JOURNAL OF MATERIALS SCIENCE **38** (2003) 1573–1577

Synthesis and characterization of chiral main chain polyesters with polar segments tailored for second harmonic generation

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The synthesis, characterization and solvatochromic behavior of a new series of chiral polyesters are reported. These polymers with π-conjugated donor-acceptor segments were synthesized with a view to be suitable for second harmonic generation. The polyesters were prepared by the reaction of diacid chlorides with biphenolic azo chromophores with Λ-conformation and optically active dihydroxy compound (isosorbide). The polymers containing isosorbide units are optically active. They showed T_g between 100°C to 160°C and are stable up to 400°C. A red shift in the longer wavelength absorption band of these polymers in UV-Vis. absorption spectra (positive solvatochromism) shows that the dipole moment of excited state is higher than that of the ground state. Therefore these polyesters are expected to have good second harmonic generation capability. © *2003 Kluwer Academic Publishers*

1. Introduction

Polymeric main chain systems which exhibit efficient second order non-linear optical property or second harmonic generation (SHG) have received considerable attention in the development of photonics—based technologies. The major advantages of such systems are their ultra fast response, high mechanical and dimensional stability, flexibility of chemical structural modification etc. In main chain systems we can have high percentage of NLO chromophores, high degree of electric field induced alignment and hence large macroscopic second-order NLO response. These systems are highly thermally stable and possess high glass transition temperature (T_g) [1–3].

Non-linear optical phenomena, typically second harmonic generation require donor-acceptor substituted π-conjugated molecular structures with non-centrosymmetry. A 'molecular engineering' approach can be used to design such polymeric materials. It was reported that chiral centers could be used as a mode for introducing non-centrosymmetry in simple organic molecules [4, 5]. Extending this idea to macromolecules, we have reported a series of main chain polyesters incorporating chiral building blocks and donor-acceptor π-conjugated systems. They showed high T_g (~200°C) and good second harmonic generation [6]. In polymeric systems, the method for attaining non-centrosymmetry is electrical poling [7, 8]. The Λ-conformation of the chromophore tends to orient dipole moments perpendicular to the molecular chain. The polar alignment of NLO chromophoric parts should be easier to be achieved by electrical poling when the dipole moments are pointing perpendicular to the polymeric chain [9, 10]. A poled structure is a metastable state. These thermodynamically unstable orientations undergo slow relaxation, which destroys the macroscopic non-centrosymmetry. Hence the orientational stability of the poled polymer is among the main concerns of the last few years. One of the strategies to achieve this is the use of polymers with high T_g [7]. The polymers must also be thermally stable up to the temperatures of poling. The use of chiral building blocks can induce macroscopic noncentrosymmetry in the material even in the absence of poling. Long polymer chain with chiral groups often prevents the tendency of the polymer to twist macroscopically. The cooperative chiral order plays a vital role in the self-assembly of ordered supramolecular structure [11].

The second-order molecular polarisability β of NLO active molecules is a function of spectroscopic and excited state properties of a molecule. It is proportional to the dipole moment change between ground state and

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excited state of the molecule as given by the equation [12],

$$\beta = \frac{3e^2h^2}{2m} f \frac{\Delta\mu_{\mathrm{ge}}}{\Delta E_{\mathrm{ge}}}$$

where, ΔE_{ge} is the energy and $\Delta\mu_{\mathrm{ge}}$, the dipole moment change and f, the oscillator strength for the transition between the ground state (g) and the first excited state which is the charge—transfer state. Molecules with large β-values are characterized by internal charge transfer (ICT) transitions, which are highly solvatochromic [13, 14]. Since for NLO molecules, the dipole moment of excited state is greater than that of ground state ($\mu_{\mathrm{e}} > \mu_{\mathrm{g}}$), they show positive solvatochromism or a red shift in UV-Vis absorption spectra when solvent polarity is increased. The objective of this work was to synthesize polymers incorporating donor-acceptor π-conjugated systems and chiral units that possess high T_{g} and thermal stability.

We selected the chromophres, bis(4-hydroxyphenylazo)-2,2′-dinitrodiphenylmethane and bis(4-hydroxyphenylazo)-2,2′-dinitrodiphenylsulphone for the present study. In this paper we report the synthesis, characterization and solvatochromic behavior of a series of polyesters, tailored to meet the requirements for second harmonic generation.

2. Experimental

2.1. Materials and methods

IR spectra were recorded on Perkin-Elmer model 882 IR spectrometer. UV-Vis spectra were recorded on a Schimadzu UV-2100 spectrophotometer. NMR spectra were obtained using a JEOL JNM-EX270 spectrometer operating at 270 MHz. DSC measurements were performed on a Perkin-Elmer DSC-7 instrument. Thermogravimetric (TG) analyses were done using a Metler 851 model SDTA/TGA instrument. Optical rotations were measured using an ELICO Model polarimeter PA-21. Inherent viscosities were measured with an automated Ubbelohde viscometer thermostated at 25°C. Reagent grade reactants and solvents were used as received. Extremely dry solvents were prepared by adopting standard procedures. Spectroscopic grade solvents were used for all measurements.

2.2. Synthesis of monomers

*2.2.1. 1,4:3,6-dianhydro-D-sorbitol (isosorbide) (**1**)*

Isosorbide was prepared by dehydration of D-sorbitol using concentrated sulphuric acid and removing the water and excess sulphuric acid with a rotary vacuum evaporator. White needle shaped crystals were obtained and used without further purification. The measured melting point was $T_{\mathrm{m}} = 61°\mathrm{C}$. The specific rotation was +42°. This is in good agreement with literature values [6].

2.2.2. 4,4′-diamino-2,2′-dinitrodiphenylmethane [6]

Diaminodiphenylmethane was nitrated using a mixture of anhydrous potassium nitrate and 98% sulphuric acid at 0°C. To an ice cold solution (0–5°C) of diamine (0.05 mol 9.9 g) in conc.sulphuric acid (18 M, 40×10^{-6} m^3), a solution of potassium nitrate (0.1 mol 10.1 g) in conc.sulphuric acid (18 M, 15×10^{-6} m^3) was added during a period of 1 h. The stirring was continued for 3 h, keeping the temperature below 5°C. The reaction mixture was poured into crushed ice and neutralized with ice-cold solution of ammonia. The yellow solid was collected on a filter, washed thoroughly with water. Crystallisation from a mixture of dioxane-alcohol afforded orange yellow flakes of **3a** (Yield–9 g) Calculated for ($C_{13}H_{12}N_4O_4$): C, 54.6; H, 4.16; N, 19.44. Found: C, 54.11; H, 4.18; N, 19.33.

2.2.3. 4,4′-diamino-2,2′-dinitrodiphenylsulphone

Diaminodiphenylsulphone was nitrated as above by taking diamine and potassium nitrate in the ratio 1:2. The product was recrystallised from alcohol-water mixture (Yield–9.2 g) Calculated for ($C_{12}H_{10}N_4O_6S$): C, 42.6; H, 2.95; N, 16.57. Found: C, 42.75; H, 2.9; N, 16.50.

*2.2.4. Bis(4-hydroxyphenylazo)-2,2′-dinitrodiphenylmethane (**2a**) [6]*

To an ice cold solution of 3a (10 g, .035 mole) in HC1 (6 M, 20×10^{-6} m^3) was added aqueous sodium nitrate solution (6 g, 15×10^{-6} m^3). The diazonium salt was added slowly to a cold alkaline solution of phenol (6.58 gm, 0.07 mol). The resulting solution on acidification gave a brown solid. It was collected, washed with water, dried and purified in a silica column using benzene and benzene-ethyl acetate mixture (Yield-7g). IR (KBr): 1540, 1345 cm^{-1} (NO_2), 3400 cm^{-1} (O—H). ^{1}H NMR ($CDCl_3$): δ (ppm) = 3.8 [2H(s), CH_2], 6.93 [4H(d), H^a], 7.76 [4H(d), H^b], 9.2 [2H(d), H^c], 8.65 [2H(d), H^d], 7.9 [2H(d), H^e], 9.9 [2H(s), OH] UV $\lambda_{\max}$: 270 nm (NO_2) and 375 nm (—N=N—). Calculated for ($C_{25}H_{18}N_6O_6$): C, 60.24; H, 3.61; N, 16.81. Found: C, 60.18; H, 3.58; N, 16.76.

*2.2.5. Bis(4-hydroxyphenylazo)-2,2′-dinitrodiphenylsulphone (**2b**)*

3b was diazotised and coupled with phenol using the procedure adopted for synthesizing 4a (Yield–7.5 g). IR (KBr): 1540, 1345 cm^{-1} (NO_2), 3390 cm^{-1} (O—H). ^{1}H NMR ($CDCl_3$): δ (ppm) = 7 [4H(d), H^a], 7.8 [4H(d), H^b], 9.3 [2H(d), H^c], 8.5 [2H(d), H^d], 8.1 [2H(d), H^e], 9.9 [2H(s), OH]. UV $\lambda_{\max}$: 275 nm (NO_2) and 380 nm (—N=N—). Calculated for ($C_{24}H_{16}N_6O_8S$): C, 52.55; H, 2.92; N, 15.33. Found: C, 52.5 H, 3.1; N, 15.15.

*2.2.6. Azobenzene-4,4′-dicarbonylchloride (**3**) [15]*

p-nitrobenzoic acid (13 g) and sodium hydroxide (50 g) were mixed in water (225×10^{-7} m^3) and solution was warmed to 50°C. A solution of glucose in water (100 g in 150×10^{-6} m^3) was then added slowly at 50°C and mixture warmed on a steam bath until a yellow precipitate started to form. It was then removed and well

TABLE I Synthesis of polyesters (**2a**/**2b** + **1** + **3**)

PE	Mass (in grams)	
	Chromophore	Isosorbide (**1**)
	2a	
1	4.98 (0.01 mol)	0
2	3.74 (0.0075 mol)	0.365 (0.0025 mol)
3	2.49 (0.0050 mol)	0.730 (0.0050 mol)
4	1.25 (0.0025 mol)	1.095 (0.0075 mol)
5	0	1.46 (0.01 mol)
	2b	
6	5.48 (0.01 mol)	0
7	4.11 (0.0075 mol)	0.365 (0.0025 mol)
8	2.74 (0.0050 mol)	0.730 (0.0050 mol)
9	1.37 (0.0025 mol)	1.095 (0.0075 mol)

For all polymers 4,4′-azobenzenedicarbonylchloride (**3**)-3.06 g (0.01 mol).

shaken until the precipitate dissolved to give a brown solution. Then a stream of air was drawn through the brown solution for three hours. This on acidification deposited the azobenzene dicaboxylic acid. The acid was refluxed with excess thionyl chloride for 24 h to give **3**. On recrystallisation from petroleum ether yielded **3** as red needles. Melting point is 165°C. The literature value is 164°C [15].

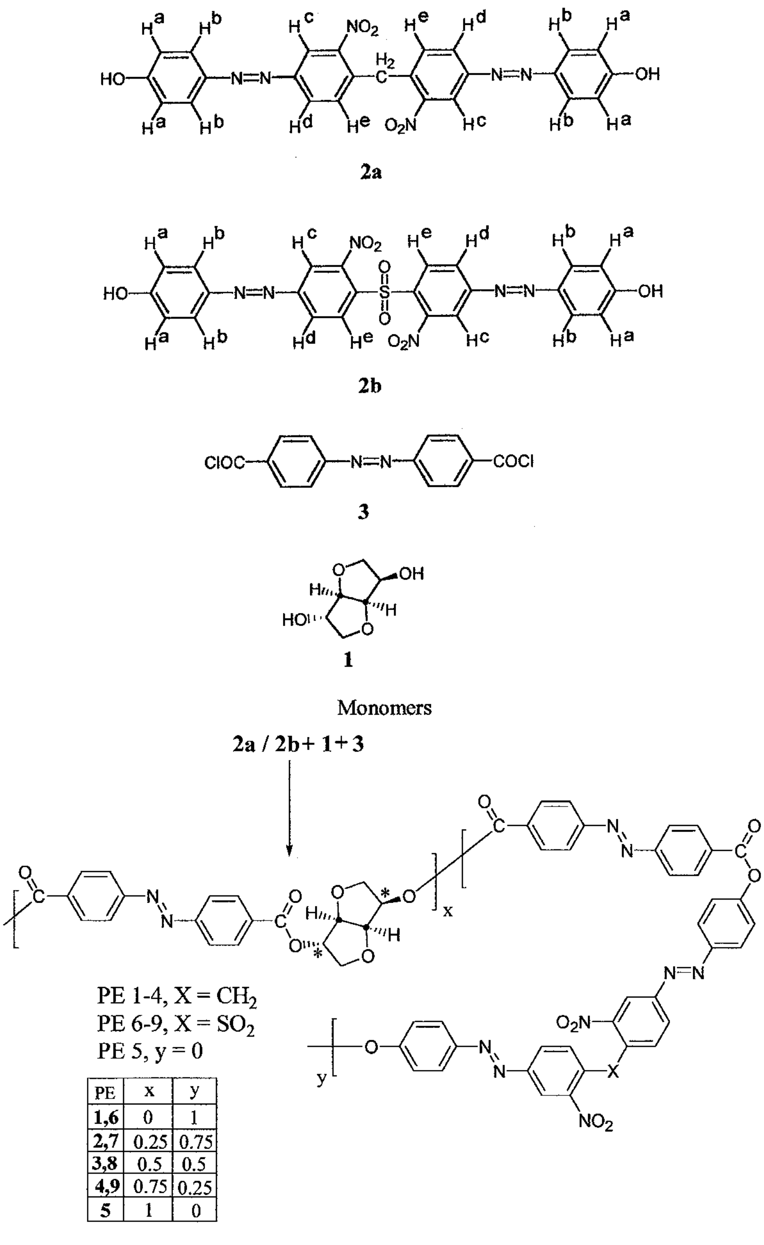
2.3. Synthesis of polyesters

The diacid chloride (**3**) was dissolved in N,N′-dimethyl acetamide (10^{-5} m^3). Fixed proportions of biphenol and isosorbide were added (see Table I). Few drops of pyridine were added as acid acceptor. The reaction mixture was stirred under nitrogen atmosphere at 160°C for 25 h. The product was precipitated in methanol, washed with acetone and dried.

3. Results and discussion

3.1. Synthesis of polyesters

Scheme-1 shows the synthesis of polyesters **1** to **9** by the reaction of **2a**/**2b** with **1** and **3**. It was found that the inherent viscosity and yields of these polymers were very much dependent on the conditions of



PE	x	y
1,6	0	1
2,7	0.25	0.75
3,8	0.5	0.5
4,9	0.75	0.25
5	1	0

Scheme 1.

polycondensation. The polymerizations were carried in different highly polar solvents like N,N′-dimethyl formamide (DMF) and DMAc with pyridine as acid acceptor. Temperature was varied from 30°C to 160°C. Polymers of good inherent viscosity in high yield were obtained in DMAc at a temperature of about 160°C. x:y (percentage incorporation) was obtained from molar ratio of starting materials. The percentage of the chromophore was varied from 0 to 100 (0, 25, 50, 75, 100). PE-**1** and **6** with $x = 0$ have the highest density of chromophore. All polymers containing isosorbide units were found to be optically active. PE-5 contained no chromophoric units. The $[\alpha]_D$ value varies from −25.0 to −42.0°. The polyesters showed almost 100% optical purity even in the molten state. Relatively good values of specific rotations have shown that no extensive racemization occurred during the polymerization stage or when polyesters were heated to melt. When optical rotation was measured after cooling from liquid phase, no change in the value of α was observed. The value of α decreased with a decrease in amount of isosorbide units. The isosorbide unit has proved to be a highly stable building block, which could impart molecular level chirality to copolymers and retain it at high temperatures [16, 17]. The polyesters **1** and **6** showed the ester carbonyl peak between 1750–1755 cm^{-1} due to the ester bonds formed by phenolic units. But polyesters **2**, **3**, **4**, **5**, **7**, **8** and **9** showed additional peaks in the region 1720–1730 cm^{-1}. The ester bonds formed by isosorbide units gave these peaks. The incorporation of isosorbide units was also indicated by the peaks in the region 1230–1235 cm^{-1} (C—O str.), 2900–2910 cm^{-1} (C—H str.) and 1465–1470 cm^{-1} (C—H bend.). The ^{1}H NMR spectra of polymers showed no peaks corresponding to the probable end groups (OH and COOH), revealing no detectable concentration of end groups. This is an indication of high molecular weight of this material [18]. The signals at δ 4.2 (CH_2), 4.7 (CH) and 4.0 (CH bridge) indicated the presence of isosorbide units in the polymer chain. The shift of δ from 3.9 to 4.64 for the CH attached to OH in isosorbide, was due to the conversion of OH to ester group. The presence of chromophore units in the main chain was established by comparing the δ values of polymers with that of chromophores. The polyesters showed peaks corresponding to that of H^a to H^b in the monomers. The δ value of H^a in chromophore was shifted from 6.93 to 7.35 due to the conversion of phenolic OH groups to ester groups during polymerization.

3.2. Thermal properties

The thermal stabilities of the polyesters were determined by TG analysis. The polymers were heated in nitrogen atmosphere from 30°C to 700°C. The initial decomposition temperature (T_i) was taken to determine the stability. All the polyesters were stable up to 400°C. The stability increased with increase in biphenol content. These values are capable for meeting thermal requirements in constructing optical devices. The glass transition temperatures were determined by DSC and these range from 100°C to 160°C. The T_g value tends to decrease with decrease in chromophore content. An endotherm was also observed in the second heating curves of polymers (see Fig. 1). This may be due to the decrease in the number of aromatic units and bulky nitro substituents in polymer backbone.

TABLE II Yield and physical properties polyesters

PE	Chromophore (%)	Chiral unit (%)	Yield	η_{inh}^{a}	$[\alpha]_D$^{b}	T_g	T_m	T_i
1	100	0	87	1.20	0	160	320	391
2	75	25	80	1.00	−25.0	137	310	378
3	50	50	85	0.98	−30.1	126	320	370
4	25	75	84	1.11	−35.0	115	325	361
5	0	100	90	1.12	−42.0	100	300	320
6	100	0	87	0.97	0	150	321	420
7	75	25	86	0.96	−26.0	130	312	412
8	50	50	83	1.03	−32.2	120	310	400
9	25	75	85	0.95	−36.2	105	305	385

^{a,b}Conc. 10^3 g m^{-3} in DMAc.
T_g, T_m and T_i in °C.

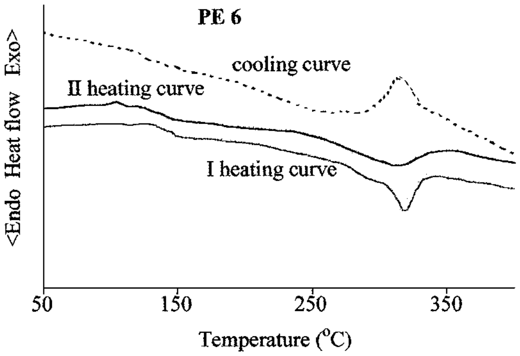


Figure 1 DSC plots of PE-**6**.

The properties of the polyesters are summarized in Table II.

3.3. UV-Visible absorption studies

The UV-Visible spectra of all polyesters were obtained in DMF. The spectra exhibited characteristic bands of nitro groups (265–270 nm, $n \rightarrow \pi^*$) and azo groups (350–360 nm, $\pi \rightarrow \pi^*$). The absorption spectra were also recorded after cooling from isotropic liquid state. There was no change in absorption maxima. This showed that all building units remained intact even in molten state i.e., no decomposition or thermal rearrangement of azo groups.

The insolubility of polymers in common organic solvents limits the extensive solvatochromic studies in solvents of different polarity. However to illustrate the dipole moment change during ICT absorption of many donor-acceptor substituted dyes two solvents of different polarity were taken [19]. So in the case of the above polymers we have determined the λ_{max} for the longest wavelength absorption in two solvents of different polarities. The solvents were DMF (1) and 1: 0.05 v/v mixture of DMF with methanol (2). The polarity parameter E_T (30) of the two solvents is 43.8 and 54.036 respectively [20]. All the polymers showed a red shift of about 15 nm in the position of longer wavelength absorption with an increase in solvent polarity or a positive solvatochromism. This indicates that the

TABLE III UV-Visible absorption studies

	λ_{max} (nm)	
PE	1	2
1	350	363
2	348	359
3	346	358
4	347	359
5	340	343
6	360	371
7	358	370
8	356	369
9	357	369

1-DMF, 2-DMF + Methanol.

total dipole moment of the polyesters are higher in excited state than in ground state so that the polymers are stabilized more in the excited state by an increase in solvent polarity. This shows that the polymers are suitable for NLO studies. The results are summarized in Table III.

4. Conclusions

In all respects these polyesters are suitable for NLO studies. The polymers were tailored with Λ-shaped chromophores so that the dipole moments are perpendicular to the polymer chain, which makes the polar alignment easier during poling. The polymers containing isosorbide units were optically active and retained it even after cooling from an isotropic liquid state. Thus the chiral building blocks induced a macroscopic chirality in the material even in the absence of poling. They exhibited high T_g values and good thermal stability. All polyesters showed moderately good positive solvatochromism in UV-Vis. absorption spectra. This indicates an intramolecular charge transfer (ICT) absorption of less polar ground state molecule leading to a polar excited state molecule i.e., $\mu_e > \mu_g$ which is characteristic of an NLO active molecule. Therefore a moderately good second harmonic generation can be expected from these chiral polyesters.

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Received 18 October 2000
and accepted 24 December 2002