Synthesis and Characterization of a New monomer for Obtaining of Polymers with Nonlinear Optical Properties

ION SAVA*
„Petru Poni" Institute of Macromolecular Chemistry, 41A, Aleea Gr. Ghica Vodă, 700487 Iaşi, Romania

A new aromatic diamine, namely 2,2-bis(3-amino-4-oxyhexyloxy-phenyl-4'-butoxyazobenzen) hexafluoropropane, containing two azobenzene side groups have been prepared by modification of 2,2-bis(3-amino-4-hydroxyphenyl) –hexafluoropropane with 4-(6-bromohexyloxy)-4'-butoxyazobenzene in the presence of K_2CO_3/KI. This monomer showed a mesophase in the range of 103-114°C and can be used for obtaining of polymers with special optical properties.

Keywords: butoxyaniline, side azobenzene groups, thermal characterization

Nonlinear optical properties of polymers are extremely important in many fields of applications (optical waveguides, photoswitching and optical data storage, alignment of photoactive species ..). Functional polymers which contain photochromic groups have generated much interest in the field of optical layer technologies. Among photochromic polymers, those with azobenzene groups are widely studied as by exposure to linear polarized light, the photochromic groups reorient perpendicular to the electric field vector of the incident light [1-4]. Many efforts are focused to develop the photoreactive polyimides because they are much more thermoresistent [5-9] than azocompounds or vinylcinamat derivatives [10-12]. The photosensitive polyimides arise a special interest due to the posibilities of photoinduced alignment in liquid crystalline [13, 14]. In order to obtain new materials it is necessary to synthesize new monomers and hence, the corresponding macromolecular compounds with special properties.

In this context the present paper proposes the synthesis and characterization of one diamine with side azobenzene groups for obtaining of polymers useful in materials with nonlinear optical properties.

Experimental part

Materials

Butoxyaniline (97%), phenol (99%), 1,6-dibromohexane (96%), $NaNO_2$ (99,9%), K_2CO_3 (anhidrous), KI (purris), acetone (p.a) were provided from different commercial sources (Sigma-Aldrich, Lancaster s.a) and were used as received.

Measurements

FTIR spectra were recorded with a FTS 3000 MX Exalibur spectrometer (Digilab/Bio-Rad, Thermo Scientific Company, USA), in atenuate reflexion mode (ATR). ^{1}H-NMR spectrum was recorded using a spectrometer Bruker Avance DRX 400 in DMSO-d_6 with TMS as internal refernce. The thermal measurements were performed with differential calorimeter type TA DSC 2010 with a heating rate of 10°C/min in nitrogen. The mesophase textures were evidenced with polarized light microscope Olympus BH2 (Japan) with a hot plate Linkam TP92.

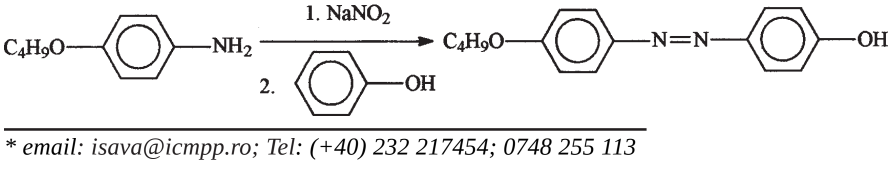
Results and discussion

The synthesis of the diamine 2,2 bis-(3-amino-4-oxyhexyloxy-phenyl-4'-butoxyazobenzene) hexafluoropropane was realized by the modification of 2,2-bis(3-amino-4-hydroxyphenyl)–hexafluoropropane with *p*-(6-bromhexyloxy)-*p'*-butoxyazobenzene, a compound which contains preformed azobenzene groups. This intermediate containing azobenzene groups was synthesized by the reaction of diazotized *p*-butoxyaniline with phenol, followed by the reaction with dibromohexane. Hereinafter are presented the reactions which lead to 2,2 bis-(3-amino-4-oxyhexyloxy-phenyl-4'-butoxyazobenzen) hexafluoropropane.

Synthesis of p-hydroxy-p'-butoxyazobenzene

This compound is obtained by a reaction which takes place in two steps at low temperatures (0-5°C) and pH 5-8 [15] : first diazotiazation of *p*-butoxyaniline followed by the coupling of the formed diazonium salt with phenol (Scheme 1). Thus, 10 mL of concentrated hydrochloric acid and 10 mL water were added to 8.25 g (0.05 mol) of *p*-butoxyaniline and the resulting solution was cooled down to 0°C. Then a solution of 3.45 g (0.05 mol) of sodium nitrite in 20 mL water was added drop-wise and the mixture was stirred at a temperature between 0 and 5°C for 15 min. The resulting clear solution of diazonium salt was slowly added to a solution of 14.1 g (0.15 mol) phenol, 6 g (0.15 mol) NaOH, 32 g (0.3 mol) Na_2CO_3 in 150 ml water at 0-5°C. Sometimes it was necessary to add extra NaOH to avoid the formation of foam. After complete addition, the mixture was stirred for 1–2 h at 0-5°C. The yellow-orange coloured precipitate was filtered off, dried and recrystallized from a mixture of ethanol:water 2:1. Melting point: 105-106°C. Yield: 72% [16].

The FTIR spectrum of this intermediate shows the characteristic absorbtion peaks of methylene units at 2937 cm^{-1} and the characteristic absorbtion bands of azobenzene which overlapps to benzene rings at 1600 cm^{-1} [16].



Scheme 1. Synthesis of *p*-hydroxy-*p'*-butoxyazobenzene.

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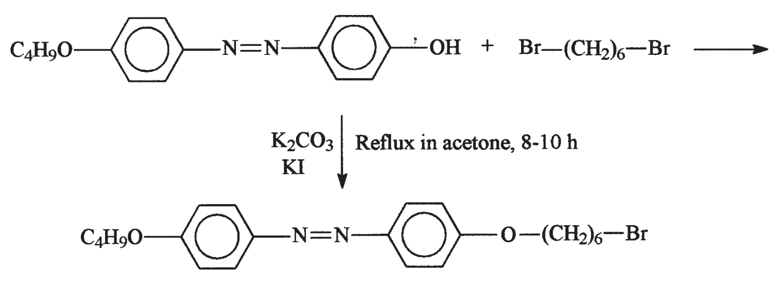
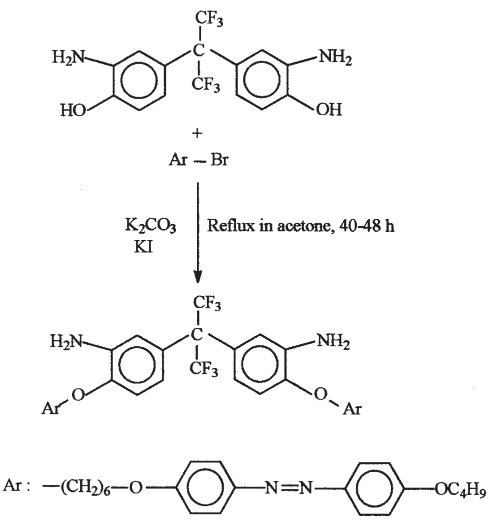
* email: isava@icmpp.ro; Tel: (+40) 232 217454; 0748 255 113



Scheme 2. Synthesis of *p*-(6-bromhexyloxy)-*p'*-butoxyazobenzene



Scheme 3. Synthesis of 2,2-bis{3-amino-4-[(*p*-oxyhexyloxy–*p'*-butoxy) azobenzene]-phenylene}-hexafluoropropane

Synthesis of p-(6-bromhexyloxy)-p'-butoxyazobenzene

This product was obtained by the reaction of the p-hydroxy-p'-butoxyazobenzene (above synthesized) with 1,6-dibromohexane by a procedure described in the literature [16]. The reaction takes place in acetone at reflux temperature, the dibromocompound being in great excess (10:1) (scheme 2).

A mixture of 81.3 g (0.33 mol) of 1,6-dibromohexane, 23.5 g (0.17 mol) K_2CO_3, 9 g (0.033 mol) *p*-hydroxy-*p'*-butoxyazobenzene and a trace of KI in 250 mL acetone was stirred vigorously and refluxed for 9.5 h (controlled by thin-layer chromatography). After cooling the precipitated salt was filtered off and filtrate was evaporated. The crude product was purified by recrystallization from a mixture of toluene:ethanol 1:2.25. Melting point: 96.5-115°C (liquid crystalline) [16].

Synthesis of 2,2-bis{3-amino-4-[(p-oxyhexyloxy–p'-butoxy) azobenzene]-phenylene}-hexafluoropropane

The above described procedure has been used to obtain this diamine by the reaction of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane with *p*-(6-bromhexyloxy)-*p'*-butoxyazobenzene (scheme 3). A mixture of 3.66 g (0.01 mol) of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane, 8.66 g (0.02 mol) of *p*-(6-bromhexyloxy)-*p'*-butoxyazobenzene, 13.8 g (0.1 mol) K_2CO_3 and a trace of KI in 250 mL acetone was stirred vigorously and refluxed for 45 h (controlled by thin-layer chromatography). After cooling the precipitated salt was filtered off and filtrate was evaporated. The crude product was purified by recrystallization from a mixture toluene:ethanol 1:2.3. Mesophase: Crystal 103°C Nematic; 114°C Izotrop. Yield: 63 %. Elemental analysis for $C_{59}H_{68}O_6N_6F_6$; Calc. %: C: 66.15; H: 6.4; N: 7.84; F: 10.64 Found % C: 67.28; 67.41; H: 6.82; 6.88; N: 7.58; 7.56; F: 10.5; 10.6.

FTIR spectrum of the synthesized diamine shows the characteristic absorbtion bands of amine group at 3460 and 3381 cm^{-1} and of metylene groups at 2938 cm^{-1} and 2871 cm^{-1}. The azobenzene group is overlapping to benzene rings at 1598 cm^{-1} and the isopropylidene bridge is present at 1237 cm $^{-1}$ [17].

^{1}H-NMR Spectrum of this diamine (fig.1) shows the following characteristics absorbtion bands: 0.95 ppm, triplet, 6H, CH_3 (**1**); 1.47 ppm, multiplet 12 H, -CH_2- (**2**);. 1.77 ppm, multiplet 12 H, O-CH_2-CH_2 (**3**); 4.075 ppm, triplet, 8H, protons –CH_2 – O (**4**); 3.98 ppm, triplet, 4H, protons -CH_2-O (**4'**); 7.11 ppm, dublet, J = 8,8Hz, 8H, aromatic protons **5**; 7.826 ppm, dublet, J = 8,8Hz, 8H, aromatic protons **6** ; 6.84 ppm, dublet, J = 6,4 Hz, 2H, aromatic protons **8**; 6.64 ppm, singlet, 2H, aromatic protons **9**; 6.52 ppm, dublet, J = 6,4Hz, 2H, aromatic protons **7**; 4.844 ppm, peak extended, 4H, NH_2 (**10**). From this spectrum analysis it can be concluded that this diamine corresponds to the

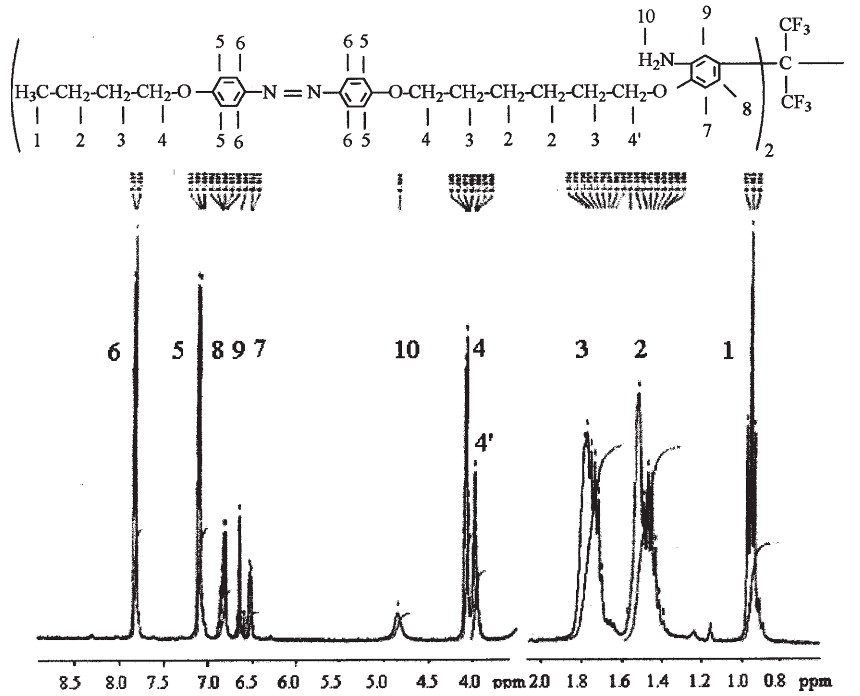


Fig. 1. ^{1}H-NMR Spectrum of 2,2-bis{3-amino-4-[(*p*-oxyhexyloxy–*p'*-butoxy) azobenzene]-phenylene}-hexafluoropropane

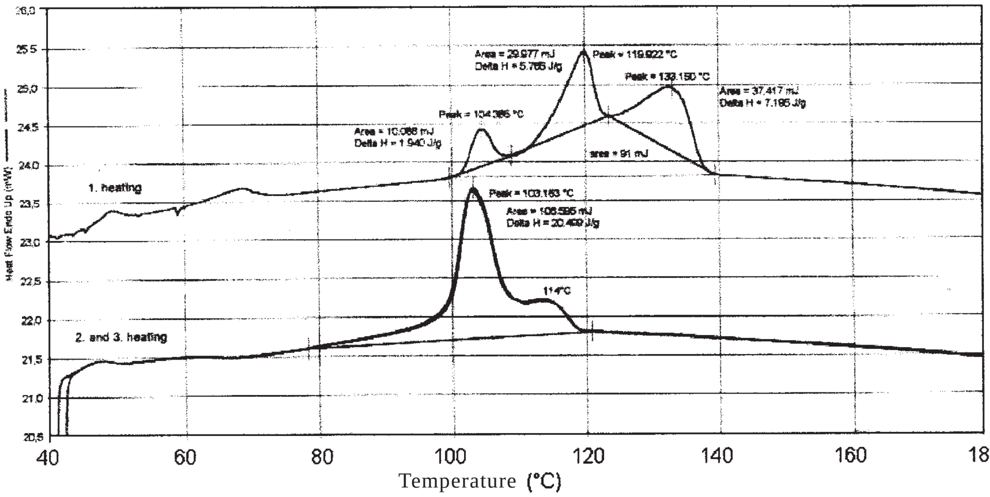


Fig. 2. Behaviour at heating of
2,2-bis{3-amino-4-[(*p*-oxyhexyloxy–*p*'-butoxy) azobenzene]-phenylene}-hexafluoropropane

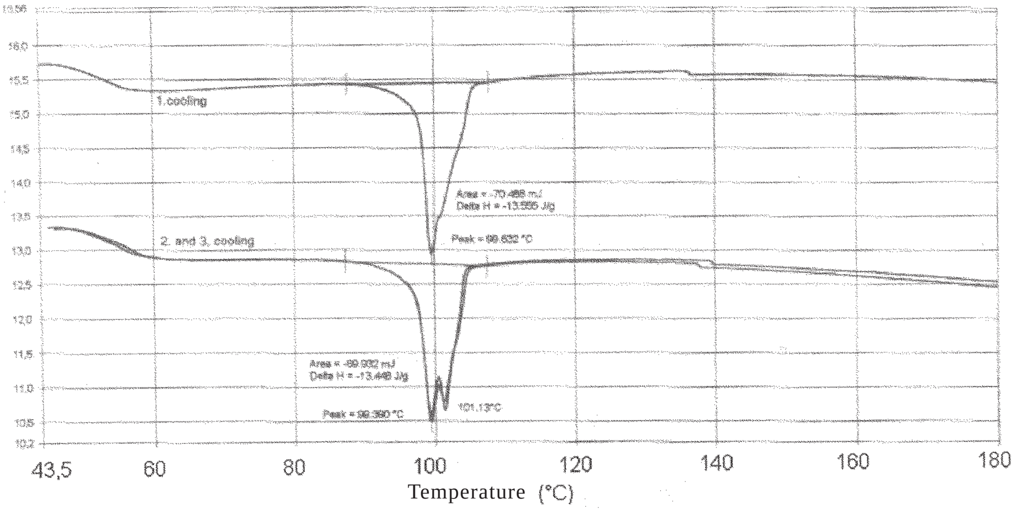


Fig. 3. Behaviour at cooling of
2,2-bis{3-amino-4-[(*p*-oxyhexyloxy–*p*'-butoxy) azobenzene]-phenylene}-hexafluoropropane

chemical structure and contains reduced quantities of impurities.

The synthesized diamine was characterized from the point of view of thermal behaviour by a repeated heating-cooling cycles. Figures 2 and 3 show the heating and the cooling curves, respectively, of this diamine. As can be seen from figure 2, at first heating this diamine presents peaks at 104°C, 119.9°C and at 133°C, respectively. The second heating shows only two transition processes at 103 °C and 114 °C and after the third heating the behaviour of the product remains unchanged. Regarding the cooling processes (fig. 3) one can notice: a pronounced peak at 99°C and a shoulder at 101°C at first cooling; two pronounced peaks at the same temperatures (99 and 101°C) at the second and third cooling. All these results suggest that this diamine shows a stable thermal behaviour proving thus that, this product is a monomer of high purity and hence, proper to further obtain macromolecular compounds with special properties.

The study of this diamine in polarized light shows the presence of a "schlieren texture", which is typical for nematic mesophase [18], in the range of 103-114°C, proving good agreement with the results obtained by thermal analysis (fig. 4).

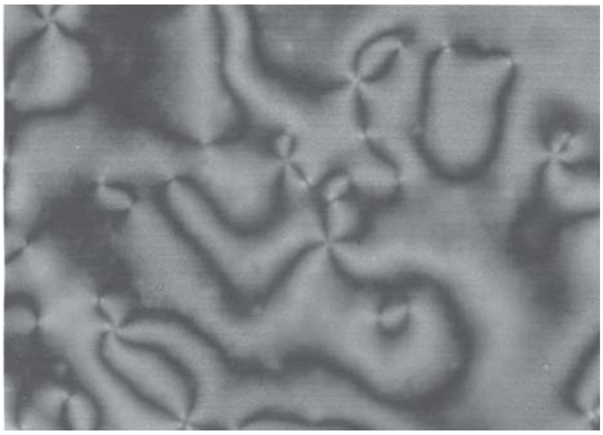


Fig. 4. Texture of 2,2-bis{3-amino-4-[(*p*-oxyhexyloxy–*p*'-butoxy) azobenzene]-phenylene}-hexafluoropropane at 112°C (400x)

This diamine has been used in the synthesis of new macromolecular compounds which presented special optical properties (photoinduced dichroism, optical anisotropy) [19, 20].

Conclusions

A new diamine which contains two side azobenzene groups has been obtained by modification of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane with 4-(6-bromhexyl-oxy)-4'-butoxyazobenzene. The structure of this diamine was evidenced by FTIR and ^{1}H-NMR spectrometry, elemental analysis and thermal behaviour. The obtained diamine was successfully used in the synthesis of polymers with nonlinear optical properties.

Acknowledgements: The author adresses warm thanks to Institute for thin films technologies and Microsensorics, Teltow, Germany and to Program CEEX, Contract nr. 107/2006 for financial support.

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Manuscript received: 25.08.2009