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Nonlinear optical properties of polymers containing a new azophenylbenzoxazole chromophore

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Abstract

The synthesis of the new highly extended chromophore 2-[4-(*N*,*N*-dihydroxyethylaminophenylazo)-phenyl]benzoxazole is described. Two polymers obtained by the polycondensation of this chromophore with propyloxyterephthalic acid and 2,4-tolylenediisocyanate and one obtained by the polycondensation of 2-[4-*N*,*N*-bis(2-hydroxyethyl)aminophenyl]-6-nitro-benzoxazole with 2,4-tolylenediisocyanate have been prepared and characterized. The polymers are amorphous and exhibit good optical clarity, satisfactory thermal stability above the glass transition temperature and are soluble in common organic solvents. Second order nonlinear optical behavior of the polymers has been studied through measurement of the electrooptic coefficient on films poled between parallel electrodes. The maximum value measured for the electrooptic coefficient (r_{33}) is 6.5 pm/V at an incident laser wavelength of 1.552 μm. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Organic polymers containing highly conjugated chromophores covalently incorporated in the side chain or in the main chain are candidate materials for applications in the field of nonlinear optics (NLO) [1–3].

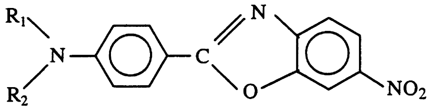
For optimum NLO behavior two important features are the intrinsic activity of the chromophore, i.e. β values, and (for second order applications) the extent and temporal stability of molecular alignment of active segments, the second feature being controlled, at least in part independently from the chromophore, by proper choice of the polymers to be prepared (i.e. glass transition, secondary interactions, cross-linking, etc.).

The design (and chemical synthesis) of NLO active molecular fragments is mainly based on the well known push–pull pattern, i.e. organic π electron conjugated systems with strong electron donor–acceptor groups. The length of the conjugation path, the efficiency of the charge transfer and the energy gap between the fundamental and the first excited electronic state are important variables to be considered in the synthesis of potentially active chromophores.

We have been examining since recently the use of chromophores containing phenylbenzoxazole groups to obtain thermoplastic polymers with NLO properties of the second order [4,5].

Phenylbenzoxazole is a chemically robust moiety. It may be functionalized to variate the structure of the chemical groups connected and relevant for the definition both of the optical properties of the chromophore and the way it is related to the polymer chain. This influences, of course, other important properties of the final material, such as solubility, chain mobility, crystallizability, T_g and poling efficiency.

Phenylbenzoxazole based chromophores **1** and **1′** were utilized to obtain polyesters (**1**) or acrylate/methacrylate copolymers (**1′**) and the second harmonic generation coefficient d_{33} was measured.



1 : [R_1=R_2=CH_2CH_2OH] **1′** : [R_1=CH_3 , R_2=$(CH_2)_6OH$]

Improving the NLO behavior of such materials may be

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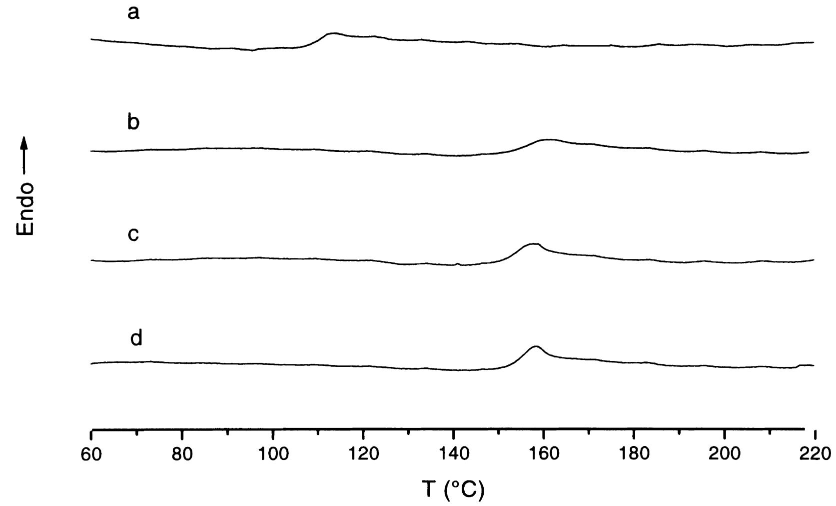
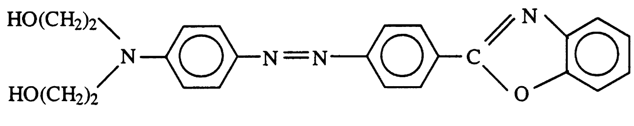


Fig. 1. DSC thermograms of melt cooled samples: (a) PE2; (b) PU1; (c) PU2; (d) PU2 previously annealed at 180°C for 14 h.

reached introducing modifications in the chromophore structure or in the polymer structure or in both; in the latter case, cross controls should be performed for detecting specific effects of the chromophore/polymer on NLO properties.

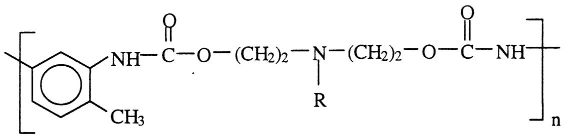
The new chromophore (**2**) that has been considered has the structure shown below



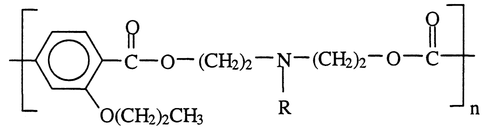
Some interesting features of this structure, in comparison with the preceding one, are its longer conjugation path and the absence of the strong electron withdrawing nitro group on the benzoxazole system, although some electron withdrawing character has been reported for benzoxazole itself [6]. Furthermore, good NLO activity has been reported for azo compounds both from theoretical calculations on aromatic azo chromophores [7] and from experimental measurements on aromatic azo polymers [8] and monomers [9], indicating this group as a good bridge for charge transfer in conjugated systems.

Modifications of the polymer structure have been considered for increasing the glass transition of the polymer and possibly stabilizing the orientation of the chromophore in the poled polymer film through secondary interactions. In this respect it should be noted that nitrogen atoms of azo and benzoxazole groups [10] are hydrogen bond acceptors; for these reasons polyurethanes were considered a possible better choice of polymers as compared to polyesters.

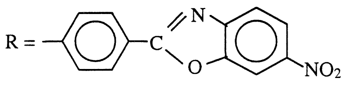
In the present paper, the synthesis and characterization of two polyurethanes and one polyester containing chromophores **1** and **2** is reported, including NLO investigation through electrooptic coefficient measurements. The chemical formula and numbering of polymers is shown below



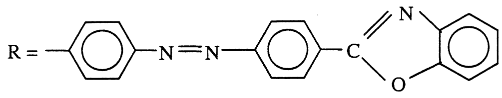
PUn



PEn



PU1, PE1



PU2, PE2

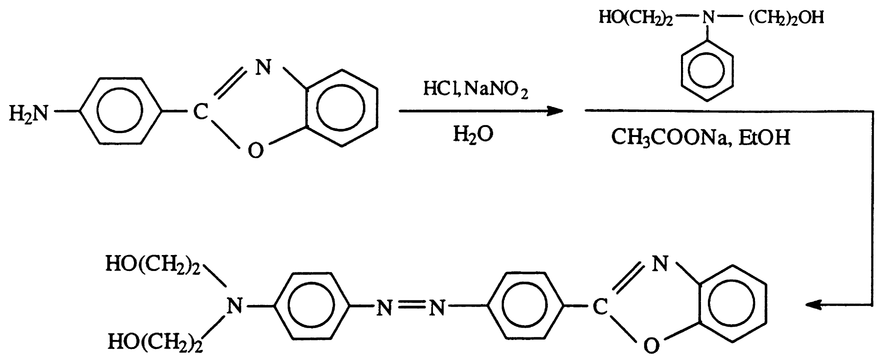
Polyurethanes have been based on 2,4-tolylenediisocyanate monomer, which has been already reported in the literature for the synthesis of NLO active polymers [11]. This monomer should allow a nonlinear and constitutionally disordered connectivity along polymer chains, with consequent possible increase of solubility and decrease of crystallization tendency. The polyester was based on 2-propyloxyterephthalic acid for similar reasons and direct comparison with our previous data on PE1 [4].

2. Experimental section

2.1. Monomer synthesis

Chromophore **1** was prepared according to the procedure already described by us [4].

Chromophore **2** was prepared according to the following sketch:



2-(4-Aminophenyl)-benzoxazole [12] and *N*,*N*-bis(hydroxyethyl)aniline [4] were prepared according to procedures already described. Commercial low in water pyridine was further dried by refluxing over potassium hydroxide pellets, under nitrogen atmosphere for 3 h, and successive distillation and recovery on activated molecular sieves. 2-Propyloxyterephthaloyl dichloride was prepared as previously described [13]. Commercial 2,4-tolylenediisocyanate was purified by vacuum distillation and stored under nitrogen.

*2-[4-(N,N-dihydroxyethylaminophenylazo)phenyl]benzoxazole (**2**).* The synthesis was performed according to the classic scheme of diazotization–coupling. For the diazotization, 5.5 g (26.2 mmol) of 2-(4-aminophenyl)benzoxazole were suspended, in a round bottom flask, in a solution containing about 30 ml of water and 6.8 ml of 37% HCl; the suspension was cooled at 0–5°C in a water–ice bath. Under stirring, a solution was obtained dissolving 2.0 g (29 mmol) of sodium nitrite and 10 ml of water was added drop by drop to the suspension. Stirring at low temperature was continued for 20 min after the addition of the nitrite solution was completed, obtaining, finally, a yellow suspension of the diazonium salt.

Separately, a solution containing 7.48 g (91.2 mmol) of sodium acetate, 4.75 g (26.2 mmol) of *N*,*N*-bis(hydroxyethyl)aniline, 100 ml of water and 50 ml of ethanol was prepared. To this solution, under stirring at room temperature, the solution of the diazonium salt was rapidly added; immediately the color of the solution turned to red and in a few seconds a red-orange crystalline precipitate of the azo compound formed. The mixture was allowed to stir for another hour, then the crystalline precipitate was collected by filtration. Final recrystallization from dioxane–hexane gave 7.8 g (74% yield) of pure **1** (m.p. 224°C). The compound is easily soluble in *N*,*N*-dimethylformamide and pyridine, and it is less soluble in ethanol. UV–VIS spectrum in acetonitrile shows two bands at 542.4 and 308.8 nm. ^{1}H NMR (CDCl$_3$): δ (ppm) = 8.4 (d, 2H); 8.0 (d, 2H); 7.9 (m, 4H); 7.5 (d, 2H); 6.9 (d, 2H); 3.7 (m, 8H).

2.2. Synthesis of polymers

Solution polymerizations were performed by refluxing under stirring, in dry pyridine, equimolar amounts of chromophore (**1**) or (**2**) and 2,4-tolylendiisocianate or 2-propyloxyterephthalic acid chloride under nitrogen atmosphere (about 3.5 ml of pyridine were used for 0.8 g of chromophore). During the reaction the solution became more and more viscous. After 2 h reaction, the mixture was diluted with equal volume of pyridine and poured in 200 ml of *n*-hexane affording precipitation of the crude polymer, as a red powder. This was then dissolved in about 20 ml of *N*,*N*-dimethylformamide and precipitated in 150 ml of methanol, collected by filtration and dried in an oven. The yields of polymerization reactions ranged between 35 and 47%. ^{1}H NMR spectra of polymers are consistent with the expected structures.

2.3. Characterization

The thermal behavior was examined by differential scanning calorimetry (Perkin Elmer DSC-7, nitrogen atmosphere, scanning rate 10 K/min). Temperature controlled polarizing microscopy was used for optical observations (Zeiss microscope combined with a Mettler FP5 micro furnace). X-ray diffraction photographs were recorded by a flat film camera utilizing Ni filtered CuK$_\alpha$ radiation. Thermogravimetric analysis was performed with a Mettler TG50 apparatus. Inherent viscosities were measured at 25.0°C in 0.5 g/dl *N*-methylpyrrolidone solutions with an Ubbelohde viscometer. Proton NMR spectra were recorded on a Varian XL 200 and on a Bruker AC 250 spectrometers. UV–VIS spectra were recorded with a Perkin Elmer Lambda 7 UV–VIS spectrophotometer.

2.4. Thin films preparation

For the NLO characterization, 0.5–2 μm thick polymer films were laid by spin coating on ITO-coated glass slides. To this purpose appropriate amounts of polymers were dissolved in freshly distilled NMP and the solutions filtered on 0.45 μm Teflon filters. The spinner used was a CONVAC 2001, operating at a rate of 2000 rpm, at a temperature of 80°C. Residual solvent was removed by heat treating the films first at 120°C for 1 h and then at 80°C, 0.5 mmHg vacuum overnight. For the refractive index measurements, 2–3 μm thick spin-cast films of the polymers were prepared on fused Silica slides. The film thickness was measured with a profilometer Alphastep.

A gold layer, 1000 Å thick, was then formed on the top of the polymer films coated on ITO, by thermal evaporation, for NLO measurements. The ITO and gold layers were used as both poling and modulation electrodes.

3. Results and discussion

3.1. Structural and thermal characterization

All synthesized polymers are amorphous, non-crystalline materials, as evidenced by combined X-ray diffraction analysis and optical observations at the polarizing microscope. Consistently, DSC thermograms of polymers, on heating, show no endothermic melting signal but only the inflexion corresponding to the glass transition, Fig. 1. Crystallinity is not observed also upon long annealing at temperatures above glass transition. Lack of crystallinity is not unexpected owing both to the lateral encumbrance of the chromophore and to the constitutional disorder induced, along polymer chains, by 2,4-tolylendiisocyanate or 2-propyloxyterephthalic acid monomer. As a result of the poor tendency to crystallize, optical quality films can be cast from DMF or NMP polymer solutions. The pattern of glass transition temperatures, which is reported in Table 1, indicate, as it is expected on the basis of greater chain rigidity and hydrogen bond formation, that polyurethanes have glass transitions higher than polyesters. Furthermore, data of Table 1 also indicate that polymers are well stable in a rather large temperature range above the glass transition, thus allowing a safe poling procedure to be performed.

3.2. NLO measurements

The refractive indices of the polymers were measured on Silica slides by a grating coupling technique, using the same wavelength of the incoming laser beam used in the next step for the electrooptic measurements (1552 nm).

Table 1
General properties of polymers

Polymer	T_g (°C)	η_{inh} (dl/g)	T_d (°C)[a]
PU1	156	0.17	330
PU2	152	0.23	308
PE1[b]	119	0.25	344
PE2	117	0.15	338

[a] Temperature of initial decomposition of the polymer (5% weight loss) estimated by thermogravimetric analysis (TGA) under nitrogen flow, at 20 K/min rate.

[b] Data from Ref. [4].

The measurement of electrooptic coefficients r_{33} was performed using the reflection technique [14,15]. The ellipsometric setup used is described in detail elsewhere [14–16]; the sample is mounted on a heating stage and a modulating voltage of 2–3 V (1 kHz frequency) is applied between the two parallel electrodes. A laser beam at 1.522 μm is incident on the back of the glass substrate at a fixed angle of 45°. It propagates through the ITO, the polymer film and is then reflected back from the bottom gold electrode. The polarization of the input beam is set at 45° to the plane of incidence so that s and p polarized waves are equal in amplitude. The modulated output intensity is measured by a lock-in amplifier. The lock-in signal depends on the phase difference between the s and p polarized waves induced by the modulation voltage [14]. From the relation between the modulating voltage and the modulated intensity it is then possible to evaluate r_{33}. The electrode poling experiment is performed in situ, by applying a high voltage while the film sample is heated at a rate of 10°C/min up to the glass transition temperature of the polymer. The value of r_{33} as a function of the time and of the temperature during the poling experiment is monitored. After some minutes at T_g the sample is cooled down to room temperature, then the electric field is switched off. For determining r_{33} with better accuracy the lock-in signal is measured at different modulation voltages. From the slope of the lock-in signal versus the modulation voltage r_{33} can be calculated [16].

NLO data of polymers, reported in Table 2, indicate that NLO activity of PU1 and PU2 are rather similar and considerably higher than PE2.

Actually, comparing NLO data of different polymers may not be fully significant, since the final NLO datum depends on several factors which may hardly be controlled and reproduced in chemically different systems (as for example, the poling efficiency, i.e. extent and temporal stability of chromophores orientation, for a given electric field applied, is related both with the chemical structure of the chromophore and with that of the polymer backbone). Therefore, possibly significant comparisons have to be limited to systems in which introduced chemical modifications are relatively small, and in any case care must be taken in drawing definitive conclusions.

Similar r_{33} values for PU1 and PU2 might indicate the intrinsic NLO activity of chromophores **1** and **2** is not very

Table 2
NLO properties of polymers

Polymer	r_{33} (pm/V)	n[a]	V_p[b] (V/μm)
PU1	6.5	1.62	120
PU2	5.0	1.69	130
PE2	1.7	1.67	60

[a] Refractive index (±0.01) at 1552 nm.

[b] Poling voltage.

different. Actually, chromophore **1** has a stronger electron withdrawing group as compared with **2**, but, for the latter, the length of conjugation path is higher. The slightly higher r_{33} value of PU1, if it is significant, would indicate a prevalence of the attractive group effect on the length of conjugation path. However, the slight difference might also reflect a more difficult orientation of chromophore **2**, during poling, owing to the higher steric encumbrance.

The small value of r_{33} observed for PE2, which contains the same chromophore as PU2, might be due to a faster relaxation of chromophore groups orientation after poling, or more probably it might be simply a consequence of the lower poling voltage applied.

Acknowledgements

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