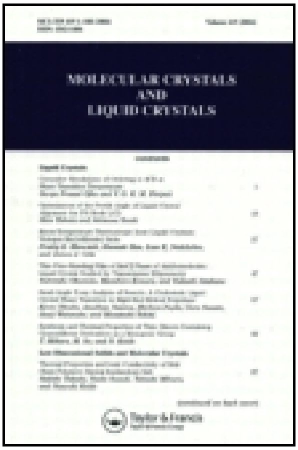


Molecular Crystals and Liquid Crystals

Nonlinear Optical Effects In Polymeric Azoesters

Oksana Nadtoka [a] , Oksana Krupka [a] , Jerome Luk [b] , Volodymyr Syromyatnikov [a] , Bouchta Sahraoui [b] & Vitaliy Smokal [a]

[a] Kyiv National Taras Shevchenko University, Macromolecular Chemistry Department, Kyiv, Ukraine

[b] Laboratory POMA, University of Angers, Boulevard Lavoisier, Angers, France

Version of record first published: 06 Jul 2012

To cite this article: Oksana Nadtoka, Oksana Krupka, Jerome Luk, Volodymyr Syromyatnikov, Bouchta Sahraoui & Vitaliy Smokal (2008): Nonlinear Optical Effects In Polymeric Azoesters, Molecular Crystals and Liquid Crystals, 496:1, 302-309

To link to this article: http://dx.doi.org/10.1080/15421400802451915

Mol. Cryst. Liq. Cryst., Vol. 496, pp. 302–309, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802451915

Nonlinear Optical Effects In Polymeric Azoesters

Oksana Nadtoka[1], Oksana Krupka[1], Jerome Luk[2], Volodymyr Syromyatnikov[1], Bouchta Sahraoui[2], and Vitaliy Smokal[1]
[1]Kyiv National Taras Shevchenko University, Macromolecular Chemistry Department, Kyiv, Ukraine
[2]Laboratory POMA, University of Angers, Boulevard Lavoisier, Angers, France

The methacrylic monomers containing azobenzene moiety with flexible alkyl spacers of different lengths and groups of different nature are synthesized, and their physicochemical properties were determined by electronic absorption, ^1H NMR spectroscopy, and element analysis. In the present work, the homopolymers built with the use of the free radical polymerization of methacrylic monomers incorporating an azobenzene side-group have been synthesized and structurally characterized. The results of photochemical and optical activities of the corresponding polymers are presented. Third-order nonlinear optical (NLO) properties of the azopolymer solutions are studied by the degenerate four wave mixing (DFWM) method.

Keywords: aryl(meth)acrylates; azopolymers; radical polymerization; third-order NLO properties

1. INTRODUCTION

Photoanisotropic materials are widely investigated for optical storage and processing applications. The most promising of them are azo-dye-polymer systems because of their large value of photoinduced birefringence. Azobenzene systems possess the advantages for high optical nonlinearities due to photoinduced *trans-cis* isomerization, molecular reorientation, and nonlinear absorption [1]. Holograms with very high diffraction efficiency and exceptional stability can be written (and erased) by laser illumination in these materials. Azobenzene

Address correspondence to Oksana Nadtoka, Kyiv National Taras Shevchenko University, Volodymyr'ka St., 64, Kyiv 01033, Ukraine. E-mail: oksananadtoka@ukr.net

polymers are interesting because they combine the properties of anisotropy with photoresponsive behavior and can give rise to applications in such areas as LC displays, NLO materials, information storage devices, etc. [2–7].

Among basic requirements to the materials exhibiting the NLO activity are the polarizability (electrons need to be greatly perturbed from their equlibrium positions), asymmetric charge distribution (incorporation of D-A molecules), and acentric crystal packing.

On the molecular level, a molecule must possess an excited state with energy close to that of the ground state, the large oscillator strength for electronic transitions from the ground to the excited state, and a large difference between the dipole moments in the ground and excited states. Such requirements are implemented due to the charge transfer between electron donating and electron withdrawing groups as a dipolar highly polarizable donor-π-acceptor (D-π-A) system.

Such factors as the increased length, increased planarity, overall increased conjugation, and the strength of donors and acceptors play a significant role in the NLO activity. In this paper, we designed a new series of photochromic polymers based on methacrylic azoesters (poly-AzoMA). The azobenzene polymers containing NLO chromophores in each side chain unit with different groups of the acceptor nature and a flexible alkyl spacer have been synthesized via free radical polymerization. On the other hand, the introduction of methacrylate chains ensures a good solubility of azobenzene compounds in different organic solvents that provides a wide potentiality for the fabrication of optical and optoelectronic devices.

In this article, we turn attention to the investigation of the influence of the push-pull electronic effect on the third-order NLO properties of polymers. For this purpose, the poly-AzoMA should have different substituents and a flexible alkyl spacer.

2. EXPERIMENTAL

2.1. Materials

The general structures and main characteristics of poly-AzoMA are shown in Figure 1 and Table 1. All the chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. The structures of all the precursors and final products were confirmed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectra were done on samples dissolved in $CDCl_3$.

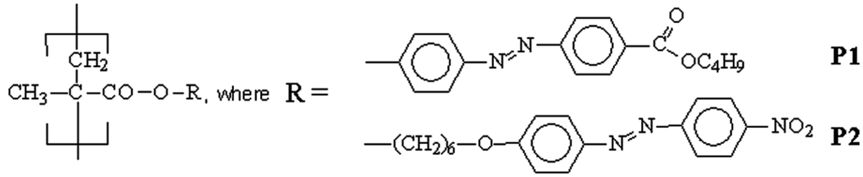


FIGURE 1 Structures of azopolymers.

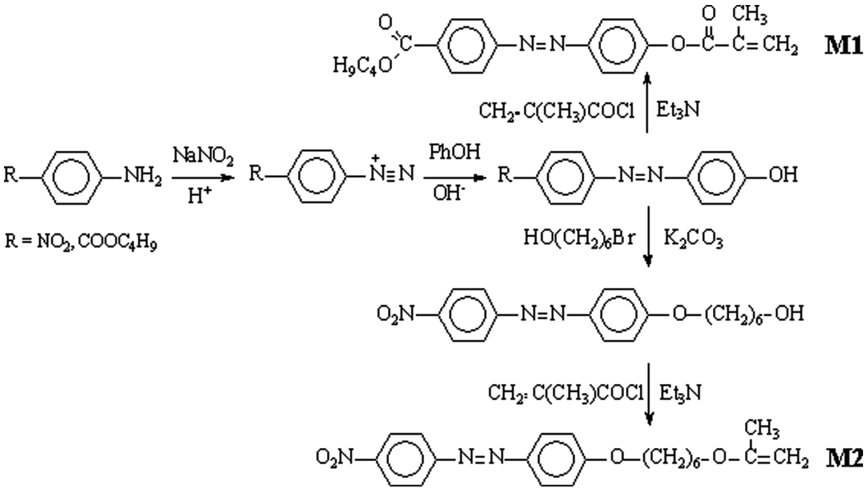
Monomer Synthesis. The synthetic route for the target azomonomers (**M1** and **M2**) is shown in Scheme 1. The corresponding monomers were synthesized by general methods. The azocompound (0.06 mole) and triethylamine (9.0 ml) were dissolved in THF (200 ml). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (6.0 ml, 0.06 mole) was added dropwise to the above mixture. The additional methacryloyl chloride was added, and the resulting mixture was stirred at room temperature overnight. Then the solution was poured into distilled water (1 l) and the obtained residue was filtered and air-dried. Recrystallization of monomers was carried out from ethanol.

4-[(Z)-[4-[(2-methyl-1-oxo-2-propenyl)oxy]phenyl]azo]-benzoic acid butyl ester (M1) Brown crystals; yield 69%; mp 63°C (by DSC). ^{1}H NMR ($CDCl_3$), δ(ppm): 7.89 (d, 2H, Ar), 7.73 (d, 2H, Ar), 7.93 (d, 2H, Ar), 6.94 (d, 2H, Ar), 6.34 (s, 1H, $=CH_2$), 5.91 (s, 1H, $=CH_2$), 2.05 (s, 3H, $-CH_3$), 1.72 (m, 9H, C_4H_9). UV-vis (ethanol) λ_{max}: 350, 485 nm. Elem. Anal. Calcd for $C_{21}H_{22}O_4N_2$: C, 38.25%; H, 6.01%; N, 7.65%. Found: C, 38.05%; H, 5.88%; N, 7.61%.

4′-(methacryloxy)hexyloxy-4-nitroazobenzene (M2) Orange crystals; yield 50%; mp 72°C (by DSC). ^{1}H NMR ($CDCl_3$), δ(ppm): 8.02 (d, 2H, Ar), 8.34 (d, 2H, Ar), 7.68 (d, 2H, Ar), 7.10 (d, 2H, Ar), 6.30 (s, 1H, $=CH_2$), 5.95 (s, 1H, $=CH_2$), 2.20 (s, 3H, $-CH_3$), 4.10 (m, 2H, $ArOCH_2$), 3.9 (m, 2H, $HOCH_2$) 1.72 (m, 4H, H_2). UV-vis (ethanol) λ_{max}: 365, 490 nm. Elem. Anal. Calcd for $C_{21}H_{25}O_5N_3$: C, 61.74%; H, 4.18%; N, 13.50%. Found: C, 61.70%; H, 4.16%; N, 13.52%.

TABLE 1 Characteristics of Polymeric Azoesters

Compound	T_g, °C	λ_{max}, nm	M_n	M_w	M_w/M_n
P1	123	331	3500	4410	1.26
P2	112	343	5000	6900	1.38



SCHEME 1 Synthetic route for the azomonomers.

Polymerization. Homopolymers were synthesized by free-radical polymerization in toluene. The polymerization was carried out in 10 wt % toluene solution of monomer with AIBN as a free radical initiator (1 wt % of monomer) at 80°C for more than 30 h. Polymers were isolated from the reaction solution by precipitation into methanol followed by reprecipitation from toluene into methanol and then dried at 20°C overnight. The synthetic procedure was described previously [8] in detail.

The obtained polymers were dissolved in dimethylformamide. The solutions of polymers were filtered through a 0.2 μm nylon filter before using.

2.2. Instruments for Characterization

The synthesized azopolymers and organic intermediates were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR (400 MHz) spectra were recorded on a "Mercury-400" spectrometer using $CDCl_3$ as a solvent. Chemical shifts are in ppm from the internal standard tetramethylsilane (TMS). The obtained results are in agreement with the proposed structures.

The phase transitions were studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC-2 instrument equipped with a IFA GmbH processor at a scan rate of 20°C/min. The calorimetry calibration was carried out according to the well-known recent recommendation [9–11] using sapphire and quartz as standard.

2.3. Degenerate Four-Wave Mixing Experiment

Nonlinear optical properties of the solutions of **P1** and **P2** ($C = 12\,g/l$) were investigated using the DFWM method. Various experimental techniques can be used for estimating the third-order nonlinearity of the given materials, even though each technique addresses only a particular facet of the nonlinearity due to the frequency dispersion of $\chi^{<3>}$. The DFWM measurements were performed using a Nd:YAG laser (Quantel Model YG472) working at 532 nm with the 30-ps duration of pulses and the 1-Hz repetition rate [12]. In this experiment, three optical pulses (two pump beams I_1 and I_2 and a probe beam I_3) were obtained by using two beam splitters (Fig. 2).

Carbon disulfide (CS_2) was used as a reference material to calibrate the DFWM measurements ($\chi^{<3>}_{CS_2} = 1.11 \times 10^{-12}$ esu). The **P1** and **P2** were contained in 2-mm-thick quartz cuvettes.

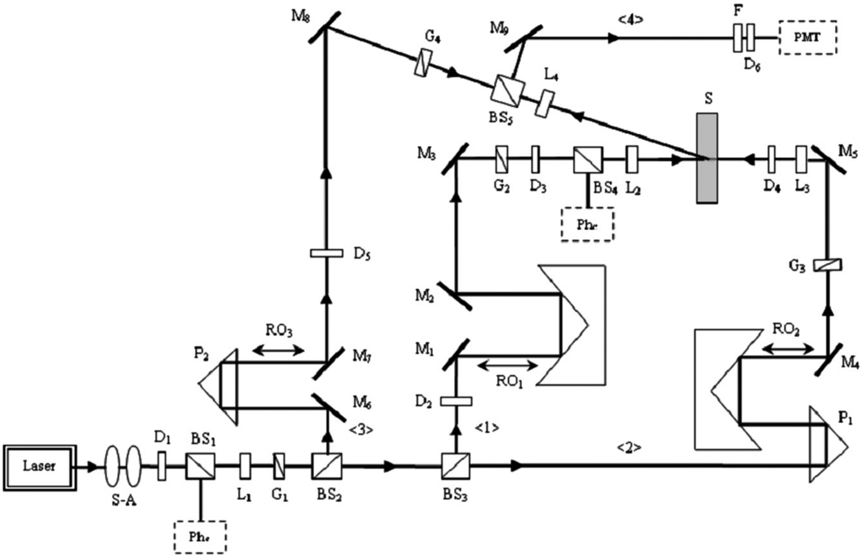


FIGURE 2 Experimental set up of DFWM: *S* – sample, *RO* – delay lines, *G* – Glan prism, Ph_s and Ph_c – synchronization and control photodiodes, *BS* – beam-splitters, PMT – photomultiplier tube, <1> and <2> – pump waves, <3> – probe wave, <4> – fourth wave.

The DFWM reflectivity (R) was calculated from the propagation equation of the four beams in interaction and took into account the linear and nonlinear absorption and can be expressed as follows [13–15]:

$$R = \frac{I_4(0)}{I_3(0)} = \frac{K^2}{\left[q\coth(qL) - \frac{\phi}{2}\right]^2}, \tag{1}$$

with

$$q^2 = \left(\frac{\phi}{2}\right)^2 - K^2, \quad \phi = -\alpha - 2\beta(I_1 + I_2),$$

and

$$K^2 = \left(\frac{48\pi^3}{n^2 c\lambda}\right)^2 \left[(\chi^{<3>\prime})^2 + (\chi^{<3>\prime\prime})^2\right] I_1 I_2, \tag{2}$$

where α, β, L, λ, and n are the linear absorption coefficient, nonlinear absorption coefficient, sample thickness, laser wavelength, and linear refractive index, respectively.

We used the nonlinear transmission measurement to determine the two-photon absorption coefficient (β) that corresponds to the imaginary parts of the third-order nonlinear optical susceptibility at 532 nm in the picosecond regime. We note that the investigated compounds exhibited only the linear absorption at the excitation wavelength.

Therefore, the only parameter that remains to be determined is the third-order nonlinear optical susceptibility $\chi^{<3>}$. Taking the linear and nonlinear absorption into account, the variation of the intensity of pump waves along the z-axis can be expressed as

$$\frac{dI}{dz} = -(\alpha + \beta I)I \tag{3}$$

The transmission can be calculated from the equation

$$T = \frac{I(L)}{I(0)} = \frac{\alpha e^{(-\alpha L)}}{\alpha + \beta I(0)(1 - e^{-\alpha L})}. \tag{4}$$

The best fit of Equation (4) to experimental data allows us to evaluate the coefficients α and β. Thus, knowing the analytic formula for the DFWM reflectivity R and measuring the I_4 intensity, we can determine the absolute value of $\chi^{<3>}$.

The geometry of the DFWM experimental setup is presented in Figure 2. As a source of excitation, we used 532-nm pulses from a Q-switched mode locked Quantel Nd:YAG laser of the 30-ps duration with a repetition frequency of 1 Hz. The first beam-splitter divides the beam to synchronize the acquisition from a fast photodiode. A Glan prism (G) and a half-plate ($\lambda/2$) allow us to modify the intensity of laser beams. The second beam-splitter reflects about 6% of the intensity (probe beam <3>). The non-reflected part of a beam goes to the next (third) beam splitter which divides it into two pump beams <1> and <2>. Their intensities satisfy the relation $I_1(z=0) = I_2(z=L)$. The probe wave <3> is a weak probe beam ($I_3 = 10^{-2}\, I_1$) which makes an angle of 12° with the direction of the two pump waves. The signal wave <4> is emitted in the opposite direction to the probe beam.

3. RESULTS

The calculated values of linear absorption coefficient (α), nonlinear absorption coefficient (β), and third-order nonlinear optical susceptibility ($\chi^{<3>}$) are collected in Table 2.

We chose NLO active substances for comparison such as Liquid Crystals (**LC**) and Cobalt Phthalocyanine (**CoPc**) which are known for their strong nonlinear optical properties [17]. We observed that the third-order nonlinear optical susceptibility ($\chi^{<3>}$) of the polymers under study is one order of magnitude higher than that of **LC**. In the case of **CoPc**, the value of the third-order nonlinear optical susceptibility ($\chi^{<3>}$) is higher than that of **P1** and **P2**. These polymers have a number of advantages, first of all their homogenized film-forming and further application in devices (microdevices such as micromachines and microelectronic mechanical systems). In general, polymeric materials have gained a wide popularity in various fields, because plastics have a low specific gravity and are chemically inert.

TABLE 2 Values of the Linear Absorption Coefficient (α) and the Absolute Values of the Third-Order Nonlinear Optical Susceptibility ($\chi^{<3>}$) of **P1** and **P2** Dissolved in **DMF**; and those for Cobalt Phthalocyanine (**CoPc**) and Liquid Crystal (**LC**) for Comparison

Sample	α, cm^{-1}	β, cm/GW	$\chi^{<3>}_{DFWM}$, 10^{-13} esu
DMF	0.19	0.01	1.38
P1	1.83	0.01	2.26
P2	4.76	0.02	3.71
CoPc	5.11	0.32	25.20 [16]
LC	9.92	≈0	0.30 [16]

4. CONCLUSION

Two homopolymers containing azoesters in the side chain were synthesized by the thermoinitiated free-radical polymerization process and characterized. In this paper, we evaluated the linear and nonlinear absorption coefficients and the third-order NLO susceptibility of various polymeric azoesters. These parameters have been measured within the degenerate four-wave mixing method at a fundamental wavelength of 532 nm in the picosecond regime. We also show that the synthesized polymer **P2** gives a larger effect on the NLO response. We suggest that the value of the third-order nonlinear optical susceptibility is determined by a steric delocalization of the active side chain of azoester.

REFERENCES

[1] Luc, J., Niziol, J., Sniechowski, M., Sahraoui, B., Fillaut, J.-L., & Krupka, O. (2008). *Mol. Cryst. Liq. Cryst.*, *485*, 248.

[2] Sutherland, R. L. (1996). *Handbook of Nonlinear Optics*. Marcer Dekker: New York.

[3] Kumar, G. S. (1992). *Azo Functional Polymers: Functional Group Approach in Macromolecular Design*. Technomic Publication: Lancaster.

[4] Demus, D., Goodby, J., Gray, G. W., Spiess, H. W., & Vill, V. (1998). *Handbook of Liquid Crystals*. Wiley-VCH: New York.

[5] Sekkat, Z. & Knoll, W. (2002). *Photoreactive Organic Thin Films*. Academic Press: Amsterdam.

[6] Fritz, A., Schonhals, A., Sapich, B., & Stumpe, J. (1999). *Macromol. Chem. Phys.*, *200*, 2213.

[7] Czaplicki, R., Krupka, O., Essaidi, Z., El-Ghayoury, A., Grote, J.G., Kajzar, F., & Sahraoui, B. (2007). *Optic Express*, *15*, 15268.

[8] Nadtoka, O., Syromyatnikov, V., & Olkhovykh, L. (2005). *Mol. Cryst. Liq. Cryst.*, *427*, 259.

[9] Wunderlich, B., Boller, A., Okazaki, I., & Ishikiriyama, K. (1997). *Thermochim. Acta*, *304–305*, 125.

[10] Ribeiro, M. & Grolier, J.-P. (1999). *Eur. J. Thermal Anal. & Calorimetry*, *57*, 253.

[11] Wunderlich, B. (2003). *Prog. Polymer Sci.*, *28*, 383.

[12] Sahraoui, B. & Rivoire, G. (1997). *Opt. Comm.*, *138*, 109.

[13] Smokal, V., Czaplicki, R., Derkowska, B., Krupka, O., Kolendo, A., & Sahraoui. B. (2007). *Synth. Met.*, *157*, 708.

[14] Smokal, V., Kolendo, A., Krupka, O., Derkowska, B., Czaplicki, R., & Sahraoui, B. (2008). *Mol. Cryst. Liq. Cryst.*, *485*, 269.

[15] Najun Li, Jianmei Lu, Qingfeng Xu, & Lihua Wang. (2006). *Opt. Mat.*, *28*, 1412.

[16] Derkowska, B., Jaworowicz, K., Krupka, O., Karpierz, M., Wojdyla, M., Bala, W., Sahraoui, B., Grote, J. G., & Kajzar, F. (2007). *J. App. Phys.*, *101*, 083112.

[17] Collings, P. J. & Patel, J. S. (1997). *Handbook of Liquid Crystal Research*, Oxford University Press: New York.