

**СИНТЕЗ, ПОЛІМЕРИЗАЦІЙНА ЗДАТНІСТЬ,
НЕЛІНІЙНО-ОПТИЧНІ ВЛАСТИВОСТІ
МЕТАКРИЛОВИХ МОНОМЕРІВ ТА ПОЛІМЕРІВ
З БЕНЗИЛІДЕНОВИМ ФРАГМЕНТОМ**

***Анотація.** Синтезовано нові метакрилові мономери та полімери з бензиліденовим фрагментом. Структура всіх сполук доведена методами ПМР та УФ- спектроскопією. Нелінійно-оптичні властивості третього порядку оксазолон-, тіозолідіон- та тіогідантоїн-вмісних похідних досліджені в розчині методом змішування чотирьох хвиль (DFWM) з довжиною хвилі 532 нм. Одержана залежність для ацетильних похідних оксазолонів, тіозолідіонів, тіогідантоїнів: $p-1b > p-3b > p-2b$. Показано, що значення нелінійно-оптичної чутливості третього порядку ($\chi^{(3)}$) кополімеру вищі порівняно з відповідним гомополімером, а для модельних сполук метакрилових мономерів вищі, ніж для полімерів завдяки стеричним ефектам.*

***Ключові слова:** оксазолон, тіозолідіон, тіогідантоїн, арил(мет)акрилати, радикальна полімеризація, нелінійно-оптичні властивості.*

