Synthesis and Characterization of Novel Polyarylates Bearing NLO Moieties

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ABSTRACT: A series of thermally stable second-order nonlinear optical polyarylates containing azo side-chain groups have been obtained by interfacial polycondensation. Theoretical calculations of the static hyperpolarizabilities, first- and second-order hyperpolarizability, were carried out. The structures of the obtained monomers and polymers were confirmed by infrared, ^{1}H NMR and ultraviolet spectroscopies. Thermal and optical properties of the obtained polymers were evaluated. The investigations show that some of the new polymers obtained in this study may find use in optical applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2195–2201, 2006

Key words: nonlinear optical polyarylates; thiazolyloazo chromophores; theoretical calculation of β_0 and γ_0

INTRODUCTION

The present study is the continuation of our research on polyarylates with nonlinear-optical (NLO) properties.[1–6] In the light of the recent communications in the literature, we know that polymeric NLO systems are composed of two components: a chromophore and polymer. To obtain the required NLO properties, these components must be correctly connected, either in the chemical or in the physical way.

In this article, we present a novel type of a polymeric system, where the chromophore molecules simultaneously play the role of side groups and are an integral part of the main backbone. The "guest-hosts" systems, which were so interesting and widely researched a few years ago, now lost the center of attention, because they do not guarantee thermal stability. Their chromophore molecules are not joined together by covalent bonds, and hence at higher temperatures, they begin to shift along the polymeric chains, and the system loses its nonlinear properties. Low thermal resistance (low values of T_g) and fast relaxation of nonlinear properties prohibit application of these systems in the design of optical and electrooptical properties.[7,8]

A better perspective awaits systems with chemical bonding between chromophores and the polymer chain. A significantly higher glass transition temperature (T_g) had been registered for these systems, from which follows an increase in thermal resistance. In an ordered structure, the relaxation of nonlinear properties is restricted in comparison with "guest-host" systems. An additional advantage is established by the possibility of obtaining high concentration of chromophores without the risk of phase separation of crystallization. Such problems occur during the synthesis of "guest-host" systems.

Much interest is still induced by systems with side chain or a main chain based on polyarylates[9] and polymethacrylates,[10,11] and lately also on polyimides[12–14] and polyurethanes.[15]

It follows from the literature that the latter-mentioned polymers are characterized by high glass-transition temperatures, which is a positive prognosis for their future applications in optoelectronics.

However, the choice of thermoresistant aromatic polyesters[16] as a basis to introduce the appropriate chromophores seems by all means correct, because contrary to polyimides, the synthesis of polyarylates can be carried out at low temperatures, and the polymer undergoes far easier transformations by traditional methods.

Dyes are the compounds that could play the role of NLO elements in polymeric systems. Communications in the literature quote the hyperpolarizability of dyes,[17,18] reaching high values for appropriate structures; e.g., dyes containing a heterocyclic ring.

Therefore, in this study, thiazole derivatives were utilized in the synthesis. The azo-dyes (special monomers) were obtained as a product of coupling diazo-

Figure 1 Structures of the obtained compounds.

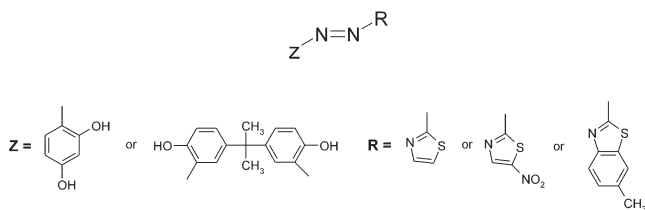**Scheme 2** Structure of MON 2.

nium salts of variously substituted 2-aminothiazole with bisphenol A or with resorcinol.[19] In this way, after the incorporation of the chromophore into the polymer chain, a new group of polyarylates was obtained, where the alkyl groups of bisphenol A play the role of electron donors, and side azo-groups with a substituted thiazole ring show properties of acceptors.
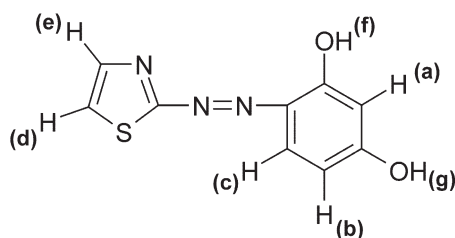
EXPERIMENTAL

Measurement

^{1}H NMR spectra were recorded with a Gemini 200 spectrophotometer. IR spectra were measured with a Specord M-80Z Carl Zeiss Jena spectrophotometer. UV/vis spectra were recorded with a Lambda 2 PerkinElmer spectrophotometer at 250–600 nm wavelength and gap width of 1 nm.
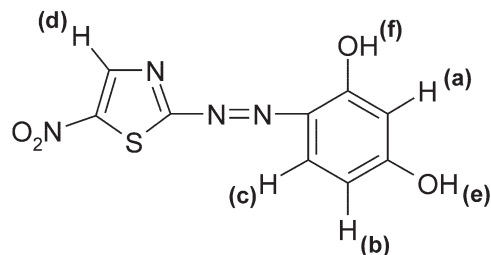
Methanol was used as solvent for monomers, and dichloromethane was used as a solvent for polymers. Refractive indexes were determined by the transmission spectrum measurement by means of a UV–vis PerkinElmer LAMBDA 40 spectrophotometer.

Synthesis

At first, the synthesis of azo dyes was performed. These dyes were then incorporated into the polymer chain as special monomers to obtain polymers with nonlinear optical (NLO) properties. The synthesis consisted of two parts: in the first one, the amino compounds were transferred to diazonium salts, and in the second one, the resultant salts were subjected to conjugation reaction with resorcinol and bisphenol-A. The obtained compounds are presented in Figure 1.

### MON 1, MON 2, MON 3 synthesis

About 0.05 mol of a thiazole derivative was dissolved in 40 mL of HCl; the solution was then cooled to 0°C, and 3.5 g of $NaNO_2$ in water was slowly added. The reaction progress was controlled by a starch iodide paper. Finally, the solution of diazonium salt was slowly poured into a well-cooled solution of 3.4 g resorcinol in 60 mL of $4N$ HCl. The resultant solution was cooled at 0°C for 30 min. Afterwards, a solution of 60 g of sodium acetate in 180 mL of water was added. The coupling reaction was carried out at 0°C during 2 h. The precipitate was washed by rinsing with water.

MON4, MON 5, MON 6 synthesis

About 0.1 mol of thiazole derivative was dissolved in a mixture of concentrated sulfuric acid and acetic acid. The solution was cooled in an ice bath. An appropriate amount of $NaNO_2$ dissolved in water was slowly added to the cooled thiazole solution with vigorous stirring. The mixture was cooled for 10 min. The diazonium salt solution was then slowly added to 0.051 mol of 1,1-dichloro-2,2,-bis(4-hydroxy-phenyl)-ethene dissolved in 208 mL of acetic acid. The clear solution was cooled for 30 min, and then, 100 g of sodium acetate in 300 mL of H_2O was added. The obtained precipitate was filtered, purified with $NaOH_{aq}$, acidified with $4N$ HCl, and crystallized from ethanol.

4-[(Thiazol-2-yl)azo]resorcinol (MON 1): Product, orange powder; yield, 49%; m.p., 220°C.
^{1}H NMR: δ = 6.48 (d, $H_{(d)}$, J = 2.4 Hz); 6.68 (d, $H_{(e)}$, J = 2.6 Hz); 7.68 (d, $H_{(b)}$, J = 4 Hz); 7.78 (s, $H_{(a)}$); 7.96 (d, $H_{(c)}$, J = 3.2 Hz); 12.43 (bs, $2H_{(f, g)}$, OH).

Scheme 1 Structure of MON 1.
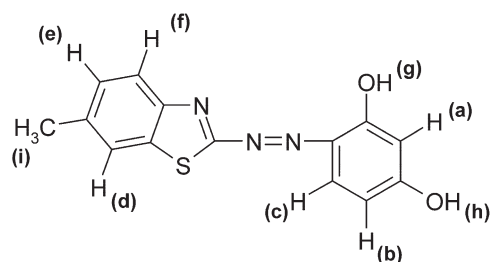
Scheme 3 Structure of MON 3.
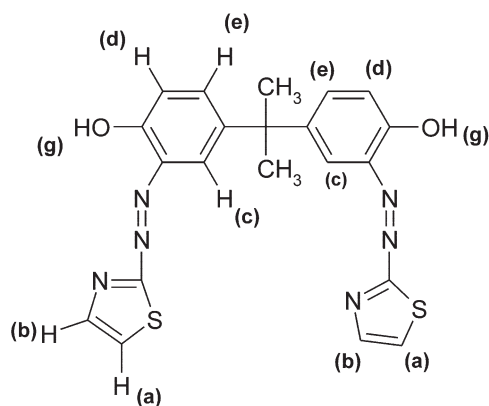
Scheme 4 Structure of MON 4.

IR (KBr): 3400 (OH); 1628 cm^{-1} (N=N—).

4-[(5-Nitrothiazol-2-yl)azo]resorcinol (MON 2): Product, violet powder; yield, 48%; m.p., 192°C.

^{1}H NMR: δ = 7.89 (m, 2H$_{(e, f)}$, OH); 8.05 (s, H$_{(a)}$); 8.38 (s, 2H$_{(b, c)}$); 8.51 (s, H$_{(d)}$).

IR (KBr): 3384 (OH); 1620 cm^{-1} (—N=N—).

4-[(6-Methylbenzothiazol-2-yl)azo]resorcinol (MON 3): Product, brown powder; yield, 42%; m.p., 231°C.

^{1}H NMR: δ = 2.50 (s, 3H$_{(i)}$, CH$_3$); 2.94 (bs, 2H$_{(g, h)}$, OH); 6.74 (d, H$_{(b)}$, J = 8.8 Hz); 7.06 (d, H$_{(c)}$, J = 8.8 Hz); 7.83 (s, H$_{(a)}$); 7.42 (s, H$_{(d)}$); 7,99 (d, 2H$_{(e, f)}$, J = 8.8 Hz).
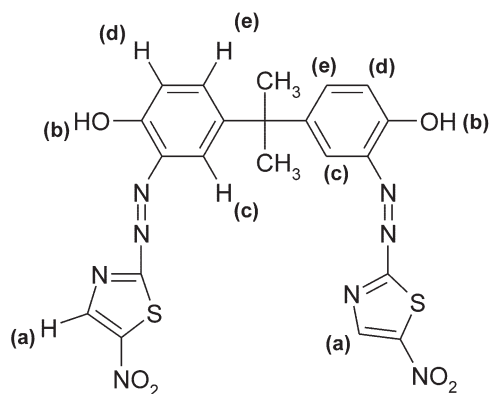
IR (KBr): 3428 (OH); 1628 cm^{-1} (—N=N—).

2,2-Bis[(3-thiazol-2-yl)azo-4-hydroxyphenyl]propane (MON 4): Product, rusty powder; yield, 58%; m.p., 178°C.

^{1}H NMR: δ = 1.95 (s, 6H, CH$_3$); 5.50 (bs, 2H$_{(g)}$, OH); 7.02–7.08 (m, 4H$_{(a),(b)}$); 7.66 (d, 2H$_{(e)}$, J = 3.2 Hz); 7.90 (d, 2H$_{(d)}$, J = 9 Hz); 8.05 (d, 2H$_{(c)}$, J = 3.4 Hz).
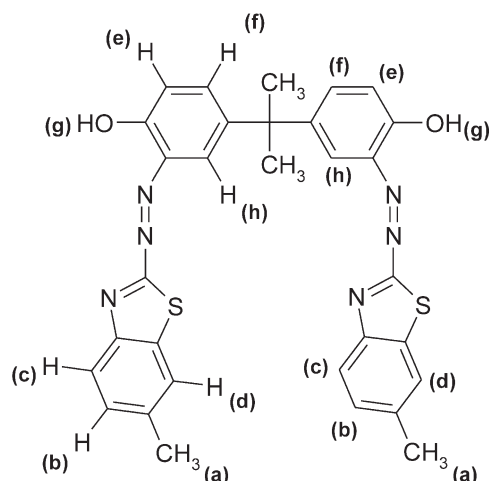
IR (KBr): 3432 (OH); 1604 cm^{-1} (—N=N—).

2,2-bis[3-(5-nitrothiazol-2-yl)azo-4-hydroxyphenyl) propane (MON 5): Product, dark brown powder; yield, 48%; m.p., 176°C.

^{1}H NMR: δ = 1.69 (s, 6H, CH$_3$); 4.05 (s, 2H$_{(b)}$, OH); 6.78–7.13 (m, 4H$_{(e),(c)}$); 7.99 (d, 2H$_{(d)}$, J = 9.6 Hz); 8.79 (s, 2H$_{(a)}$).

Scheme 6 Structure of MON 6.

IR (KBr): 3452 (OH); 1592 cm^{-1} (—N=N—).

2,2-Bis[3-(6-methylbenzothiazol-2-yl)azo-4-hydroxy-phenyl]propane (MON 6): Product, cherry powder; yield, 56%; m.p., 182°C.

^{1}H NMR: δ = 2.01 (s, 6H, CH$_3$); 2.29 (s, 6H$_{(a)}$); 3.15 (sb, 2H$_{(g)}$, OH); 7.09–7.40 (m, 6H$_{(h),(e),(f)}$); 7.79–7.97 (m, 6H$_{(b),(c),(d)}$).

IR (KBr): 3352 (OH); 1604 cm^{-1} (—N=N—).

Polymer synthesis

The polymers were obtained by interfacial polycondensation of bisphenol A, special monomers, and a mixture of acidic chlorides (iso- and terephthalic at a 1 : 2 ratio) in the presence of an interfacial transfer catalyst TEBA-Cl. Physicochemical and optical studies of the polymers obtained were carried out. General formulas for polyarylates are presented in Figure 2.

To confirm that the special monomer was indeed introduced into the main polymer chain, the UV–vis spectra were obtained for selected polyarylates (Fig. 3).
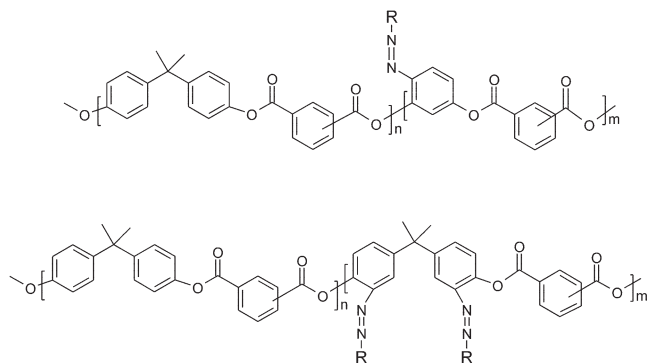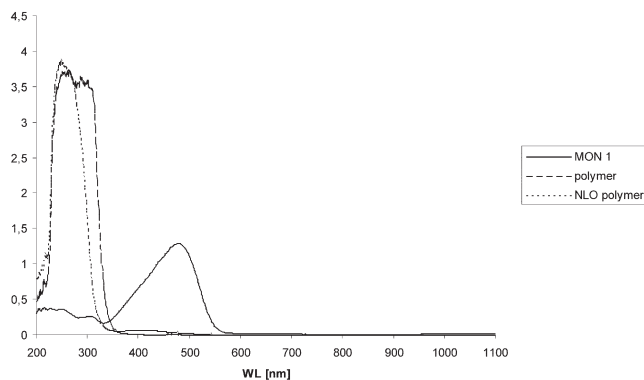

Scheme 5 Structure of MON 5.

Figure 2 Structures of the obtained polymers.

Figure 3 The UV–vis spectra of polymer containing special monomer.

RESULTS AND DISCUSSION

Theoretical calculations

The possibility of the application of chromophores as special monomers in NLO polymer synthesis depends mainly on the values of chromophore hyperpolarizability. These values can be estimated by theoretical calculations.[20] In our research, the compound's geometry optimization, static first-order hyperpolarizability, and dipole moment calculation were performed using the HF method, with the 6–21G basis included in the Gaussian 98 program (Table I) and PM3 method included in MOPAC93 (Table II). The values of the average first-order hyperpolarizability were evaluated from the following formula:

$$\beta_{av} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}$$

where $\beta_i = \beta_{iii} + \dfrac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$.

Calculations of the second-order hyperpolarizability were performed by the MOPAC93 package utilizing the semiempirical PM3 method (Fig. 4). The results are listed in Table II.

TABLE I
Results of Theoretical Calculations Obtained in Gaussian98

	Dipole moment (D)	Average β_0 (esu)
MON 1	2.01	1.04×10^{-29}
MON 2	8.61	2.70×10^{-29}
MON 3	1.46	8.88×10^{-30}
MON 4	4.04	4.14×10^{-30}
MON 5	10.21	2.40×10^{-29}
MON 6	3.85	1.38×10^{-29}

TABLE II
Results of Theoretical Calculations Obtained in MOPAC93

	Dipole moment (D)	Average β_0 (esu)	Average γ_0 (esu)
MON 1	4.37	1.32×10^{-29}	7.21×10^{-35}
MON 2	19.67	2.84×10^{-29}	1.29×10^{-34}
MON 3	2.21	1.46×10^{-29}	1.38×10^{-34}
MON 4	17.81	7.23×10^{-30}	3.66×10^{-35}
MON 5	24.17	2.62×10^{-29}	1.82×10^{-34}
MON 6	7.80	1.18×10^{-29}	2.17×10^{-34}

The β_0 and γ_0 values for the chromophores obtained differ by one order of magnitude from those characterizing dyes with an azomethine bond, which shows that they can be the better candidates for the synthesis of compounds bearing NLO properties.

Intrinsic viscosity

The polymers dissolved best in tetrachloroethane, dichloromethane, and chloroform. In the remaining solvents (hexane, toluene, and ethyl acetate), they underwent swelling or did not dissolve at all. The type of polymer did not affect the results of the solubility studies. All the polymers exhibited very good film-formation properties, yielding good quality resistant membranes.

The measurement of molecular weights of polyarylates were carried out by the viscosimetric method, at 25°C. The coefficients in the M-H equations are not known, and therefore, only the intrinsic viscosity was determined. For each of the polymers, three solutions in dichloromethane were prepared, with the following concentrations: 0.002, 0.0032, and 0.005 g/mL.

The experimental results are presented in graphs of $\eta_{red} = f(c)$ relation. The intrinsic viscosity was determined by extrapolation of the $\eta_{red} = f(c)$ dependence down to the zero concentration. A comparison of results is presented in Table III. Gel permeation chromatography was performed to check the distribution of molecular weights.

The polyarylates with 1% concentration of a dye based on resorcinol and 2-amino-5-nitrothiazole [PAR 9] had the highest intrinsic viscosity value.

The lowest value of intrinsic viscosity was determined for the polymer with 4% concentration of a special monomer based on bisphenol A and 2-amino-5-methylbenzothiazole [PAR 19]. A general relationship was noted that intrinsic viscosity decreased with an increase in the percentage concentration of the special monomer in the polymer.

Polymers PAR 7 PAR 8 and also PAR 12 and PAR 14 were an exclusion to this relationship. For the case of polymers with the dye based on bisphenol and substituted 2-aminothiazole, an opposite relation-
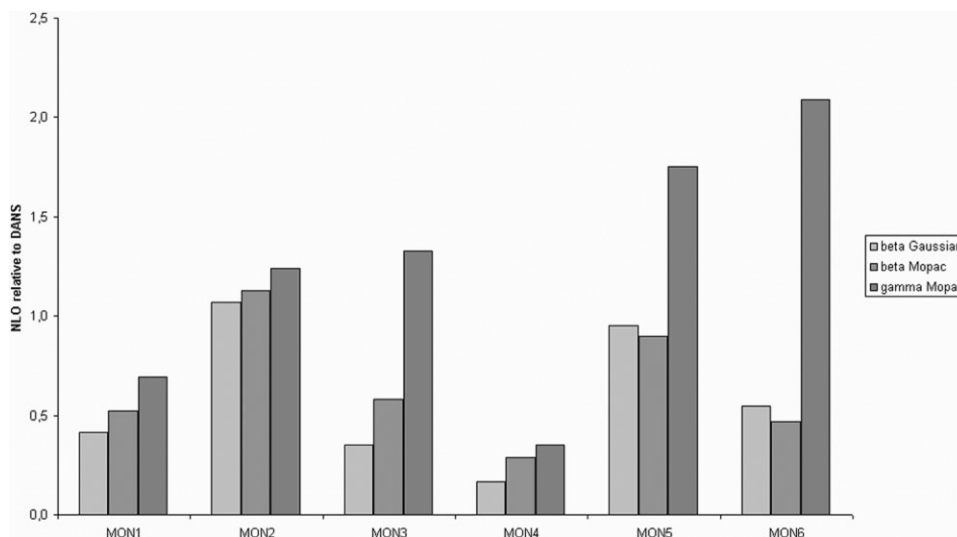
Figure 4 The values of hyperpolarizabilities relative to DANS ($\beta_0 = 4.04 \times 10^{-29}$ esu, $\gamma_0 = 1.04 \times 10^{-34}$ esu).

ship was observed, i.e., intrinsic viscosity increased with an increase in the percentage concentration of the special monomer.

Thermal properties

The analysis was carried out under the atmosphere of air with a heating rate of 20°C/min in temperature range 100–300 °C. Mass of the samples was 13–17 mg.

Selected three polyarylates were subjected to analysis. They were characterized by different intrinsic viscosity values. The second polyarylate contained an azo monomer. The glass transition temperatures are presented in Table IV.

The polymers exhibit high thermostability. Their glass transition temperatures exceed 200°C, and the temperatures of decomposition are above 300°C.

Optical measurements

The measurements of refractive indexes and absorption coefficients were performed for selected polymers containing special azo bonds as monomers. The transmittance was recorded with a UV–vis PerkinElmer Lambda 40 spectrometer (Fig. 5). The measurements were carried out for polymer film samples based on the quartz substrate. The samples investigated contained 6% of the special monomer. The transmittance measurements were carried out for the 400–1100 nm wavelength range.

From the analysis of experimental data, the refractive indexes and absorption coefficients were determined. The refractive index dependence on wavelength is presented in Figure 6.

The values of refractive indexes for the polymers investigated were low, in the range of 1.52–1.61. The curves diminish with an increase in wavelength and then assume a constant value.

From the literature data, it follows that an increase in the chromophore concentration in the polymer matrix is accompanied by a respective increase in the refractive index. Therefore, we expect a similar correlation between the chromophore concentration and the refractive index. The polymeric films we investi-

TABLE III
Intrinsic Viscosity of the Polyarylates

Polymer	Special Monomer	Concentration (%)	Intrinsic viscosity (10^2 cm^3/g)
PAR 0	None	0	1.122
PAR 2	MON 1	2	1.672
PAR 4	MON 1	6	1.137
PAR 5	MON 4	1	0.719
PAR 6	MON 4	2	0.676
PAR 7	MON 4	4	0.849
PAR 8	MON 4	6	1.187
PAR 9	MON 2	1	2.080
PAR 10	MON 2	2	1.613
PAR 12	MON 5	2	0.709
PAR 14	MON 5	6	0.724
PAR 18	MON 6	2	0.580
PAR 19	MON 6	4	0.312

TABLE IV
Result of the Glass Transition Temperature Measurement

Polymer	Special monomer content (%)	Glass transition temperature (°C)
PAR 10	2	200
PAR 14	6	203
PAR 19	4	211
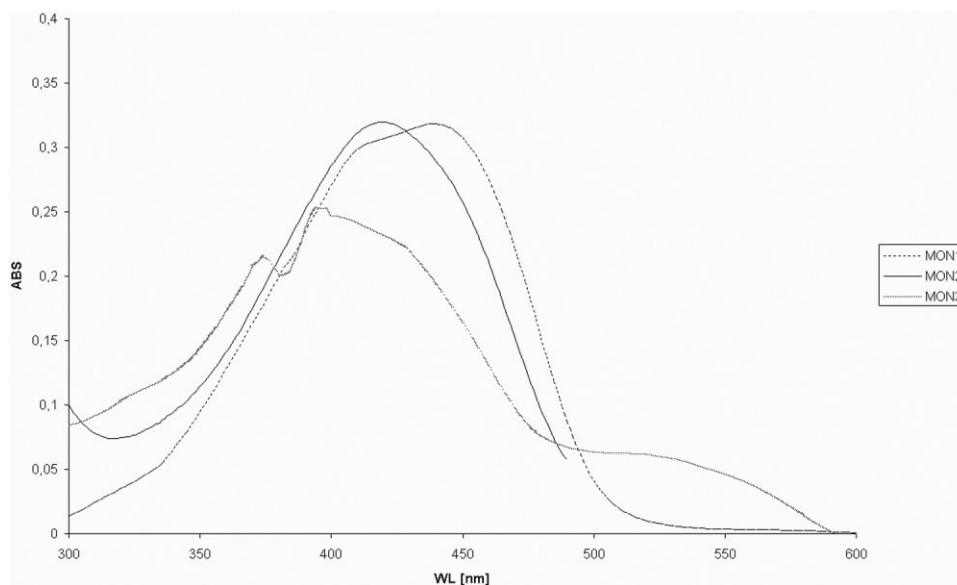
Figure 5 UV–vis spectra of (a) MON 1, MON 2, and MON 3; (b) MON 4, MON 5, and MON 6.

gated exhibited also low absorption coefficients. In the case of polymers PAR8 and PAR15, their values were in the range of 52–127, for the wavelength range of 400–1200. Only for polymer PAR13, the absorption coefficient is slightly higher.

CONCLUSIONS

On the basis of the presented investigations, it can be concluded that polyarylates are a group of polymers that could find possible application in optoelectronics.

In comparison with the group of PMMA derivatives and polyimides, widely used in NLO, their electric properties are better and the glass transition temperatures higher. The values of optical coefficients are also more suitable for applications, with comparable temporal stability of NLO properties.

These compounds can be synthesized by simple and cost-effective chemical processes, which is a fair prognosis for their applications in optoelectronics. A prototype of an optical modulator is an evidence for this.[4]
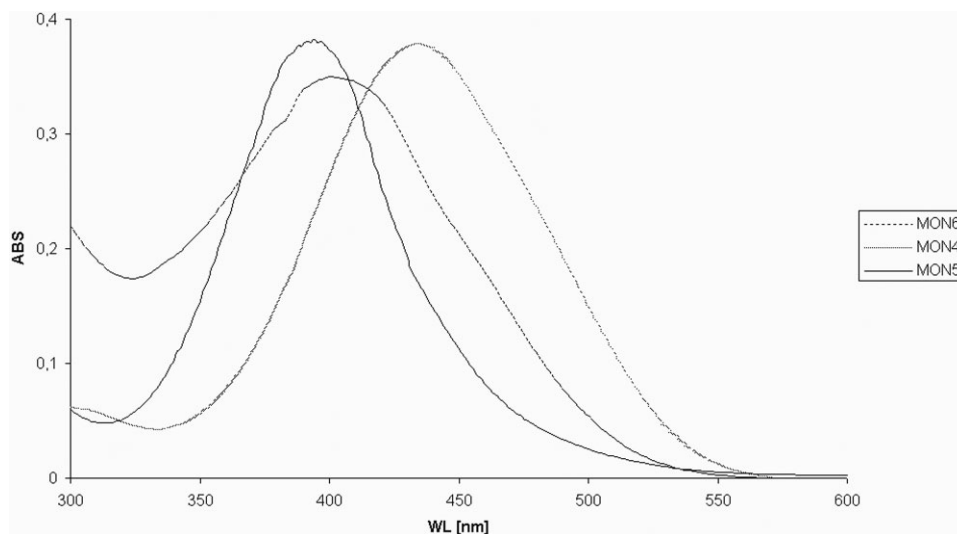
Figure 6 UV-Vis spectra of MON 4, MON 5 and MON 6.
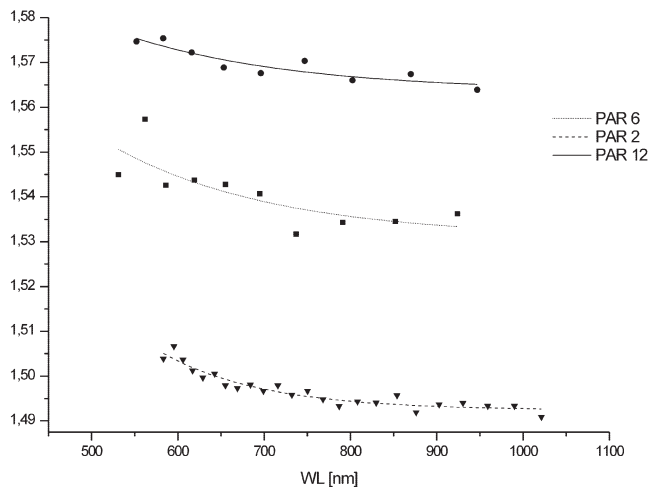
Figure 7 The values of refractive index. 77×58mm (600 × 600 DPI).

References

1. Zadrożna, I.; Parzuchowski, P.; Brzozowski, Z.; Milburn, G. H. W. J Appl Polym Sci 1999, 71, 1017.
2. Zadrożna, I.; Mysłek, M.J Appl Polym Sci 2001, 80, 1374.
3. Pura, B.; Osuch, K.; Zadrożna, I.; Piramidowicz, R.; Wierzbicki, M. Mol Phys Rep 2004, 39, 229.
4. Pura, B.; Zadrożna, I.; Mączeński, Z.; Tadeusik, A.; Ratusznik, G. In Proceedings of the International School of Quantum Electronics, 39th course Microresonators as building blocks for VLSI photonics, Erice, Sicily, Italy, October 18–25, 2003.
5. Zadrożna, I.; Kaczorowska, E.; Woliński, J. In 11th International Conference on Polymers and Organic Chemistry, Prague, July 18–23, 2004.
6. Zadrożna, I.; Wierzbicki, M.; Kaczorowska, E.; Osuch, K. In 11th International Conference on Polymers and Organic Chemistry, Prague, July 18–23, 2004.
7. Lindsay, G. A. Tren Polym Sci 1997, 5, 91.
8. Kajzar, F.; Lee, K. S.; Jen, A. K. Adv Polym Sci 2003, 161, 1.
9. Noniewicz, K.; Brzozowski, Z. React Funct Polym 1997, 33, 343.
10. Xie, H. Q.; Liu, Z. H.; Liu, H.; Guo, J. S. Polymer 1998, 39, 2393.
11. Shirai, M.; Kawane, A.; Okamura, H.; Tsunooka, M. Polymer 2004, 45, 7519.
12. Jeng, R. J.; Chang, C. C.; Chen, C. P.; Chen, C. T.; Su, W. C. Polymer 2003, 44, 143.
13. Leng, W. N.; Zhou Y. M.; Xu, Q. H.; Liu, J. Z. Polymer 2001, 42, 9253.
14. Bruma, M.; Hamciuc, E.; Schultz, B.; Kopnick, T.; Kaminorz, Y.; Robinson, J. J Appl Polym Sci 2003, 87, 714.
15. Zhang, T.; Xi, K.; Chen, H.; Yu, X. J Appl Polym Sci 2004, 91, 190.
16. Zhang, H.; Westermoreland, P. R.; Farris, R. J.; Coughlin, E. B.; Plichta, A.; Brzozowski, Z. K. Polymer 2002, 43, 5463.
17. Ostroverkhov, V.; Petschek, R. G.; Singer, K. D.; Twieg, R. J. Chem Phys Lett 2001, 340, 109.
18. Dalton, L. R. J Phys: Condens Matter 2003, 15, R897.
19. Vogel, A. I. Vogel's Textbook of Practical Organic Chemistry; Longman: London, 1978.
20. Garin, J.; Orduna, J.; Andreu, R. Synth Met 1999, 102, 1531.