

Novel Optical Material: Polyarylates with Azomethine Side-Chain Groups

I. ZADROŻNA, M. MYSŁEK

Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Received 3 January 2000; accepted 28 May 2000

ABSTRACT: A number of NLO polymers were obtained, in which aromatic polyester is a matrix and the chromophores are incorporated into the form of a side chain. Special monomers are based on 2,2-bis(3-amino-4-hydroxyphenyl)propane; they contain an azomethine bond and various electron-acceptor groups (nitro, cyanide, and fluoride) as substituents in the side-chain aromatic ring. The effect of the type of the electron-acceptor substituent, its substitution position in the aromatic ring with respect to the azomethine bond, and special monomer concentration on the optical, mechanical, and thermal properties of the whole system was studied. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1374–1382, 2001

INTRODUCTION

Optically nonlinear polymers became recently the object of interest and intense studies are now being carried out in many laboratories worldwide.^{1–10} Easy processing (including the possibility of producing thin films, which enables the miniaturization of systems), low price, lightweight, and high-polarization possibilities are the advantages resulting from applying polymers as materials of NLO properties.¹¹ These features make polymeric materials very attractive for use in optoelectronic devices, which may revolutionize computational and communication technologies.¹²

It was found that many polymers studied so far, despite good optical properties, did not fulfill the stability condition at elevated temperature over a given time period. It has been shown that the polymer glass transition temperature (T_g) is the decisive parameter of the stability of the system^{13–17} and the best results are obtained for polymers exhibiting T_g values above 120°C.

A low-absorption coefficient in the range of the wavelengths applied, low specific conductivity at the orientation temperature, good optical properties, good dielectric properties, good film- and fiber-forming properties, as well as high mechanical strength are other conditions, which should be fulfilled by a polymer¹⁸ to be a material of good NLO properties.

Such properties are exhibited by aromatic polyesters, and, hence, the interest in such compounds in the studies on polymeric NLO systems.¹⁹ Studies carried out until now on NLO polyarylates did not provide satisfactory results. The use of a guest–host system²⁰ (in which the chromophore was not chemically bonded with the polymer matrix) or of systems in which the chromophore formed the polymer backbone, which weakened the physical–chemical properties of the entire system, was the main reason for this failure.²¹

Studies on polyarylates with chromophore molecules incorporated in the form of a side chain are presented in this article. Organic compounds comprising a conjugated π -bond system and exhibiting an acceptor–donor electronic effect are the monomers applied for the studies. These chro-

Correspondence to: I. Zadrozna.

Journal of Applied Polymer Science, Vol. 80, 1374–1382 (2001)
© 2001 John Wiley & Sons, Inc.

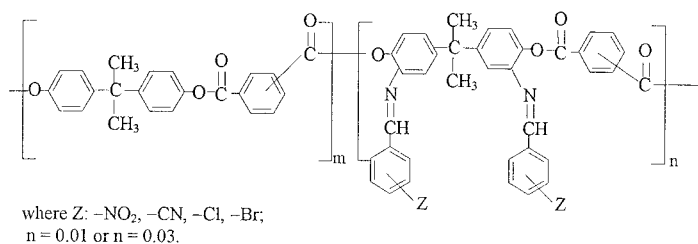


Figure 1 General formulas for polyarylates.

mophores contain an azomethine bond in their structure, which plays the role of a link between the polymer backbone and side chain, designed in such a way for the nitrogen atom to be found at the polymer backbone aromatic ring (contrary to the compounds studied earlier).^{21,22} The structure of these monomers consists of a number of electron-acceptor groups (Z), substituted at various positions of the aromatic ring.

An aromatic polyester obtained from interface polycondensation is the matrix of the polymer (Fig. 1).

Sixteen polymers were designed and obtained, for which various physical-chemical investigations were carried out, studying the influence of

- The type of substituent Z;
- Its substitution position (*ortho*-, *meta*-, *para*-) with respect to the azomethine bond;
- The number of chromophore groups (percentage contents of the special monomer in the polymer matrix: 0, 1, and 3%).

RESULTS

Monomers

UV-sensitive monomers were obtained from the reaction of 2,2-bis(3-amine-4-hydroxyphenyl)propane with appropriate benzoic aldehydes. The amine was obtained from the reduction of the nitro group of 2,2-bis(3-nitro-4-hydroxyphenyl)propane. The compound subjected to reduction was obtained from the nitration of 2,2-bis(4-hydroxyphenyl)propane.

Thus, the nitration of 2,2-bis(4-hydroxyphenyl)propane was the first step of the monomer synthesis. The facility of phenol nitration resulted in the problem of multisubstitution of the aromatic ring by the nitro group.^{23,24} Therefore, new methods and conditions of carrying out this reaction were sought.²⁵ A completely novel method of nitrating bisphenol A in a two-phase system was elaborated (Fig. 2).²⁶

A water-ether (diethyl Et₂O or *tert*-butylmethyl *t*-Bu-O-Me) system was applied. Sodium nitrate (1 mol) dissolved in a diluted mineral acid aqueous solution was the nitrating reagent. The bisphenol (0.5 mol) dissolved in the organic phase was added in portions to the aqueous phase. The reaction proceeds very mildly at ambient temperature. 2,2-Bis(3-nitro-4-hydroxyphenyl)propane precipitates during the reaction. The second nitro-substitution product is of a liquid form. The solid product, after filtering off from the postreaction mixture, was purified by crystallization from ethyl alcohol and was used for the further reaction stage, that is, the reduction of the nitro groups to a corresponding amine.

The reaction involving sodium borohydride was chosen from many possible reduction reactions of the nitro group to an amine. Metal hydrides do not reduce a majority of nitro compounds. However, aromatic and heterocyclic nitro compounds easily undergo (and in good yield) the reduction to corresponding amines upon the influence of sodium borohydride in an aqueous-alcohol solution in the presence of a catalyst (Fig. 3).

To a catalytic amount (0.002 mol) of palladium deposited on charcoal (palladium black), dis-

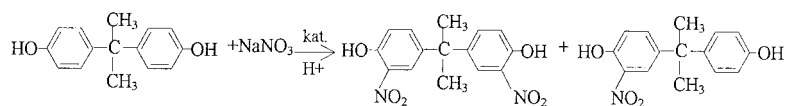


Figure 2 Nitration reaction of bisphenol A.

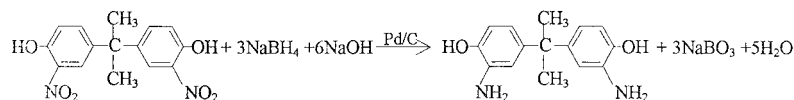
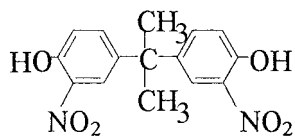


Figure 3 Reduction reaction.

solved in 20 mL of water, sodium borohydride (0.14 mol) dissolved in 30 mL of water was added and, in portions, a basic solution of sodium nitro-bisphenolate (0.01). The reaction was carried out at room temperature in an argon atmosphere. The postreaction mixture was acidified with hydrochloric acid to pH \sim 2 to remove the unreacted borohydride and then neutralized with a saturated solution of NaHCO₃. After extraction with diethyl ether, drying, and solvent evaporation, a corresponding amine was obtained, which was a solid product. This product was further utilized for the condensation with respective aldehydes in order to obtain special monomers. A number of benzaldehyde derivatives containing various electron-acceptor groups (*Z*) substituted at different positions of the aromatic ring were used for the condensation (Fig. 4).²⁷

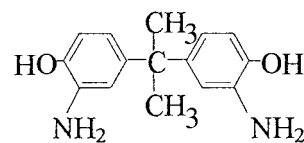
The reaction mixture, 2,2-bis(3-amine-4-hydroxyphenyl)propane (1 mol), an appropriate benzoic aldehyde (2.2 mol), and ethyl alcohol was heated to the boiling point of the solvent. The reaction was carried out under such conditions for 24 h. After ethanol evaporation, the postreaction mixture was alkalinized with a sodium base and extracted with ethyl ether. Depending on the benzoic aldehyde used, appropriate special monomers were obtained in the form of solid products.

SPECTROSCOPY



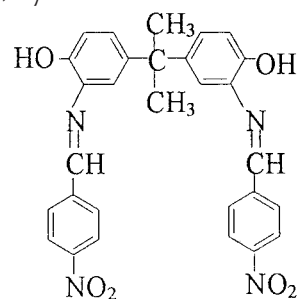
2,2-Bis(3-nitro-4-hydroxyphenyl)propane

¹H-NMR δ = 1.75 (s, 6H, CH₃); 7.11 (d, 2H_b, *J* = 8.8 Hz); 7.33 (dd, 2H_a, *J* = 2.44 Hz; *J* = 8.8 Hz); 8.04 (d, 2H_c, *J* = 2.38 Hz); 10.39 (s, 2H, OH); IR (KBr) = 3240 (ν_{valen} OH), 2968 (ν_{asym} CH₃), 2974 (ν_{sym} CH₃), 1536 (ν_{asym} NO₂), 1324 (ν_{sym} NO₂), 1260 (ν_{valen} C—O); cm⁻¹; *T*_{top} = 134–135°C; *R*_f: 0.371.



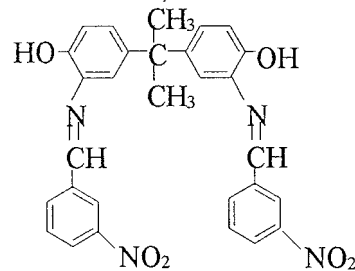
2,2-Bis(3-amino-4-hydroxyphenyl)propane

¹H-NMR δ = 1.47 (s, 6H, CH₃); 1.49 (d, 4H, NH₂, *J* = 5.6 Hz); 2.89 (s, 2H, OH); 6.84–6.33 (m, 6H, H_{aromat}); IR (KBr) = 3412 (ν_{valen} N—H); 3380 (ν_{valen} N—H); 2924 (ν_{valen} O—H); 1602 (ν_{deform} N—H); 1296 (ν_{valen} C—N); 1192 (ν_{valen} C—O); 780 (ν_{bend} N—H); cm⁻¹; *T*_{top} = 248–250°C; *R*_f: 0.181.



2,2-Bis[3-(iminomethyl-4-nitrophenyl)-4-hydroxyphenyl]propane

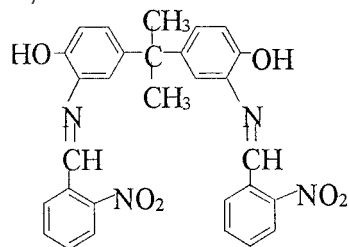
¹H-NMR δ = 1.29 (s, 6H, CH₃); 5.64 (s, 2H, OH); 8.46–7.71 (m, 14H, H_{aromat}); 10.22 (s, 2H, N=CH); IR (KBr) = 2924 (ν_{valen} O—H); 2884 (ν CH₃); 1608 (ν C=N); 1536 (ν_{asym} NO₂); 1346 (ν_{sym} NO₂); 1228 (ν_{valen} C—O); cm⁻¹; *T*_{top} = 88–90°C; *R*_f: 0.208.



2,2-Bis[3-(iminomethyl-3-nitrophenyl)-4-hydroxyphenyl]propane

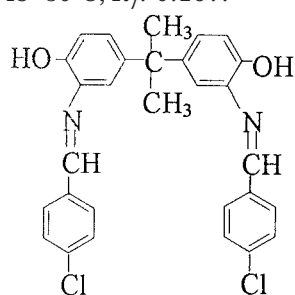
¹H-NMR δ = 1.24 (s, 6H, CH₃); 2.86 (s, 2H, OH); 8.72–7.76 (m, 14H, H_{aromat}); 10.16 (s, 2H, N=CH); IR

(KBr) = 2924 (ν_{valen} O—H); 1616 (ν C=N); 1534 (ν_{asym} NO₂); 1352 (ν_{sym} NO₂); 1204 (ν_{valen} C—O); cm⁻¹; T_{top} = 43–45°C; R_f : 0.122.



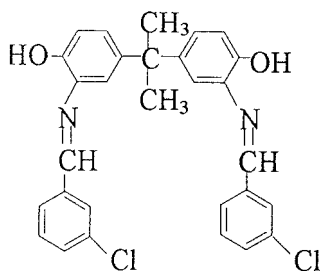
2,2-Bis[3-(iminomethyl-2-nitrophenyl)-4-hydroxyphenyl]propane

¹H-NMR δ = 1.27 (s, 6H, CH₃); 2.64 (s, 2H, OH); 8.18–7.83 (m, 14H, H_{aromat}); 10.36 (s, 2H, N=CH); IR (KBr) = 2928 (ν_{valen} O—H); 2856 (ν CH₃); 1572 (ν C=N); 1522 (ν_{asym} NO₂); 1376 (ν_{sym} NO₂); 1188 (ν_{valen} C—O); cm⁻¹; T_{top} = 48–50°C; R_f : 0.167.



2,2-Bis[3-(iminomethyl-4-chlorophenyl)-4-hydroxyphenyl]propane

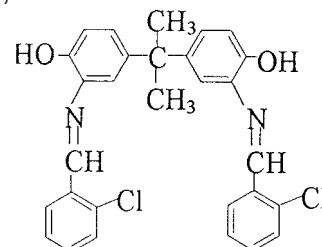
¹H-NMR δ = 1.27 (s, 6H, CH₃); 4.21 (s, 2H, OH); 8.03–7.51 (m, 14H, H_{aromat}); 10.02 (s, 2H, N=CH); IR (KBr) = 2920 (ν_{valen} O—H); 2850 (ν CH₃); 1684 (ν C=N); 1464 (ν_{deform} C—O); 1284 (ν_{valen} C—O); 1092 (ν Cl); cm⁻¹; R_f : 0.512.



2,2-Bis[3-(iminomethyl-3-chlorophenyl)-4-hydroxyphenyl]propane

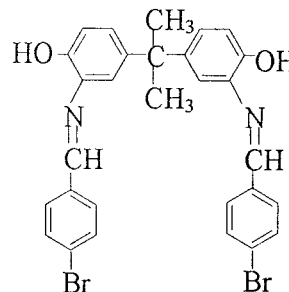
¹H-NMR δ = 1.29 (s, 6H, CH₃); 4.19 (s, 2H, OH); 7.98–7.25 (m, 14H, H_{aromat}); 10.04 (s, 2H, N=CH); IR

(KBr) = 2928 (ν_{valen} O—H); 2745 (ν CH₃); 1596 (ν C=N); 1376 (ν_{deform} C—O); 1276 (ν_{valen} C—O); 1076 (ν Cl); cm⁻¹; R_f : 0.219.



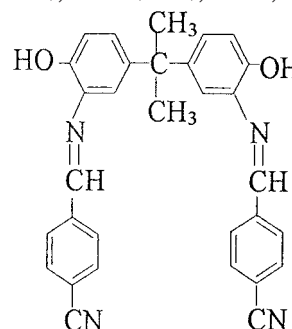
2,2-Bis[3-(iminomethyl-2-chlorophenyl)-4-hydroxyphenyl]propane

¹H-NMR δ = 1.34 (s, 6H, CH₃); 4.19 (s, 2H, OH); 7.92–7.43 (m, 14H, H_{aromat}); 10.44 (s, 2H, N=CH); IR (film) = 2932 (ν_{valen} O—H); 2536 (ν CH₃); 1592 (ν C=N); 1268 (ν_{valen} C—O); 1072 (ν Cl); cm⁻¹; R_f : 0.625.



2,2-Bis[3-(iminomethyl-4-bromophenyl)-4-hydroxyphenyl]propane

¹H-NMR δ = 1.27 (s, 6H, CH₃); 2.99 (s, 2H, OH); 7.97–7.68 (m, 14H, H_{aromat}); 10.03 (s, 2H, N=CH); IR (KBr) = 2924 (ν_{valen} O—H); 2856 (ν CH₃); 1586 (ν C=N); 1068 (ν_{valen} C—O); 1012 (ν Br); cm⁻¹; R_f : 0.367.



2,2-Bis[3-(iminomethyl-4-cyanophenyl)-4-hydroxyphenyl]propane

¹H-NMR δ = 1.27 (s, 6H, CH₃); 4.67 (s, 2H, OH); 8.22–7.86 (m, 14H, H_{aromat}); 10.16 (s, 2H, N=CH); IR (KBr)

Table II Limiting Viscosity Number of Polyarylates

Special Monomer Content (%)	Limiting Viscosity Number (100 cm ³ /g)							
	<i>o</i> -NO ₂	<i>m</i> -NO ₂	<i>p</i> -NO ₂	<i>o</i> -Cl	<i>m</i> -Cl	<i>p</i> -Cl	<i>p</i> -CN	<i>p</i> -Br
1	1.42	0.81	0.32	0.62	0.55	0.79	0.66	0.21
3	0.89	0.49	0.18	0.43	0.35	0.17	0.32	0.63

It was observed that polymers with a 1% content of the special monomer most often exhibit higher limiting viscosity numbers than do polymers with a 3% content of that monomer. At the same time, the size and position of substitution of the electron-acceptor group in the side-chain aromatic ring have a considerable effect on the value of the polymer limiting viscosity number and, hence, its molecular weight.

Tensile Strength

Tensile strength measurement is one of the methods of studying the mechanical properties of polymers and it consists in subjecting strips of a polymer film of known cross sections to static stretching with a determined rate. The measurement was carried out according to the Polish standard PN-81/C-89034 on an Instron Model 1115 apparatus (Table III).

No essential effect of the incorporated side chains on the mechanical properties of these polymers was found, since they showed values close to that of a polyarylate not containing chromophores in its structure (58.86 MPa). Thus, it can be assumed that the NLO polymers obtained will maintain their good mechanical properties, similar to that of pure polyarylates.

Glass Transition Temperature

The glass transition temperature was determined from the differential scanning calorime-

try traces. Polyarylates comprising chromophores with nitro groups as special monomers were studied (Table IV).

The results obtained indicate an influence of both the number of side chains in the polymer, as well as the substitution position of the electron-acceptor group in the side-chain aromatic ring on the glass transition temperature. The highest T_g value (214.1°C) was obtained for the *o*-NO₂ polymer (1%) and the lowest (174.3°C) for the *p*-NO₂ polymer (3%). An increase in the number of side chains (increase in the special monomer concentration) in the polymer causes a weakening of interactions between the particular polymer chains and, hence, a decrease in the T_g value. The elongation of the side chain (group at the *para* position) has a similar effect, which also causes a decrease in the glass transition value. However, all the results obtained indicate good thermal properties of the polymers and it seems that these polymers can be good candidates for NLO applications.

Optical Studies

The refractive index and absorption coefficient measurements were carried out for polymers containing chromophores with nitro groups as special monomers. Transmission measurements were recorded using an UV-vis spectrometer, a Perkin-Elmer Lambda 40, and were performed on polymeric films placed on a quartz base.

Table III Tensile Strength of Polyarylate Layers

Special Monomer Content (%)	Tensile Strength (MPa)							
	<i>o</i> -NO ₂	<i>m</i> -NO ₂	<i>p</i> -NO ₂	<i>o</i> -Cl	<i>m</i> -Cl	<i>p</i> -Cl	<i>p</i> -CN	<i>p</i> -Br
1	46.30	41.39	57.89	58.90	68.47	71.09	45.48	55.87
3	56.71	62.80	36.89	63.52	32.39	21.21	54.51	47.36

Table IV Glass Transition Temperature of Selected Polymers

Special Monomer Content (%)	Glass Transition Temperature (°C)		
	<i>o</i> -NO ₂	<i>m</i> -NO ₂	<i>p</i> -NO ₂
1	214.1	203.3	189.9
3	177.2	175.9	174.3

Samples from polymers in which organic compounds comprising nitro groups substituted at various positions of the aromatic ring (*ortho*, *meta*, *para*) were taken for the measurements. Polymers with a 1 and 3% content of the special monomer were studied. In total, six new polymers were studied.

Diagrams obtained from measurements carried out with the *p*-NO₂ polymer (1%) are presented in this article. The diagrams for the other polymers are very similar. Transmission measurement was made within the wavelength range above 200 nm for a polymer film deposited on quartz (Fig. 5).

The refractive index and absorption coefficient diagrams were obtained after appropriate transformations.²⁸ These diagrams showed small values of the refractive index (Fig. 6).

Figures for various polymers range from 1.48 to 1.64 for wavelengths from 400 to 1000 nm exhibit an initial decreasing character with an

increase in wavelength and then reach a constant value. The position of substitution of the characteristic group in the side-chain aromatic ring has no effect on the refractive index value. An increase in the concentration of the chromophore in the polymer matrix causes an increase in the refractive index value. The films obtained show also low absorption coefficient values (Fig. 7).

The light absorption coefficient values obtained for all the polymers range from 21 to 40 for wavelengths from 400 to 1000 nm. The substitution position of the characteristic group in the side-chain aromatic group affects the absorption coefficient value and the lowest results were obtained for the substitution in the *ortho* position and the highest for the *meta* position. An increase in the chromophore concentration in the polymer matrix causes an increase in the refractive index value.

The refractive index $n(\lambda)$ and susceptibility χ for different compositions of polymers with nitro groups were determined. The values of susceptibility χ are from 1.48×10^{-9} to 1.64×10^{-9} (esu) for wavelengths from 400 to 1000 nm.

CONCLUSIONS

NLO polymers comprising special monomers were obtained by simple reactions, which can also be applied on an industrial scale. Good mechanical, thermal, and optical properties of the compounds obtained were found from the physical-

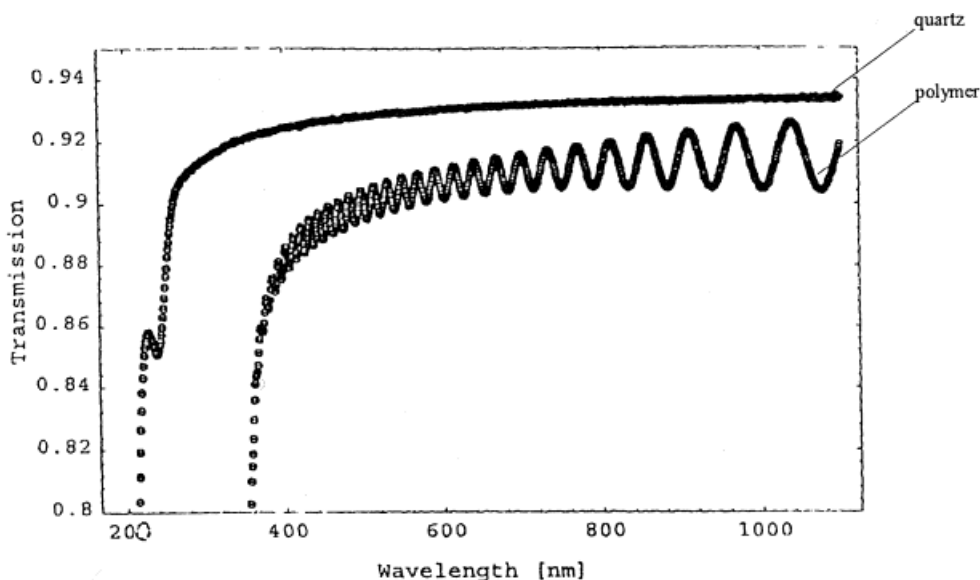


Figure 5 Transmission spectrum for polyarylate *p*-NO₂ (1%) and quartz.

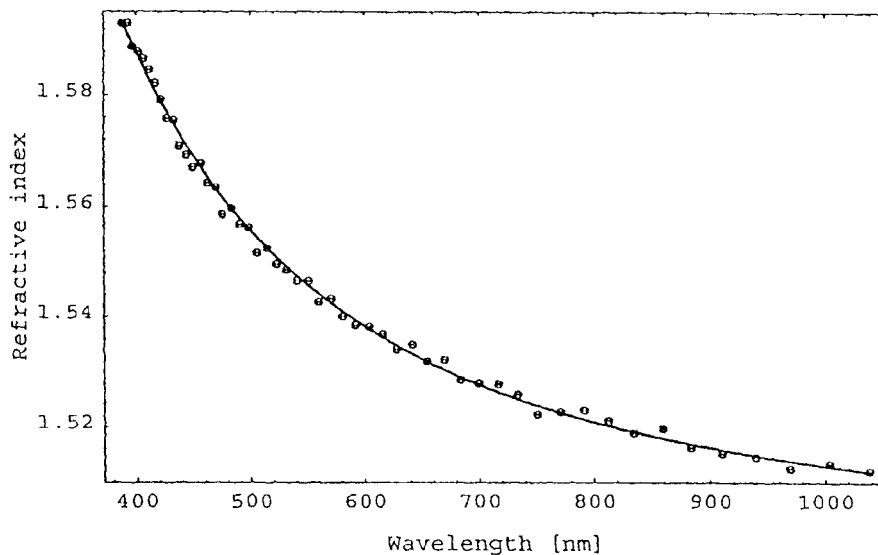


Figure 6 Refractive index for polyarylate p -NO₂ (1%) film deposited on quartz.

chemical studies carried out. All the new polymers dissolve well in chlorinated solvents and exhibit good film-forming properties.

Polymer solutions exhibit high limiting viscosity number values, from 0.087 to 1.375 (100 cm³ g⁻¹). An increase in the concentration of the special monomer in the polymer causes most often a decrease in the polymer molecular weight.

The glass transition temperature values determined, from 174.3 to 214.1°C, indicate good thermal properties of the new NLO systems. These polymers should also exhibit good thermal stability, since all of them show T_g values above 120°C,

which was the assumption when designing these polymers.

Tensile-strength studies of polymer films confirm their good mechanical strength, similar to that of a polyarylate not containing chromophores (58.86 MPa). The tensile strength values obtained range from 21.2 to 71.1 MPa. The polymer films obtained on a quartz base show good optical properties: low refractive index values (1.48–1.64) and low light absorption coefficient values (21–40 cm⁻¹) for the 400–1000-nm wavelength. Thus, it seems that the polymers obtained are good candidates for applications in nonlinear optics.

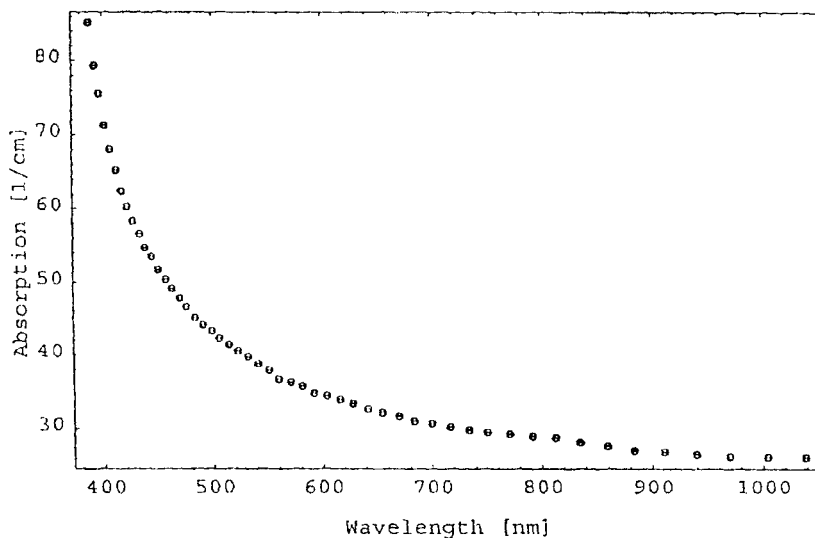


Figure 7 Absorption spectrum for polyarylate p -NO₂ (1%) film deposited on quartz.

REFERENCES

1. Wijekoon, W. M.; Zhang, Y.; Karna, S. P.; Prasad, N. *J Opt Soc Am B* 1992, 9, 1832–1842.
2. Prasad, N.; Ulrich, D. R. *Non-linear Optical and Electroactive Polymers*; Plenum: New York, 1988.
3. Burland, D. M. *Chem Rev* 1994, 94, 31–75.
4. Brzozowski, Z.; Zadrożna, I.; Lato, E. *Polym Compos* 1994, 2, 253A–258A.
5. Nuken, O. *Prog Polym Sci* 1997, 22, 93–183.
6. Kamiński, R. *Macromol Rep A* 1994, 31, 217–223.
7. Szymańska, E. *Macromol Rep A* 1994, 31, 643–650.
8. Brzozowski, Z. *Polimery* 1984, 29(10–12), 415–421.
9. Allen, D. E.; DeMartino, R. N. U.S. Patent 4 978 479, 1990.
10. Koide, N.; Ogura, S.; Aoyama, Y. *Mol Cryst Liq Cryst* 1991, 198, 323–330.
11. Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem Rev* 1994, 94, 31–75.
12. Lindsay, G. A. *TRIP* 1997, 5(3), 91–96.
13. Servay, T. K.; Winkelhahn, H. J.; Schulze, M.; Boeffel, M. *Phys Chem* 1993, 97, 1272–1280.
14. Noniewicz, K.; Brzozowski, Z.; Zadrożna, I. *J Appl Polym Sci* 1996, 60, 1071–1082.
15. Brzozowski, Z.; Zadrożna, I.; Kowalczyk, T.; Syromyatnikov, V. S. *Polym Compos* 1995, 3, 421.
16. Zadrożna, I.; Brzozowski, Z.; Noniewicz, K.; Dyrda, M. *Polym Compos* 1997, 5, 57.
17. Brzozowski, Z.; Zadrożna, I. *Novel UV-Sensitive Polyarylates Confirmed by NMR*, XIII European Experimental NMR Conference, Paris, May 1996.
18. Noniewicz, K.; Brzozowski, Z. *React Funct Polym* 1997, 33, 343–349.
19. Hayden, L. H.; Sauter, G.; Ore, F.; Pasillas, P. *J Appl Phys* 1990, 68, 456–465.
20. Choi, D.; Wijekoon, W. M.; Kim, H.; Prasad, N. *Chem Mater* 1994, 6, 234–238.
21. Parzuchowski, P.; Zadrożna, I. *J Appl Polym Sci* 1999, 71, 1017–1028.
22. Zeegers, P. J. *J Chem Ed* 1993, 70, 1036–1037.
23. Gaude, D.; Le Goaller, R. *Synth Commun* 1986, 1, 63–68.
24. Zadrożna, I.; Sakowska, M. *Pol. Patent* 333385, 1999.
25. Zadrożna, I.; Sakowska, M. *Pol. Patent* 333196, 1999.
26. Zadrożna, I.; Sakowska, M. *Pol. Patent* 333197, 1999.
27. Wyszomirska, A.; Zadrożna, I. *Polym Compos* 1998, 6, 541–549.
28. Zadrożna, I.; Parzuchowski, P.; Brzozowski, Z.; Milburn, G. H. W. *J Appl Polym Sci* 1999, 71, 1017–1028.