JOURNAL OF
Materials
CHEMISTRY

Chiral polyesters with azobenzene moieties in the main chain, synthesis and evaluation of nonlinear optical properties

Damodaran Bahulayan† and Krishnapillai Sreekumar*

Department of Chemistry, University of Kerala, Kariavattom Campus, Trivandrum 695 581, Kerala, India

Received 21st January 1999, Accepted 27th April 1999

The synthesis, characterization and evaluation of nonlinear optical properties of a new series of chiral copolyesters containing push–pull electronic azobenzene mesogenic groups in the main chain are reported. The copolyesters showed liquid crystalline behaviour with high glass transition temperatures (~ 200 °C), stable liquid crystalline mesophases (up to 360 °C) and high second harmonic generation (SHG) efficiency. The second order nonlinear susceptibility values were measured as a function of the percentage of the chiral building unit and the temporal stability was found to be significant over a long duration of time.

Introduction

Much interest has been directed at the use of organic compounds as materials for nonlinear optical applications in recent years.[1–3] There is a myriad of possibilities among organic small molecules and polymers, which allow considerable flexibility in the molecular design. One of the formidable challenges associated with present day chemical synthesis is the construction of multimolecular assemblies with tailor made properties. This is possible by engineering interactions/spatial relationships between pre-selected constituent molecular building blocks.[4,5] An emerging field of interest is nonlinear optics. The use of organic compounds with high second order nonlinear optical properties allows full exploitation of their desirable qualities by allowing long interaction lengths, large power densities with modest power input, ultra-fast response times and damage resistance to optical radiation.[6–8] Nonlinear optical phenomena, typically, frequency doubling (infrared into visible) require molecular structures with donor–acceptor and/or conjugated functionalities which will not crystallise into centrosymmetric space groups.[9,10] Many organic molecules and polymers which can exhibit high second harmonic generation (SHG) activity, require special techniques like poling under an electric field to remove the centre of symmetry and orient themselves in a directional fashion so that they are practically applicable for device fabrication.[11,12] The main approaches in this regard centre on attempts to design molecules with structural features that favour packing in an acentric crystal structure and incorporating donor–acceptor moieties. These molecules are doped into polymer matrices, cast into films and poled under a large electric field. This process is advantageous because of good mechanical properties and ease of device fabrication. But, there are limitations regarding loading of the chromophore molecules. Also, when the external field is removed, the films relax back to random orientation and become SHG inactive. A novel and facile way to overcome this difficulty is to use main chain liquid crystalline polymers incorporating chiral units and/or donor–acceptor building blocks. The contribution of π-electrons in determining SHG activity has been well established. We have tried to couple the dual effects of molecular chirality and macroscopic chirality with donor–acceptor π-electron systems to design polymers with inbuilt directional orientation, thereby giving good SHG activity.[13] The incorporation of donor–acceptor π-electron systems provides a pathway for the redistribution of electronic charges across the entire length or parts or segments of the polymer molecule under the influence of an external field (optical or electric).[14] The use of chiral building units can prevent crystallization into centrosymmetric space groups. Long polymers in solution often crystallise into a hexagonal columnar phase. When the polymers contain chiral groups, this close packing into a triangular lattice competes with the tendency of the polymers to twist macroscopically. Similarly to the twist grain boundary phase of chiral smectics, macroscopic chirality can proliferate when screw dislocations enter the crystal.[15] In addition to this, cooperative chiral order plays a vital role in the self assembly of ordered supramolecular structures. The present paper describes the synthesis, characterization and evaluation of the nonlinear optical properties of a set of chiral polyesters containing azobenzene mesogenic groups.

Experimental

Materials and methods

Infrared spectra were recorded on a Perkin-Elmer Model 882 IR spectrometer. UV–Vis spectra were recorded on a Shimadzu UV-2100 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL 90 MHz NMR spectrometer with TMS as internal standard. Optical rotations were measured using an ELICO Model polarimeter PA-21 at a wavelength of 535 nm in a cuvette of 10 cm length. Thermogravimetry and differential scanning calorimetric measurements were made on a TGA V5 OD Dupont 200 TGA instrument and an MDSC VI. IA TA Inst. 2000 instrument respectively. Inherent viscosities were measured with an automated Ubbelohde viscometer, thermostatted at 25 °C. Molecular weights were determined by GPC measurements.

Second harmonic generation activities were measured by the Perry and Kurtz method.[16] Measurements were done both by the thin film method and the powder method using a Spectra Physics GCR-R series Nd:YAG laser (1064 nm, 11 ns, 400 mJ pulse^{-1}). For comparison, the standards used were urea and 2-methyl-4-nitroaniline (MNA). Thin films of thickness 1 μm were prepared by a spin coating technique. For powder measurements, the samples were ground and graded by use of standard sieves (100–150 μm) and loaded on a microscopic slide with a sample thickness of 1 mm. Urea and MNA samples used as standards were also powdered and sieved (100–150 μm) after drying under high vacuum. They were also mounted with the same thickness as the polyester samples. The laser beam was directed unfocused on to the

---

†*Present address*: Clays and Clay Minerals Division, Regional Research Laboratory (CSIR), Trivandrum 695 019, India.

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 second harmonic signal at 532 nm was detected by a photomultiplier and stored on a Philips model PM 3323 digital oscilloscope.

Preparation of monomers

1,4 : 3,6-Dianhydro-D-sorbitol (isosorbide). 1,4 : 3,6-Dianhydro-D-sorbitol (isosorbide) was prepared by the dehydration of D-sorbitol (E. Merck, Germany) using concentrated sulfuric acid and removing the water and excess sulfuric acid with a rotary vacuum flash evaporator. White needle shaped crystals (mp 61 °C) were obtained and used without further purification. Terephthaloyl chloride was obtained from E. Merck (Germany).

4,4′-Diaminodiphenylmethane. Diaminodiphenylmethanes (DDM) were prepared by the condensation of the corresponding aniline with formaldehyde following Scanlan's procedure.[17] In a typical experiment, 40% formaldehyde solution (4 g) was added drop-wise with effective shaking to a cold solution of aniline (9.4 g) in a minimum quantity of dil. HCl (0.1 M). The yellow solution obtained was heated in a water bath at 65–70 °C for 6 h. The reaction mixture was neutralized by adding solid sodium carbonate. It was steam distilled to remove any unreacted amine. The solid residue was dissolved in dil. HCl and decolorized with charcoal and then neutralized. The product precipitated was collected, washed well with water and dried (~10 g). On crystallization from ethanol, colourless flakes of 4,4′-diaminodiphenylmethane were obtained (mp 88–93 °C).

4,4′-Diamino-3,5,3′,5′-tetramethyldiphenylmethane (mp 126 °C) was prepared by adopting the same procedure for the condensation of 2,6-dimethylaniline with formaldehyde.

4,4′-Diamino-2,2′-dinitrodiphenylmethane. Nitration of the DDM's was accomplished by using a mixture of anhydrous potassium nitrate and 98% sulfuric acid at 0 °C.[18] To an ice-cold solution (0–5 °C) of 4,4′-diaminodiphenylmethane (0.05 M, 9.9 g) in conc. sulfuric acid (18 M, 40 ml), a solution of potassium nitrate (10.1 g) in conc. sulfuric acid (18 M, 15 ml) was added during a period of 1 h. The stirring was continued for another 3 h, keeping the reaction mixture below 5 °C. The reaction mixture was poured into crushed ice and neutralized with ice-cold aqueous ammonia. The yellow solid was collected on a filter, washed thoroughly with water and dried (~14 g). Crystallization of this product from dioxane–alcohol mixture afforded 4,4′-diamino-2,2′-dinitrodiphenylmethane as orange–yellow flakes (mp 206–208 °C)[18] [Analysis, found: C 54.11, H 4.18, N 19.33%; required for $C_{13}H_{12}N_4O_4$: C 54.16, H 4.16, N 19.44%]. 4,4′-Diamino-3,5,3′,5′-tetramethyl-2,2′-dinitrodiphenylmethane (mp 226 °C): [Analysis, found: C 59.33, H 5.62, N 16.34%; required for $C_{17}H_{20}N_4O_4$: C 59.30, H 5.8, N 16.28%].

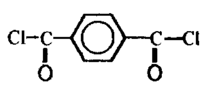
Bis(4-hydroxyphenylazo)-2,2′-dinitrodiphenylmethane. The diazonium chloride prepared by reacting an ice-cold solution of 4,4′-diamino-2,2′-dinitrodiphenylmethane (10 g) in hydrochloric acid (6 M, 20 ml) with aqueous sodium nitrite solution (6 g in 15 ml water), on coupling with phenol at 0–5 °C gave a brown solid (the pH of the solution was maintained at 7.5–8 by adding solid sodium acetate before the addition of phenol). It was collected, washed with water and dried. Crystallization of the product from dioxane–alcohol mixture afforded bis(4-hydroxyphenylazo)-2,2′-dinitrodiphenylmethane (mp 257 °C). [Analysis, found: C 60.18, H 3.58, N 16.81%; required for $C_{25}H_{18}N_6O_6$: C 60.24, H 3.61, N 16.86%]. IR(KBr) cm^{-1}: 1540, 1320 (NO_2), 1625 (–N=N–), 3400 (OH); UV, λ_{max} (nm): 270, 415. ^1H NMR (δ): 9.8, [2H(s) (OH)], 8.1–8.4, [8H(m) (phenyl)], 7.3–6.9 [2H(m) (phenyl)], 3.5 [2H(s) (CH_2)]. Bis(4-hydroxyphenylazo)-2,2′-dinitro-3,5,3′,5′-tetramethyldiaminodiphenylmethane (mp 271 °C). [Analysis, found: C 62.75, H 4.58, N 15.20; required for $C_{29}H_{26}N_6O_6$: C 62.81, H 4.69, N 15.16%]. UV, λ_{max} (nm): 268, 410. ^1H NMR: (δ) 1.3 [12H(d) (CH_3)], 9.8 [2H(s) (OH)], 8.1–8.4 [8H(m) (phenyl)], 7.3–6.9 [2H(m)(phenyl)], 3.5 [2H(s) (CH_2)].

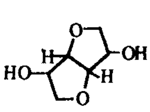
Polycondensation

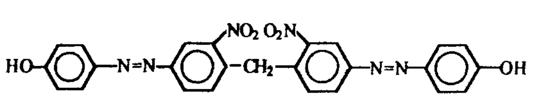
The polyesters were prepared by the condensation of the monomers, terephthaloyl chloride (2 equiv.), isosorbide (1 equiv.) and azobiphenol (1 equiv.) in a mixture of dimethylacetamide and 1,2-dichlorobenzene (1 : 4 v/v) at 160 °C for 18 h. The mole percentages of isosorbide and the azobiphenols were varied from 0 to 100% to obtain the polyesters **5a–g** and **6a–g**. After the reaction, the products were precipitated by adding the cooled reaction mixture into methanol.

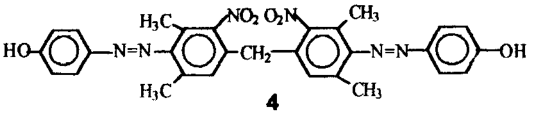
Results and discussion

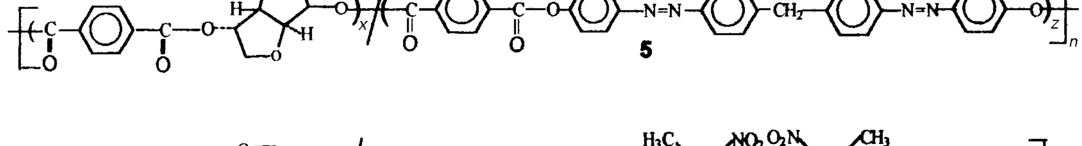
The polyesters **5a–g** and **6a–g** were prepared by the polycondensation of terephthaloyl chloride (**1**) with 1,4 : 3,6-dianhydro-D-sorbitol (isosorbide) (**2**), which acts as the chiral

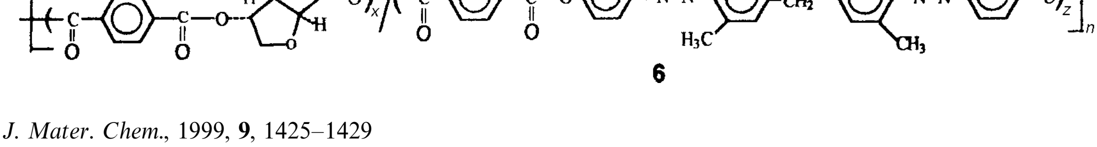

1


2


3


4


5


6

building unit, and an azobiphenol, bis(4-hydroxyphenylazo)-2,2′-dinitrodiphenylmethane (**3**) or bis(4-hydroxyphenylazo)-2,2′-dinitro-3,5,3′,5′-tetramethyldiphenylmethane (**4**). The polycondensation reaction was conducted in a solvent mixture of dimethylacetamide and 1,2-dichlorobenzene (1:4 v/v). Preliminary studies on the condensation reaction in solvents like dioxane, tetrahydrofuran and dimethylacetamide resulted in polyesters with low inherent viscosity. This was attributed to the possibility of side reactions, especially, formation of ether linkages and exchange reactions leading to cyclic byproducts. Hydrogen chloride, which is produced during the reaction is soluble in the above solvents, and it catalyses the side reactions. But when an aromatic solvent like 1,2-dichlorobenzene is used, this problem can be avoided, since hydrogen chloride, being insoluble, is evolved and swept out of the reaction mixture without interfering in the course of the reaction.[19] The easy removal of hydrogen chloride drives the reaction in the desired direction, to the desired extent and polyesters with comparably high molecular weight can be obtained. There is the possibility of controlling the reaction by adjusting the temperature and duration of the reaction so that polyesters with comparable molecular weights and good mechanical properties together with good solubility are obtained. Temperatures around 160 °C can be used, since isosorbide is highly thermally stable and it does not undergo racemization at this temperature.[20,21] Comparatively high molecular weight polymers have been obtained and the ^{1}H NMR spectrum indicated the incorporation of all the reactive monomeric units. But the sequence of the copolymer or the copolymer composition was not obtainable from the 90 MHz NMR spectrum. Also, no information about the relative reactivities of the different monomers is available. The ^{1}H NMR spectrum of the polyesters showed a closely spaced triplet signal at δ 4.6 (CH_2), a doublet at 5.3 (CH) and 5.7 (CH bridge) indicating the presence of isosorbide units. The spectra also showed signals at δ 3.5 (s, CH_2), 1–1.13 (d, CH_3 for **6**) and an aromatic A_2B_2 pattern at 8.1–8.4 (phenyl linked to N=N) and 7.6–7.8 (phenyl linked to –COO–). These are indicative of the azobiphenol and terephthaloyl units.

UV spectra of all the polyesters were obtained in DMF at room temperature. The spectra exhibited characteristic bands of phenyl groups (220–240 nm), nitro groups (270 nm, n–π*) and azo groups (390–420 nm, π–π*). The UV spectra were also recorded after cooling from the isotropic liquid state. There was no change in the absorption maxima. This showed that all the building units remained intact even in the molten state. In many cases of azo polymers, some extent of decomposition of the polymer or thermal rearrangement of the azo groups was observed on heating to high temperatures.[22] The high temperature stability of the polyesters was revealed from the IR spectra also. There was no change in the vibrational frequency values after cooling from the isotropic liquid state.

The polyesters showed almost 100% optical purity even in the molten state. Relatively high values of specific rotation (α) have shown that no extensive racemization occurred during the polymerization stage or when the polyesters were heated to melt. When the optical rotation was measured after cooling from the liquid phase, no change in the value of α was observed. The value of α decreased with a decrease in the 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. The properties of the copolyesters are summarised in Table 1.

Table 1 Yields and properties of polyesters

Polyester	Isosorbide content (%)	Yield (%)	η_{inh}[a]	$\bar{M}_n$	$\bar{M}_w/M_n$	$[\alpha]_D^{25}$[b]
5a	100	95	0.45	51 000	1.3	−210.0
5b	80	90	0.51	45 000	1.7	−190.2
5c	60	93	0.82	47 000	1.3	−162.1
5d	50	90	0.81	42 000	1.5	−152.5
5e	40	85	1.13	32 000	2.0	−116.1
5f	20	85	0.71	35 000	1.8	−75.1
5g	0	95	0.85	48 000	1.4	0
6a	100	90	0.46	45 000	1.4	−199.2
6b	80	92	0.54	48 000	1.7	−185.2
6c	60	87	0.71	52 000	1.5	−160.5
6d	50	92	0.85	51 000	1.7	−142.2
6e	40	85	0.71	42 000	1.6	−100.1
6f	20	87	0.81	48 000	1.8	−65.2
6g	0	91	1.01	53 000	1.7	0

[a] Concentration, 2 g l^{-1} in acetonitrile–trifluoroacetic acid (4:1) at 25 °C. [b] Concentration, 5 g l^{-1} in acetonitrile–trifluoroacetic acid (4:1) at 25 °C.

Thermal properties of the polyesters

Thermogravimetric studies were conducted for the polyesters from 30 to 600 °C. The polyesters were stable up to 400 °C. After that decomposition occurred in two stages. The temperature of initiation of both the decomposition stages depended on the extent of the biphenol unit; the higher the percentage of biphenol, the higher the value of the decomposition temperature. For the polyesters **5a**–**g** and **6a**–**g**, these varied in the range 410–450 °C for the first stage (10–15% mass loss) and 540–570 °C for the second stage. After the second stage, a residue of 43–57% was observed for the polyesters.

In the DSC curves, for all the polyesters upon heating, a weak step-down in heat capacity corresponding to the glass transition (T_g) was observed at a temperature of 200–250 °C. There was a gradual decrease in T_g values with a decrease in the amount of isosorbide units. After the glass transition, a broad endothermic peak was observed for the polyesters associated with the mesophase–isotropic transition analogous to the liquid crystalline behaviour. It seems that higher mole fractions of the biphenol stabilize the LC phase and the isotropization temperature rises above 350 °C. On cooling, the transitions were reversible with a supercooling of few degrees. Due to the non-availability of a hot-stage polarized microscope, optical photographs of the polyesters could not be obtained. They would have provided a clear picture of the texture of the LC phase and helped us in characterizing it.

The dynamic mechanical behaviour of the polyesters was studied in the linear viscoelasticity range at 1 Hz frequency. The transition temperatures of the dynamic mechanical processes were evaluated as a function of temperature and copolymer composition. For the different polyesters, there was a gradual decrease in the storage modulus (G') with increase in temperature. A pronounced decrease in G' values was observed at regions corresponding to β and α relaxation processes. Later, in the regions of isotropization relaxations, a complex viscoelastic behaviour was observed involving a decrease in G' values followed by an increase and finally reaching a plateau. This corresponded almost identically to the isotropization region in the DSC curve. This peculiar viscoelastic behaviour has been ascribed to the interplay of two conflicting tendencies: the usual decrease in modulus with increasing temperature and an unusual modulus increase due to an increase in the constraints on the mesogens as a transition from a locally organized region to a random chain arrangement occurs.[23] For the loss modulus (G'') also, similar changes were observed with increase in temperature. The β-relaxation process which is more concerned with the relaxation modes of the mesogenic units, was seemingly more sensitive to the copolymer composition. Typical DSC curves of the polyester **5d** are given in Fig. 1. Fig. 2 represents the dynamic mechanical transitions of the polyester **5d**. The thermal properties of the polyesters **5a**–**g** and **6a**–**g** as evaluated by DSC and DMA are summarised in Table 2.

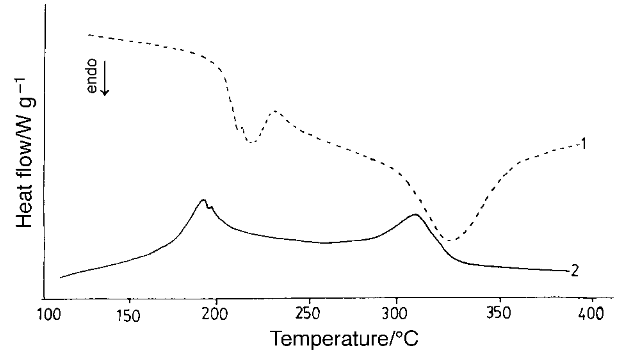


Fig. 1 DSC curves (1, heating and 2, cooling) of **5d**.

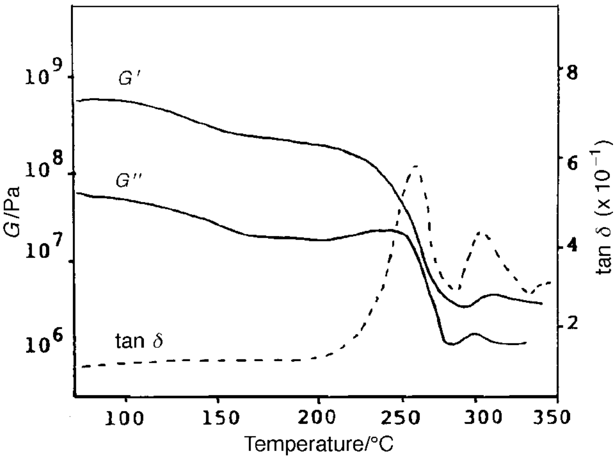


Fig. 2 Plots of dynamic mechanical transitions *vs.* temperature of **5d**.

Table 2 Thermal properties of polyesters

Polymer	T_g/°C	T_i/°C[a]	T_β/°C[b]	T_α/°C[b]	T_i/°C[b]
5a	250	280–310	180	220	295
5b	242	290–322	188	229	314
5c	230	295–325	195	232	320
5d	215	302–330	201	238	325
5e	208	311–342	214	244	335
5f	205	320–348	221	251	340
5g	198	330–357	230	260	351
6a	261	281–314	178	215	300
6b	255	288–325	188	220	310
6c	240	297–333	198	231	321
6d	233	311–348	210	240	338
6e	225	321–354	219	251	347
6f	213	333–367	228	268	355
6g	203	345–375	237	282	365

[a] From DSC measurements, heating rate 10° min^{-1} in nitrogen. [b] From DMA studies, heating rate 5° min^{-1} at 1 Hz in nitrogen.

Table 3 Optical properties of the polyesters

Polyester	SHG activity[a] Urea	MNA	β[b]/10^{-30} esu	Refractive index[c]
5a	0.82	0.87	2.359	1.8257
5b	0.87	0.90	2.441	1.8107
5c	0.90	1.05	2.826	1.8012
5d	0.95	1.35	3.655	1.7570
5e	0.68	0.85	2.301	1.8011
5f	0.55	0.65	1.764	1.7725
5g	0.45	0.58	1.576	1.8152
6a	0.85	0.90	2.430	1.8211
6b	0.87	0.92	2.486	1.8005
6c	0.92	1.11	2.998	1.7771
6d	0.97	1.47	3.979	1.7910
6e	0.80	0.93	2.531	1.8151
6f	0.65	0.72	1.954	1.7952
6g	0.57	0.61	1.647	1.7815

[a] SHG of urea and MNA = 1. [b] Static hyperpolarizability based on MNA (β of MNA = 2.7 ± 10^{-30} esu). [c] Refractive index at 535 nm.

Second harmonic generation

The second harmonic generation efficiency of the polyesters was examined by the powder reflection technique of Kurtz and Perry[16] and by reflection from a thin film deposited on Teflon tapes.[24] A laser beam from an Nd : YAG pulsed laser (1064 nm, 11 ns pulses) was used. The measurements were recorded in comparison with urea and 1-methyl-2-nitroaniline (MNA). The results are shown in Table 3. The second harmonic signal was observed at 532 nm. As the absorption maxima of the polyesters were quite different from that of the SH signal, there was no possibility of reabsorption of this signal by any of the samples and therefore no resonance enhancements were observed. Hence the static hyperpolarizability (excitation energy = 0 eV) was determined. The absolute value of β was determined from eqn. (1),

$$\beta = \frac{3e^2}{2m}\,\frac{h^2\, f\Delta\mu_{ge}}{\Delta E_{ge}{}^3} \qquad (1)$$

where E_{ge} is the energy of transition, μ_{ge}, the dipole moment change and f, the oscillator strength of the first excitation. The energy of transition is found from the band maximum of the UV–Vis absorption spectrum and the oscillator strength, f of the transition from the area under the band. The change in dipole moment was determined by a solvatochromic method.[25] All the polyesters showed moderately good efficiency in exhibiting SHG ability. Even those samples with zero mole percentage of isosorbide units (**5g** and **6g**) showed considerable ability. It is not fully clear how the polyesters **5g** and **6g** could show good SHG ability even without the presence of isosorbide units. Some of the samples (**5d** and **6d**) were even better than MNA. This was more conspicuous when the thin film technique was used. It was observed that when semicrystalline polymer films were deposited on ordered polymer substrates like Teflon, Teflon surfaces showed excellent ability to induce orientation in polymer thin films grown on them.[26] The semicrystalline grains of the polyester exhibit a greater degree of alignment along one particular direction. This is attenuated by the directional property of the azomesogenic group, due to a preferred *trans* orientation.[27] The directional orientation of the polyester molecules is highly enhanced by the helical organization of the macromolecular chains. The centre of symmetry is necessarily broken when the preferred helicity is achieved in the supramolecular organization.[28] The extent of chiral order is dependent on the enantiomer concentration. The fact that the polyesters **5** and **6** show no racemization, even in the isotropic liquid state reveals that absolute chiral order prevails. Here, the polymer backbone itself is chiral, supplementing the directional order of the azomesogenic group and the donor–acceptor π-electron system; there is a preference for one sense of the helix, which leads to the high SHG ability. Probably, this is the reason why even polyesters **5g** and **6g** with no isosorbide units or polyesters **5a** and **6a** with no azobiphenol units exhibit comparably good SHG ability.

The temporal stability of the SH signal was monitored at 100 and 200 °C. The polyester samples except **5f**, **5g**, **6f** and **6g** retained 100% SH signal intensity at 200 °C. But for the samples **5f** and **6f**, SH signal intensities were reduced to 90% of their original values when the samples were heated at 200 °C for 25 h. For samples **5g** and **6g** which did not contain any isosorbide units, the decrease in SH signal intensity was more catastrophic. The variation in the temporal stability of the SH

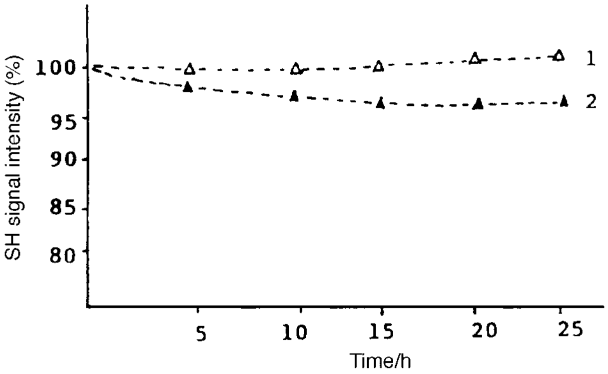


Fig. 3 Variation of SH signal intensity with temperature and time of **5d** 1, at 100 °C; 2, at 200 °C.

signal could be correlated to the glass transition temperature (T_g) of the samples.[29] Polyesters **5g** and **6g** possessed the lowest T_g values. They also did not contain isosorbide units. It could therefore be assumed that the presence of isosorbide units was essential in stabilizing the SHG ability at high temperature. The variation of temporal stability of the SH signal with temperature is presented in Fig. 3.

Conclusions

A series of polyesters containing an azomesogenic group and a chiral building block in the main chain has been prepared and characterized. They exhibited good thermal properties, have high T_g values. Some of the dynamic mechanical transitions were peculiar; additional directional order as a result of the presence of the azomesogenic group and macroscopic chirality resulted in an unusual increase in storage modulus (G') values at high temperatures. All the polyesters showed moderately good SHG capability. One could have expected a dramatic enhancement in SHG ability for the polyesters where there was a cumulative influence of the directional property of the azomesogenic groups and the prevailing chiral order of the polymer chains. But the results were not encouraging. There may be loss of macroscopic chirality due to some unforeseen reasons, probably due to steric compulsions. The polymer chains characterized by helical structures are noncentrosymmetric at the molecular level. But in randomly oriented polymer films obtained by solvent evaporation, noncentrosymmetry may be lost. Alignment of the molecular helices by application of an electric field across the solution with simultaneous evaporation of the solvent could give high SHG activity. Poling the polymer films at temperatures above the glass transition temperature can induce macroscopic chirality and the resulting directional order can be locked. Better results may be obtained by shifting to the Maker–Fringe or HRS methods. Measurement of the SH signal by the thin film technique proved to be promising because of the added organizational order induced by the Teflon substrate. The temperature stability of the SH signal was also significantly higher.

Acknowledgement

The authors sincerely thank Professor C. P. Joshua for the inspiration he has rendered them to pursue research in polymer photochemistry.

References

1 D. M. Burland, R. D. Miller and C. W. Walsh, *Chem. Rev.*, 1994, **94**, 31.
2 (*a*) D. Chemla and J. Zyss, *Nonlinear Optical Properties of Organic Materials and Crystals*, Academic Press, Orlando, FL, Vol. I and II, 1994; (*b*) P. N. Prasad and D. Williams, *Nonlinear Optical Effects in Molecules and Polymers*, John Wiley and Sons, New York, 1991.
3 (*a*) T. J. Marks and M. A. Ratner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 155; (*b*) D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 690; (*c*) B. Kippelen and N. Peyghambarian, *Chem. Ind. (London)*, 1995, 917.
4 (*a*) G. H. Wagmiere, *Linear and Nonlinear Optical Properties of Molecules*, VCH, Weinheim, 1993; (*b*) H. S. Nalwa and S. Miyata (Eds.), *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press, New York, 1997.
5 (*a*) K. J. Drost, A. K.-Y. Jen and V. P. Rao, *CHEMTECH*, 1995, 16; (*b*) S. R. Marder, B. Kippelen, A. K.-Y. Jen and N. Peyghambarian, *Nature*, 1997, **388**, 845.
6 B. Kippelen, R. Meyers, N. Peyghambarian and S. R. Marder, *J. Am. Chem. Soc.*, 1997, **119**, 4559.
7 R. Dagani, *Chem. Eng. News*, 1996, 22.
8 S. K. Asha, P. C. Ray and S. Ramakrishnan, *Polym. Bull.*, 1997, **39**, 481.
9 A. J. Heeger and D. R. Ulrich (Eds.), *Nonlinear Optical Properties of Polymers*, North Holland Press, New York, 1988.
10 J. V. Selinger and R. L. B. Selinger, *Phys. Rev. Lett.*, 1996, **76**, 58.
11 L. Yu, Y. Chen, W. K. Chan and Z. Peng, *Appl. Phys. Lett.*, 1994, **64**, 2489.
12 L. R. Dalton, A. W. Harper, R. Ghosn, W. H. Steier, H. Ziari, H. Fetterman, Y. Shi, R. V. Mustacich, A. K.-Y. Jen and K. J. Shea, *Chem. Mater.*, 1995, **7**, 1060.
13 (*a*) D. Bahulayan, V. Thomas and K. Sreekumar, *Proc. SPIE, Smart Materials, Structures and MEMS*, 1998, **3321**, 413; (*b*) K. A. Maniram and K. Sreekumar, *Proc. SPIE, Smart Materials, Structures and MEMS*, 1998, **3321**, 67.
14 S. R. Marder, J. E. Sohn and G. D. Stucky (Eds.), *Materials for Nonlinear Optics, Chemical Perspectives*, ACS Symp. Ser. **455**, American Chemical Society, Washington, DC, 1991.
15 R. D. Kamien and D. R. Nelson, *Phys. Rev. Lett.*, 1995, **74**, 2499.
16 S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
17 J. T. Scanlan, *J. Am. Chem. Soc.*, 1935, **57**, 890.
18 C. P. Joshua and P. K. Ramdas, *Synthesis*, 1974, 573; *Tetrahedron Lett.*, 1974, 4359.
19 J. M. Aducci, F. Nie and R. W. Lenz, *ACS Polym. Prep.*, 1990, **31**, 63.
20 H. R. Kricheldorff and N. Probst, *Macromol. Rapid Commun.*, 1995, **16**, 231.
21 H. R. Kricheldorff and N. Probst, *High Perform. Polym.*, 1995, **7**, 469.
22 S. Kumar and D. C. Neckers, *Chem. Rev.*, 1989, **89**, 17.
23 L. Lestel, G. Galli, M. Laus and E. Chiellini, *Polym. Bull.*, 1994, **32**, 669.
24 M. S. Paley, D. S. Frazier, S. P. McManus, S. E. Zutaut and M. Sanghadasa, *Chem. Mater.*, 1993, **5**, 1641.
25 M. S. Paley, J. M. Harris, H. Losser, J. C. Baumert, G. C. Bjorklund, D. Jundt and R. J. Tweig, *J. Org. Chem.*, 1989, **54**, 3774.
26 J. C. Wittman and P. Smith, *Nature*, 1991, **352**, 414.
27 (*a*) Y. Wu, Y. Demachi, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *Macromolecules*, 1998, **31**, 349, 355; (*b*) D. Y. Kim, L. Li, X. L. Jiang, V. Shivshankar and S. K. Tripathy, *Macromolecules*, 1995, **28**, 8835.
28 M. Kauranen, T. Verbiest, J. J. Maki and A. Persoons, *J. Chem. Phys.*, 1994, **101**, 8193.
29 D. Yu, A. Gharavi and L. Yu, *Appl. Phys. Lett.*, 1995, **66**, 1050.

Paper 9/00567F