

Studies on Second Harmonic Generation Efficiency by a Series of Chiral Polyesters

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ABSTRACT: A series of optically active main-chain polyesters were synthesized by high-temperature polycondensation from biphenolic azo chromophores, (2R,3R)-(+)-diethyl tartrate and terephthaloyl chloride. The polyesters showed glass transition temperatures in the range of 100–135°C and were thermally stable to 350°C. The second harmonic generation efficiency of the polyesters was studied by the powder method and as thin films with 2-methyl-4-nitroaniline as a reference. The SHG efficiency of the polymers was com-

pared with that of low molecular weight chromophores. The polymers with chiral units showed good second harmonic generation efficiency. The SH signal also showed good temporal stability. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2468–2473, 2003

Key words: polyesters; nonlinear optics; second harmonic generation; polar order; chiral polymers

INTRODUCTION

Polymeric main-chain systems which exhibit an efficient second-order nonlinear 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 ultrafast response, high mechanical and dimensional stability, flexibility of chemical structural modification, etc. For a nonvanishing macroscopic response in polymers, the donor–acceptor π -conjugated segments or chromophores must be incorporated into noncentrosymmetric structures such as poled polymers, LB films, and supramolecular helical organizations. With such an approach, molecular dipole moments have a net orientation along the polar axis of the macroscopic sample or the material possesses a polar order.^{1–4}

A promising development in the field of nonlinear optical polymers is the use of chiral main-chain polymers incorporating donor–acceptor π -conjugated segments or chromophores. Chiral polymers can provide a noncentrosymmetric media with a nonvanishing second-order susceptibility and polar ordering of chromophores can be achieved through chemical synthesis. The permanent dipole moment of such a structure is very large due to the coherent addition of segmental dipole moments.^{5–10} In this article, we re-

port the synthesis and characterization of a series of optically active polyesters and their second harmonic generation ability, determined by powder and thin-film methods.

EXPERIMENTAL

Measurements and shg experimental setup

IR spectra were recorded on a Perkin–Elmer Model 882 IR spectrometer. UV-vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer. ¹H-NMR spectra were obtained using a JEOL JNM-EX270 spectrometer with TMS as the internal standard. DSC measurements were performed on a Perkin–Elmer DSC-7 instrument at a heating rate of 10°C min⁻¹. Thermogravimetric analyses were done using a Metler 851 Model SDTA/TGA instrument at a heating rate 10°C min⁻¹. Optical rotations were measured using an ELICO Model polarimeter PA-21. Reagent-grade reactants and solvents were used as received. Terephthaloyl chloride and diethyl tartrate were obtained from E. Merck (Darmstadt, Germany). Extremely dry solvents were prepared by adopting standard procedures. Spectroscopic-grade solvents were used for all measurements.

The experimental setup consists of a Q-switched Nd:YAG laser (Spectra Physics, 1064 nm, 11 ns, 400 mJ pulse) and is illuminated to the sample through the UV-vis cut filter. The second harmonic signal at 532 nm was detected by a photomultiplier tube and displayed on a CCD. Measurements were done by both the thin-film method and the powder method. For

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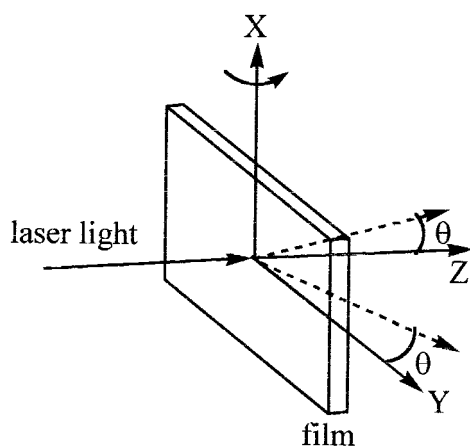


Figure 1 Film geometry.

powder measurements, the samples were ground and graded using standard sieves (100–150 μm) and loaded onto a microscopic slide with a sample thickness of 1 mm. 2-Methyl-4-nitroaniline (MNA) samples, used as standards, were also powdered and sieved (100–150 μm) after drying under a high vacuum. They were also mounted with the same thickness as that of the polymer sample. The laser beam was directed unfocused onto the sample kept at a 45° angle to the laser beam; the emission was collected from the front face of the sample at a 90° angle.

The solutions were filtered through a 0.5- μm syringe filter, spin-coated on a clean glass substrate, and dried at 100°C in a vacuum for 30 h. The thickness obtained, measured with a profilometer, was in the range of 1 μm . The film geometry is shown in Figure 1. The SHG intensity was detected by varying θ , which is changed by rotating the sample with regard to an axis X in the film plane.

Synthesis of polymers

Synthesis of polyesters (TPE-1 and -5)

Terephthaloyl chloride (**3**) (1 equiv) was dissolved in hot dry *N,N*-dimethylacetamide (DMAc). To this solution was added the chromophore (**1a** or **b**) (1 equiv). A few drops of pyridine were added. The mixture was heated under stirring for 50 h at 160°C. The product was precipitated in cold methanol and filtered. The dark-colored solid obtained was washed with methanol and acetone. After filtration and drying, the product was obtained as a brown solid.

TPE-1. UV (DMF): 370 (N=N), 320 (NO₂). IR (KBr, cm^{-1}): 1755 (C=O str. ester), 1345, 1535 (N—O str. NO₂). ¹H-NMR (DMSO-*d*₆): 5.3 (s, methylene), 8.8–7.3 (m, aromatic). ¹³C-NMR (DMSO-*d*₆): 172 (ester carbon), 34 (methylene carbon), 120–157 (aromatic ring carbons).

TPE-5. UV-vis (DMF, nm): 365 (N=N), 329 (NO₂). IR (KBr, cm^{-1}): 1758 (C=O str. ester), 1350, 1538 (N—O str. NO₂). ¹H-NMR (DMSO-*d*₆): 8.9 (s, aromatic), 8.5, 8.1, 7.7, 7.8, 7.4 (d, aromatic). ¹³C-NMR (DMSO-*d*₆): 173 (ester carbon), 120–157 (aromatic ring carbons).

Synthesis of polyesters (TPE-2, -3, -4, -6, -7, and -8)

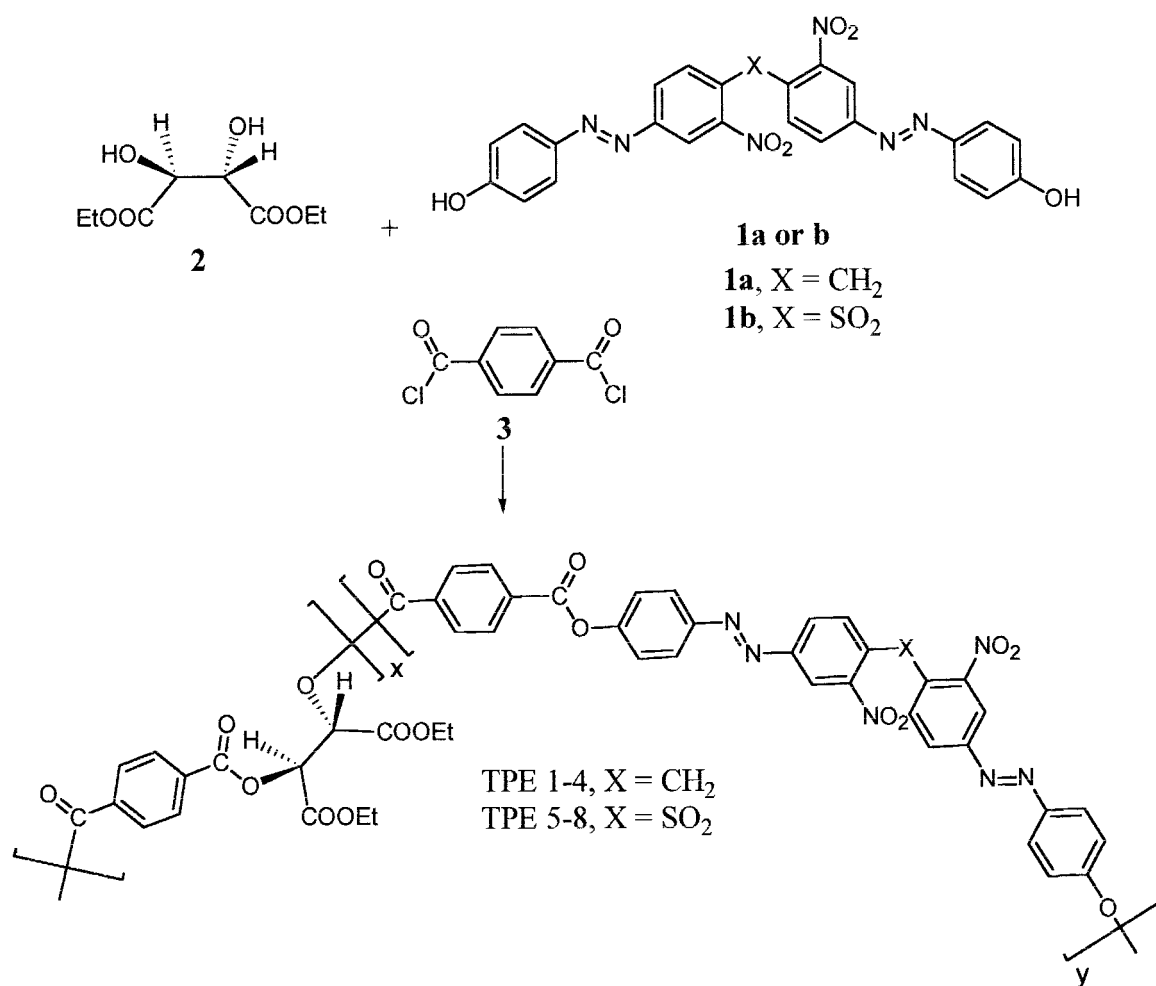
Terephthaloyl chloride (1 equiv) was dissolved in hot DMAc. To this solution was added appropriate mol percentages of the chromophore (**1a** or **b**) and diethyl tartrate (**2**). A few drops of pyridine were added. The mixture was heated under stirring for 50 h at 120°C. The product was precipitated in cold methanol and filtered. The dark-colored solid obtained was washed with methanol and acetone. After filtration and drying, the product was obtained as a brown solid.

The spectral patterns of **TP-2**, **-3**, and **-4** are similar:

UV-vis (DMF, nm): 365 (N=N), 320 (NO₂). IR (KBr): 3000, 2960, 2900 (C—H str. in tartrate unit), 1755–1760 (C=O str. in ester formed by phenolic unit), 1736–1740 (C=O str. ester group in diethyl tartrate), 1720–1725 (C=O str. in ester formed by tartrate), 1345–1350, 1530–1535 (N—O str. NO₂), 1465–1470 (C—H bend of CH₂ group), 1380–1385 (C—H bend of CH₃ group). ¹H-NMR (DMSO-*d*₆): 1.2 (t, CH₃ in tartrate unit) 4.1–4.3 (q, CH₂ in tartrate unit], 5.1–5.4 (s, CH in tartrate), 5.7 (s, methylene), 8.8–7.3 (aromatic). ¹³C-NMR (DMSO-*d*₆): 174–177 (ester carbon in tartrate unit), 170–173 (carbon in ester formed by phenolic unit), 164–167 (carbon in ester formed by tartrate), 122–160 (aromatic ring carbon atom), 76–74 (CH), 60–64 (CH₂), 14–16 (CH₃), 34–38 (methylene).

The spectral patterns of **TPE-6**, **-7**, and **-8** are similar:

UV-vis (DMF, nm): 370 (N=N), 315 (NO₂). IR (KBr, cm^{-1}): 3050, 2970, 2900 (C—H str. in tartrate unit), 1755–1760 (C=O str. in ester formed by phenolic unit), 1735–1740 (C=O str. ester group in diethyl tartrate), 1720–1725 (C=O str. in ester formed by tartrate), 1345–1350, 1530–1535 (N—O str. NO₂), 1340–1350, 1150–1155 (S—O str. SO₂), 1465–1470 (C—H bend of CH₂ group), 1380–1385 (C—H bend of CH₃ group). ¹H-NMR (DMSO-*d*₆): 1.3 (t, CH₃ in tartrate unit) 4.1–4.5 (q, CH₂ in tartrate unit], 5.0–5.4 (s, CH in tartrate), 8.8 (s, aromatic), 8.5–7.3 (d, aromatic). ¹³C-NMR (DMSO-*d*₆): 174–177 (ester carbon in tartrate unit), 170–173 (carbon in ester formed by phenolic unit), 164–167 (carbon in ester formed by



Scheme 1 Synthesis of polyesters.

tartrate), 118–160 (aromatic ring carbon atom), 76–74 (CH), 60–64 (CH₂), 14–16 (CH₃).

RESULTS AND DISCUSSION

Polymer synthesis and characterization

The polyesters were synthesized by high-temperature polycondensation of biphenolic chromophores, bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylmethane (**1a**) and bis(4-hydroxyphenylazo)-2,2'-dinitrodiphenylsulfone (**1b**)^{6,10} with (2R,3R)-(+)-diethyl tartrate (**2**) and terephthaloyl chloride (**3**) (see Scheme 1). Polyesters containing tartrate units are optically active. The optical rotation increased with the increase in the composition of diethyl tartrate units (see Table I). All polyesters except TPE-1 and -5 showed three strong peaks between 1725 and 1760 cm⁻¹. The peaks correspond to the carbonyl stretching vibration due to three types of ester bonds. The peaks can be assigned as 1735–1740 cm⁻¹ (due to ester group in tartrate), 1720–1725 cm⁻¹ (due to ester bonds formed by tartrate), and 1755–1760 cm⁻¹ (due to ester bonds formed by biphe-

nols). The frequency of C=O stretching is reduced in the case of ester bonds formed by tartrate, which is due to conjugation with the phenyl ring. In the case of ester bonds formed by phenolic units, the phenyl group attached to oxygen can reduce the extent of conjugation. Polyesters TPE-1 and -5, which contain no diethyl tartrate group, showed only one peak in this region between 1755 and 1760 cm⁻¹ given by phenolic ester units.

The percentage composition of chiral units and chromophore units in a terpolymer can be determined from the IR spectrum in the absorbance mode.¹¹ Let the two units give two different ester carbonyl peaks at x cm⁻¹ and y cm⁻¹, respectively. On the basis of the Beer–Lambert law, it is possible to relate the absorbance of carbonyl groups to their concentration in the polymer as (by neglecting the effect of chemical surroundings)

$$A_{\text{C=O}}(x \text{ cm}^{-1}) \propto C_{\text{chiral unit}}$$

$$A_{\text{C=O}}(y \text{ cm}^{-1}) \propto C_{\text{chromophore}}$$

TABLE I
Composition and Properties of Polyesters

TPE	Target composition ^a	Measured composition ^b	$[\alpha]_D^{25}$ ^c	T_g ^d (°C)	IDT ^e (°C)
1	100 : 0	100 : 0	0	135	340
2	75 : 25	80 : 20	-11.3	128	325
3	50 : 50	56 : 44	-15.5	117	317
4	25 : 75	23 : 77	-23.0	110	310
5	0 : 100	0 : 100	-30.0	80	260
6	100 : 0	100 : 0	0	129	367
7	75 : 25	78 : 22	-12.1	123	358
8	50 : 50	57 : 43	-16.2	114	350
9	25 : 75	24 : 76	-22.7	105	341

^a Feed composition (chromophore:diethyl tartrate).

^b From IR spectrum (chromophore:diethyl tartrate).

^c Concentration 1 g L⁻¹.

^d From DSC.

^e Temperature at which decomposition starts (from TG plot).

Percentage composition of chiral unit

$$= \frac{A_{C=O}(x \text{ cm}^{-1})}{A_{C=O}(x \text{ cm}^{-1}) + A_{C=O}(y \text{ cm}^{-1})}$$

Percentage composition of chromophore unit

$$= \frac{A_{C=O}(y \text{ cm}^{-1})}{A_{C=O}(x \text{ cm}^{-1}) + A_{C=O}(y \text{ cm}^{-1})}$$

The ratio of chromophore and chiral units in the polymer can be determined from the area of the absorbance of peaks corresponding to the carbonyl vibration at 1755–1760 cm⁻¹ and 1720–1725 cm⁻¹. The ratio of chromophore and diethyl tartrate in the feed and the measured, from IR spectra, are given in Table I.

The ¹H-NMR spectrum of chiral polyesters showed peaks between 4.1 and 4.5 (quartet, CH₂), 1.4–1.2 (triplet, CH₃), and 5–4.9 (singlet, CH) given by the tartrate groups in the chain. The absence of peaks corresponding to OH and COOH protons can be taken as an indication of high molecular weight. The ¹³C-NMR spectrum of TPE-1 and -5 showed only one peak above 160 ppm at 170–173 due to the ester carbonyl carbon atom since the polymer contains only one type of ester bonds formed by phenolic units. In the case of polyesters incorporating diethyl tartrate units, two more signals were observed in this region. The signals between 174 and 177 ppm were due to the ester bond in diethyl tartrate. The other between 164 and 167 was due to the ester bond formed by diethyl tartrate. The polyesters incorporating chiral units showed signals at 74, 61, and 14 ppm due to CH, CH₂, and CH₃ groups.

The DSC plots showed that the polymers possess a relatively high glass transition temperature range from 105 to 135°C. The TG analysis showed that the initial decomposition temperature (IDT) of the polymers varied from 260 to 367°C. Therefore, the polyesters are stable to these temperatures. As the relaxation

of long-range order in polymers is related to segmental motion, the high glass transition temperature and the thermal stability of a polymer can give a sufficient temperature window for NLO measurements even at elevated temperature.^{12–14} The T_g values and the IDT values are given in Table I.

Shg studies

Powder method

The second harmonic generation efficiency was measured in comparison with that of 1-methyl-2-nitroaniline (MNA). The laser beam (1064 nm) was directed unfocused onto the sample kept at a 45° angle to the laser beam; the emission (532 nm, green light) was collected from the front face of the sample at a 90° angle. The intensity of green light emitted by MNA was taken as 1. The intensity of the green light emitted by all polymers was compared with that of MNA at the same angle. This gives the SHG efficiency of the polymer. The results are given in Table II. Some chiral polymers showed better activity when compared to MNA. The role of supramolecular organization of the polymer matrix in the orientation correlation of the

TABLE II
SHG Activity of Polyesters by Powder Method

TPE	SHG efficiency	E
1	0.38	1.5
2	0.85	3.4
3	1.31	5.2
4	1.20	4.2
5	0.42	1.9
6	0.92	4.2
7	1.29	5.9
8	1.17	5.4

Film thickness is 1.0 μm.

NLO chromophores was demonstrated by comparing the β values of the polymer and the chromophore, respectively.¹⁵ For this, the SHG activity of the chromophores and that of polymers obtained by the powder method were compared. The ratio E defined as

$$E = \frac{\text{SHG activity of polymer}}{\text{SHG activity of chromophore}}$$

gives the enhancement in SHG activity when the chromophores are polymerized with chiral compounds to form optically active polymers. SHG efficiency of chromophores **1a** and **1b** are 0.25 and 0.22, respectively, by the powder method. The hyperpolarizabilities of the polyesters were found to be much larger than those of the respective chromophores. The four to six times enhancement in SHG activity is noticeable even when the strong —OH donor in the chromophore is converted to a weak ester donor group in the polymer. This finding indicates that the chromophores are organized in a noncentrosymmetric environment when they are incorporated in to a main-chain chiral polymer.

As thin films

In this method, the SHG efficiency of the polymers was also determined by taking MNA as the standard. A laser beam of wavelength 1064 nm was passed through the film. The intensity of the green light (532 nm) was measured at $\theta = 45^\circ$ (θ as given in Fig. 1). This intensity was given a value of 1. The intensity of the green light emitted by all the polymer films at different angles was compared with that of MNA. This gives the SHG efficiency of the polymer at different angles.

The SHG efficiency of the polyesters was measured at different values of angle θ (Table III). All polyesters were SH inactive at $\theta = 0^\circ$. The achiral polyesters, **TPE-1** and **-5**, which contain no chiral units, showed no second harmonic generation even at other angles. This is due to the absence of polar order along the

TABLE III
SHG Activity of Polyesters in Thin Films

Polyesters	SHG activity		
	$\theta = 0^\circ$	$\theta = 45^\circ$	$\theta = 60^\circ$
1	0	0	0
2	0	1.00	1.25
3	0	1.45	1.70
4	0	1.20	1.35
5	0	0	0
6	0	1.10	1.30
7	0	1.60	1.80
8	0	1.25	1.40

Film thickness is 1.0 μm .

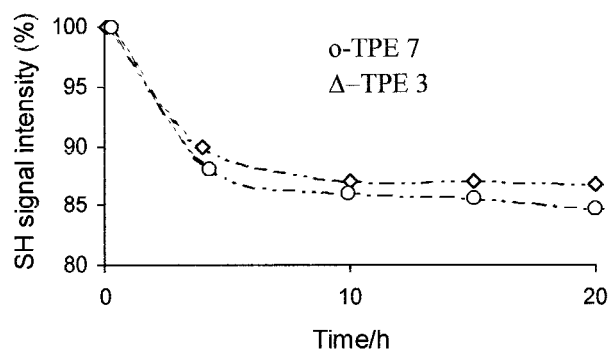


Figure 2 Variation of SHG intensity with time at 100°C.

plane of the thin film. As the composition of the chiral monomer in the polyesters increased, they became SHG active. The value was found highest for **TPE-3** and **-7** at values of all angle of incidence. For **TPE-4** and **-8**, the values of SHG efficiency were less than those of **TPE-3** and **-7** even though they had a high chiral monomer concentration. This lowering may be due to the low chromophore density along the polymer axis. The SHG efficiency of chiral polyesters increased with an increase in θ . This increase showed that the film of chiral polyesters has a polar order along the plane of the film. A macroscopically isotropic medium, that is, no polar order, containing microscopic chiral molecules can show a second-order NLO property, but only sum and difference frequency generations. The permutation symmetry of the nonlinear susceptibility tensors forbids second harmonic generation in such materials.⁷ Since the thin films of the polyesters showed second harmonic generation, there is a polar order in these films.

In the above systems as the concentration of the chiral units increased, the SHG activity increased only to 50%. Above this composition, even though the chiral order increases, the SHG activity decreased due to the decrease in chromophore density. Thus, in the present systems, polymers containing chiral units and chromophore in the ratio 50:50 optimizes the conditions of chiral order and chromophore density. Since we lack experimental facilities to study the detailed conformational behavior of the polymers, we are unable to explain the influence of diethyl tartrate units in the polymer conformation. The chance for the existence of a long-range helical order in such terpolymer systems is rare since the arrangement of chiral units and chromophore is highly random.

The thermal stability of the SHG signal of the film was studied by monitoring the intensity of $I_{2\omega}$ at 100°C for 25 h. The SH intensity was reduced only to 85% of the initial intensity (Fig. 2). Thus, the SHG in the thin films of chiral polymers also possesses a high temporal stability and indicates the thermal stability of the dipole orientation in the polymer.

CONCLUSIONS

A series of chiral polyesters containing donor-acceptor substituted π -conjugated segments in the main chain were synthesized with a view to find that they act as a potential noncentrosymmetric medium for second harmonic generation. The polyesters containing chiral units showed an enhanced SHG activity compared to that of others. The SHG activity of the chromophores was increased by four to six times when incorporated into the polymer. This shows that chromophore segments are in a noncentrosymmetric supramolecular organization and each segment contributes coherently to the hyperpolarizability of the polymer. The variation of SHG efficiency with the angle of incidence showed that there exists a polar order along the axis of the film. The temporal stability shows that the chiral organization and, hence, the dipole orientation are stable in these systems. The high T_g value of the polymers also supports the thermal stability of the orientation. Thus, chiral polymers incorporating donor-acceptor substituted π -conjugated segments can offer themselves as promising materials in the field of nonlinear optics.

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