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Synthesis and characterisation of polyesters with nonlinear optical properties

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Abstract

Eight new homo- and copolymers have been obtained by polycondensation of terephthalic acid and propyloxyterephthalic acid with two different second order NLO-active chromophores derived from 4-[*N,N-bis*(2-hydroxyethyl)amino]-benzaldehyde. Polymers exhibit good optical clarity, satisfactory thermal stability above the glass transition temperature and most of them are soluble in common organic solvents. Second order nonlinear optical properties of two corona poled polymer films were evaluated by second harmonic generation (SHG) measurements with an incident radiation of 1542 nm. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Among the different approaches studied to develop a processable material with high second order NLO properties, covalent incorporation of high β chromophores into amorphous polymers appears by now to be the most advantageous one [1–3]. In effect, polymers seem particularly attractive because of the versatility of their molecular structures, a property that makes it possible to meet converging demands such as large dielectric susceptibility, optical clarity, physical and mechanical stability. Besides, processability into various forms, and the possibility of inducing orientation of the NLO-active moieties by application of an electric field, make such poled polymers a promising class of organic second order NLO materials.

Some mobility of the chromophores within the polymeric material plays at the same time a positive role, allowing a good degree of poling to be reached under an applied electric field, and a negative one, letting eventually this orientation relax in the absence of the poling field. The intrinsic conformational mobility of the polymer chain and the way the chromophore is anchored to the polymer backbone are relevant parameters which have to be taken into account in the design of a second order NLO polymer. We report here on the synthesis of several linear condensation polymers bearing chromophores which are tightly bound to the backbone chain. To this purpose, two bifunctional monomeric chromophores having an asymmetric π-conjugated structure (*D*-π-*A* electron systems) [4–6] have been prepared. In both cases the strong electron releasing group has been derived from 4-[*N,N-bis*(2-hydroxyethyl)amino]-benzaldehyde. Condensation with molecules containing electron withdrawing groups such as nitro or cyano, leads to two different conjugated systems: one phenyl-olefin (Monomer 1, already appeared in the literature [7]) and one phenylbenzoxazole (Scheme 1).

All polymers (Scheme 2) were prepared by solution polycondensation of the bifunctional monomers 1 and 2 with terephthalic and propyloxyterephthalic acid chlorides in such a way that the backbone structure is characterised by an alternating sequence of rigid groups and of short conformationally flexible segments bearing the chromophores. This is not an uncommon feature[3,7] although other possibilities are available, like that of making rigid segment and chromophore to coincide [8]. The presence of a terephthalic group and of an alkoxy substituted derivative as a co-monomer, at variable molar ratios, allows some modulation of T_g and of the polymer solubility.

The NLO properties of two representatives homopolymers, **P1** and **P2**, have been examined by second harmonic generation measurements.

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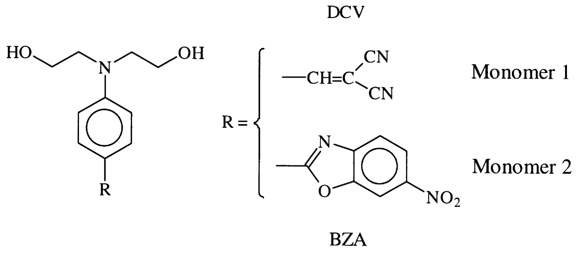


Scheme 1.

2. Experimental section

2.1. Materials

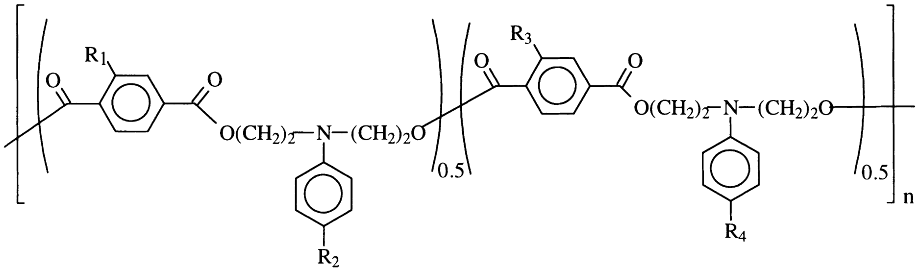
Most of the solvents and reagents were used as purchased. Commercial terephthaloyl chloride 99% was recrystallised from hexane.

Tetrahydrofuran (THF) was purified by treatment with basic alumina. Dry pyridine was obtained by refluxing commercial pyridine with potassium hydroxide pellets for 3 hours under nitrogen atmosphere, subsequent distillation and recovery on molecular sieves. Commercial *N*-methyl-2-pyrrolidone (NMP) was distilled under vacuum over calcium hydride and collected on molecular sieves.

2.2. Monomer synthesis

4-[*N*,*N*-*bis*(2-acetyloxyethyl)amino]-benzaldehyde. This compound was obtained according to a literature procedure [9]. The steps of reaction consist in the synthesis of *N*,*N*-*bis*(2-hydroxyethyl)aniline, protection of hydroxy groups by acetylation and formylation in the *para* position, according to a Vilsmeier reaction.

4-[*N*,*N*-*bis*(2-hydroxyethyl)amino]-benzaldehyde. The acetate protecting groups were hydrolysed by refluxing 13.6 g (0.0464 mol) of 4-[*N*,*N*-*bis*(2-acetoxyethyl)amino]-benzaldehyde in a mixture of 50 ml of ethanol and 12.3 g (0.186 mol) of KOH 85% dissolved in 50 ml of water, for 20 minutes. After cooling, ethanol was removed from the solution at reduced pressure. About 50 ml of water were added to the residue, solution was neutralised with HCl (37%), and the mixture was extracted with chloroform (3 × 30 ml). The aqueous phase was saturated with NaCl and extracted again with chloroform (3 × 15 ml). The combined extracts were washed with a $NaHCO_3$ aqueous solution. After solvent was removed at reduced pressure, a brown-yellow micro-crystalline solid was obtained, which melts at about 65°C. Yield 81%.^{1}H NMR (acetone-d6): δ 9.64 (s, 1H), 7.61 (d, 2H), 6.62 (d, 2H), 3.74 (t, 4H), 3.64 (t, 4H). *Legenda*: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet.



	R_1	R_2	R_3	R_4
P1	H	DCV	H	DCV
P2	$O(CH_2)_2CH_3$	BZA	$O(CH_2)_2CH_3$	BZA
P3	H	BZA	H	BZA
P4	$O(CH_2)_2CH_3$	DCV	$O(CH_2)_2CH_3$	DCV
P5	$O(CH_2)_2CH_3$	DCV	$O(CH_2)_2CH_3$	BZA
P6	H	BZA	$O(CH_2)_2CH_3$	BZA
P7	H	DCV	H	BZA
P8	H	DCV	$O(CH_2)_2CH_3$	DCV

Scheme 2.

4-(2,2-dicyanovinyl)-[*N,N-bis*(2-hydroxyethyl)]-aniline (Monomer 1). In 16 ml of hot o-dichlorobenzene 8.36 g (0.0400 mol) of 4-[*N,N-bis*(2-hydroxyethyl)amino]-benzaldehyde and 2.64 g (0.0400 mol) of malononitrile were dissolved. To the solution 0.2 g (0.004 mol) of acetamide and 0.3 g (0.004 mol) of ammonium acetate were added and the mixture was heated under nitrogen atmosphere for 1 hour. After cooling at room temperature the solution was poured in 200 ml of hexane and vigourously stirred for about 30 minutes. The product was recovered by filtration, re-dissolved in chloroform and treated with activated carbon. The organic solution was concentrated and the compound was crystallised from chloroform/hexane (3:2). The resulting orange crystalline solid was obtained with 53% yield. UV-vis spectrum in acetonitrile shows two bands: $\lambda_{max} = 280.0$ nm, $\epsilon_{max} = 5000$ Lmol^{-1}cm^{-1}; $\lambda_{max} = 431.2$ nm, $\epsilon_{max} = 55000$ Lmol^{-1}cm^{-1}. ^{1}H NMR (acetone-d$_6$): δ 7.89 (d, 1H), 7.86 (dd, 2H), 6.95 (dd, 2H), 3.83 (t, 4H), 3.75 (t, 4H). The phase behaviour of this compound was found to be not entirely coincident with that reported by Wang et al. [7]. The point is shortly addressed in the results and discussion section.

***N,N-bis*(2-hydroxyethyl)-4-[(4-nitro-2-hydroxyphenyl)imino]-methyl]-benzenamine**. In a typical preparation, 20.3 g (0.0971mol) of 4-[*N,N-bis*(2-hydroxyethyl)amino]-benzaldehyde and 16.5 g (0.107 mol) of 2-amino-5-nitrophenol were dissolved in 230 ml of o-dichlorobenzene. The solution was refluxed for 2 hours under stirring in nitrogen atmosphere. After cooling at room temperature the solution was poured in 500 ml of hexane. The brown-red solid recovered by filtration is dried and used for following reaction step without any purification. mp = 202.1°C. Yield 94%. ^{1}H NMR (CDCl$_3$) data are consistent with the expected formula.

2-[4-[*N,N-bis*(2-hydroxyethyl)amino]]-phenyl-6-nitrobenzoxazole (Monomer 2). The synthesis of Monomer 2 has been accomplished by ring closure of the above-reported Schiff base [10]. Under stirring, 10.1 g (0.0292 mol) of *N,N-bis*(2-hydroxyethyl)-4-[(4-nitro-2-hydroxyphenyl)imino]-methyl]-benzenamine was dissolved in 250 ml of tetrahydrofuran dried on basic alumina. To the solution 12.7 g (0.0286 mol) of lead (IV) acetate was added in portions while the red color turned to tan. The mixture was stirred for a few minutes to give a solution with a little amount of suspended solid, then filtered, concentrated and poured into about 500 ml of hexane to precipitate a dark red solid which was recovered by filtration. The solid was extracted in ethanol and crystallised first from ethanol and finally from anhydrous chloroform/hexane solution. The yield was 20%. UV-vis spectrum in acetonitrile shows two absorption bands: $\lambda_{max} = 304.0$ nm, $\epsilon_{max} = 15000$ L mol^{-1}cm^{-1}; $\lambda_{max} = 401.6$ nm, $\epsilon_{max} = 34000$ L mol^{-1}cm^{-1}.^{1}H NMR (acetone-d$_6$): δ 8.45 (d, 1H), 8.27 (dd, 1H), 8.06 (d, 2H), 7.77 (d, 1H), 6.94 (d, 2H), 3.82 (t, 4H), 3.70 (t, 4H).

2.3. Synthesis of polymers

All polymers were prepared by solution polycondensation of monomer 1 and/or monomer 2 with terephthaloyl chloride and/or 2-propyloxyterephthaloyl chloride (the latter was synthesised following a procedure already described [11]).

A typical preparation of **P1** is given as a representative example. A 50 ml, two-neck, cone-shaped flask was equipped with a nitrogen gas inlet, a magnetic stirrer and a condenser. Under dry nitrogen, 0.8058 g (0.00502 mol) of Monomer 1 and 0.6358 g (0.00502 mol) of terephthaloyl chloride were dissolved in 1.5 ml of dry pyridine. The reaction mixture was stirred for 2 hours at reflux and became more and more viscous. After final addition of 5 ml of pyridine the reaction mixture was poured into vigorously stirred hexane (200 ml). The precipitated polymer was filtered, re-dissolved in 40 ml of DMF and poured into 200 ml of a solution of methanol/water (4: 1). The polymer was then washed with methanol, filtered and dried at 80°C for 8 hours. The product yield was 90%.

IR (KBr): 3080 (w, ar.C-H), 2960 (vw, aliph.C-H), 2220 (s, C $\equiv$ N), 1721 (vs, C$=$O), 1607 (vs), 1567 (vs), 1516 (vs), 1156 (vs), 1268 (vs, C-O) cm^{-1}.

Another procedure of polymerisation under milder conditions has been tried, with substantially equivalent results. In the case of **P1**, terephthaloyl chloride (0.8600 g, 0.00424 mol) dissolved in NMP (1 ml) was added dropwise to a solution of Monomer 1 (0.6786 g, 0.00264 mol) in dry pyridine (0.6 ml) and NMP (1 ml). The solution was stirred for 1 hour at 5–10°C under a slow stream of nitrogen and then the temperature was raised to 60°C for additional 3 hours. After cooling, the reaction mixture was poured into stirring hexane and the precipitated polymer was recovered as in procedure I. The yield of the product was 85%.

For both the procedures, IR (KBr) and ^{1}H NMR (Py-d$_5$, DMSO-d$_6$) spectra of all polymers were in good agreement with the postulated structures.

2.4. Thin films preparation

Polymers **P1** and **P2** were dissolved in freshly distilled NMP at concentration of 10% w/w polymer. The solutions were filtered on teflon filter with 0.45 μm porosity, and spin coated on ITO-coated glass slides, for SHG measurements, or quartz slides for refractive indices measurements; the films so obtained were dried in a vacuum oven at 80°C for three days. The film thickness ranged between 0.5 and 2 μm, as measured with an Alphastep profilometer.

2.5. Nonlinear optical Measurements

The second harmonic generation experimental setup, described in detail elsewhere [12], involved a Q-switched Surelite Nd:YAG laser ($\lambda = 1064$ nm, frequency up to 10 Hz, 8.5 mJ per pulse), pumping a methane Raman cell with output at 1542 nm. The beam intensity was measured

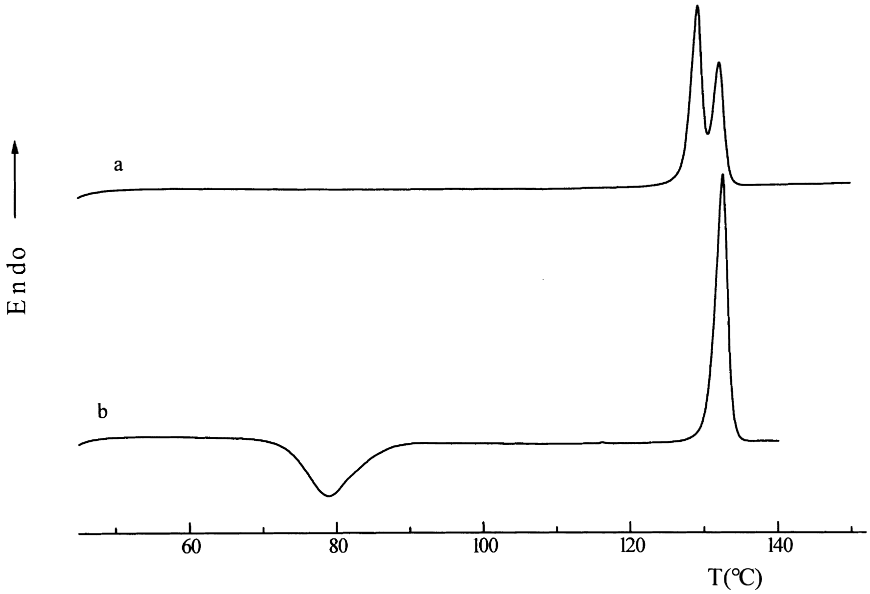


Fig. 1. DSC behaviour of Monomer 1. Solution crystallised sample, heating run. Phase I + phase II (curve a). Melt crystallised sample, heating run. Phase II.

performing a Maker fringes reference experiment with a quartz crystal (110) ($d_{11} = 0.45$ pm/V) [13]. The films were held on a computer controlled goniometer stage and heated with temperature control of ± 0.1°C. Corona poling technique was used to orient the film sample, placed at a constant distance of 2 cm from the tungsten needle. The applied corona voltage was 6.0 kV. The poling experiments were performed by measuring the SHG growth at a fixed angle of 35°. The polymer films were first heated to 140°C and there kept for a 15 min isotherm. The temperature was then lowered to 90°C at 3°C/min, for a 30 min isotherm. Finally, the samples were cooled down to room temperature at 1°C/min and the electric field was turned off.

2.6. Characterisation

The thermal behaviour was examined by differential scanning calorimetry utilising a Perkin-Elmer DSC-7 apparatus, in dry nitrogen atmosphere, with a temperature scanning rate of 10 K/min. Temperature-controlled polarising microscopy (Zeiss microscope combined with a Mettler FP5 microfurnace) was utilised for optical observations. X-ray diffraction photographs were recorded by flat-film camera utilising Ni-filtered CuKα radiation. Thermogravimetric (TGA) Mettler TG50 apparatus was utilised for monitoring the thermal stability of polymers. The intrinsic viscosity of NMP polymer solutions was measured utilising an Ubbelohde viscometer at 25.0°C. The ^{1}H NMR spectra were recorded on a Varian XL200 and on a Bruker AC 250 spectrometer. UV-vis spectra were recorded by mean of a Perkin-Elmer Lambda 7 UV/VIS spectrophotometer. IR spectra of polymers were recorded on solution cast films (chloroform or pyridine as solvents) on KBr disks using a Bruker IFS 66 FT spectrometer. The refractive indices of the thin films were measured on quartz slides using transmission spectroscopy; the real part of the refractive indices fitted a Sellmeyer-type dispersion formula [14-15].

3. Results and discussion

Cromophores – The chromophore bearing molecules (Monomer 1 and Monomer 2) were synthesised from the same precursor, 4-[*N,N-bis*(2-hydroxyethyl)amino]-benzaldehyde, and two different electron-acceptor containing molecules. Both of them exhibit solid-state polymorphism. Monomer 1 crystallises from chloroform/hexane solution in two different crystal forms melting at different temperatures, namely: form I ($T_m = 129.2$°C, $\Delta H_m = 85.6$ Jg^{-1}); form II ($T_m = 132.6$°C, $\Delta T_m = 93.1$ Jg^{-1}), with a weight ratio depending on crystallization conditions. Fig. 1 (curve a) shows the first DSC heating run for a solution crystallised sample containing forms I and II in the weight ratio 3/2. Crystallisation from the melt does not occur readily at a cooling rate of 10 K/min. However it takes place during the successive heating run forming form II only (Fig. 1, curve b). Finally, it has to be noticed that the melting temperature found for form I is fairly consistent with the temperature range found by Wang et al. [7] (127.8–129.6°C) who do not refer about solid state polymorphism.

The solid state polymorphism exhibited by Monomer 2 is of different type. Solution crystallised and melt crystallised samples show no differences. A solid state transition occurs at 140.3°C ($\Delta H = 45.1$ Jg^{-1}) while melting takes place at 178.0°C ($\Delta H = 69.4$ Jg^{-1}).

UV-vis data of monomers show maximum absorption at wavelengths in the 300–450 nm range ($\lambda_{max} = 431.2$ nm for Monomer 1; $\lambda_{max} = 401.6$ nm, for Monomer 2). This implies

Table 1
General properties of polymers

Polymers	T_g (°C)	$[\eta]^a$ (dL/g)	$T_{dec}^{\ b}$ (°C)
P1	127	0.39	369
P2	119	0.25	344
P3	208	c	316
P4	94	0.34	369
P5	107	0.25	350
P6	131	c	339
P7	141	0.24	350
P8	107	0.36	361

[a] Measured at 25°C in NMP.

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

[c] The polymer is not soluble in common solvents.

that these chromophores are transparent at the second harmonic wavelength (771 nm) of the laser radiation used for SHG measurements. The same holds for polymers **P1** and **P2**, whose UV-vis largest absorption band is found at $\lambda_{max} = 422.4$ nm for **P1**, and at $\lambda_{max} = 389.6$ nm for **P2**, in the same solvent (acetonitrile) used for the corresponding monomers.

Polymers – The thermochemical stability of all polymers, as examined by TGA technique, is fairly good both under nitrogen and in air. The 5% weight loss temperature largely exceeds 300°C (Table 1). For polymers **P1** and **P2**, which have been used in SHG experiments, a weight loss of 0.1% has been measured on samples kept at 180°C for 3 hours, which is a much more demanding thermal treatment than that of the poling process.

All polymers, either as prepared or having undergone some thermal treatment, do not show any evidence of crystallinity. A significant segment of the DSC heating curve for polymers **P1** and **P2** is reported in Fig. 2 as an example merely showing the evidence of glass transition. DSC curves at higher temperatures, within the examined range (<210°C), are entirely featureless. Glass transition temperatures, measured by DSC data, are reported for all polymers in Table 1. X-ray diffraction data are consistent with a virtual absence of crystallinity. The diffraction pattern of as prepared or compression moulded samples of **P1** and **P2** are characterised by two diffuse halos centred at $\sin(\theta)/\lambda = 0.086$ and 0.123 Å^{-1}, for **P1**, and at $\sin(\theta)/\lambda = 0.104$ and 0.128 Å^{-1}, for **P2**.

As the result of the poor tendency to crystallise, optical quality films can be cast from chloroform or DMF polymer solutions at room temperature (except for **P3** and **P6**, which are not soluble in these conditions). In fact, from observations at the polarising microscope, no optical anisotropy or light scattering caused by crystallites or grain boundaries was detected in any of the film samples. No optical or dimensional modification was detectable after a thermal treatment in air up to 200°C.

From the data reported in Table 1 it is apparent that T_g's increase with increasing content of benzoxazolic chromophore and of non substituted terephthalic acid. However, solubility is negatively influenced by the same parameters. Polymer **P3**, showing the highest glass transition temperature (208°C), was not used for SHG experiments because its poor solubility prevented the formation of good quality thin films. 100% benzoxazolic chromophore content was only compatible with 100% propyloxyterephthalic co-monomer. For this reason, polymers **P1** (highest T_g, highest dicyanovinylaniline chromophore content) and **P2** (highest T_g for a soluble polymer with the highest benzoxazolic chromophore content) were utilised for SHG measurements.

As reported in the literature for similar samples [16–19], the d_{33} time decay at 30°C presented an initial fast relaxation process, followed by a much slower one. The data analysis method used a double Kohlrausch–Williams–Watts

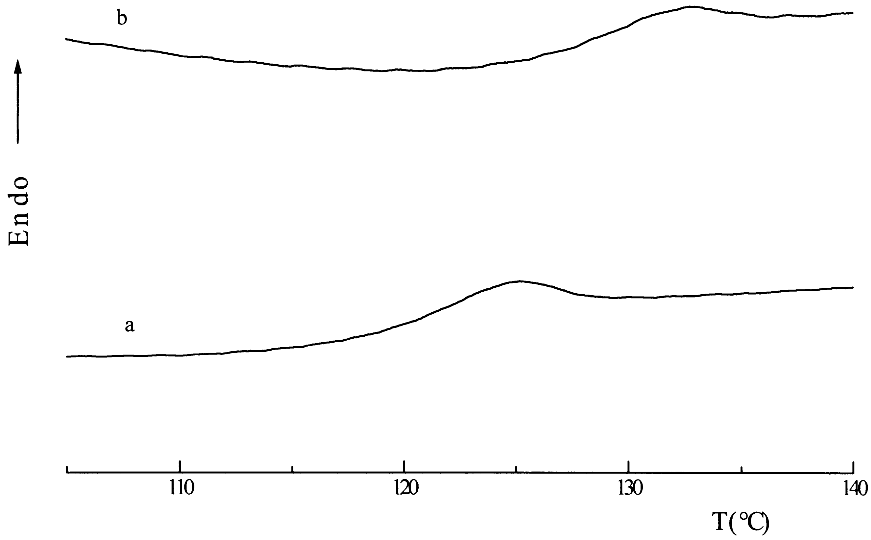


Fig. 2. DSC behaviour of polymers P1 (curve a) and P2 (curve b). Previously untreated samples.

Table 2
NLO properties of polymers P1 and P2

Polymers	$\langle\tau\rangle$ (s)[a]	*n* (771 nm)[b]	*n* (1542 nm)[b]	d_{33} (pm/V)
P1	1500	1.539	1.522	6.6[c]
P2	1100	1.566	1.544	3.6[d]

[a] Relaxation time constant (± 15%).
[b] Refraction index (± 0.3%) at the corresponding wavelength; [c,d] Second harmonic generation coefficient ([c] ± 0.6; [d] ± 0.4).

exponential fit [20], where the first time constant τ_1 was ascribed to the neutralisation of surface charges and the second one τ_2 to a real reorientation process. As result of the fast SHG signal decay, second order nonlinear susceptibilities were measured starting the Maker fringes experiment 500 s after the end of the poling and then extrapolated to time zero; in this way we can reasonably neglect the first exponential term of the double KWW function. The τ_2 mean values (that now can be named $\langle\tau\rangle$), together with those of d_{33} and of the refraction indices at first and second harmonic frequency, are shown in Table 2.

The higher second order NLO activity measured for **P1** compared to that of **P2** could be ascribed either to a different intrinsic NLO activity between the chromophores DCV and BZA, or to a better poling process realised for **P1**, owing to the fact that DCV chromophore is less bulky than BZA, so that its mobility inside the polymer matrix is less hindered. However, the higher time constant $\langle\tau\rangle$ found for **P1** makes the first hypothesis more likely.

The data obtained for **P1** can be compared with that of a polyurethane bearing in the backbone chain a chromophore whose structure is very similar to that of DCV, except for the presence of one more cyano group [21]. Surprisingly, the d_{33} value measured for **P1** is almost three times higher than the value reported for that polymer. However, the temporal stability of the latter is clearly higher, although the T_g's of the two polymers are not so different. A possible explanation for this fact is that strong interactions such as hydrogen bonding could negatively influence the efficiency of the poling process by hindering molecular motions, but at the same time they could also enhance the stability of the orientational polar order once it has been obtained.

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