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Isosorbide based chiral polyurethanes: optical and thermal studies

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Abstract A new class of chiral polyurethanes containing amido linkages in the polymer backbone have been synthesized by reacting toluene diisocyanate with isosorbide (IS) chiral moiety and the chromophores [*N*,*N*′-ethane-1,2-diyl bis(6-hydroxy hexanamide), *N*,*N*′-butane-1,4-diyl bis(6-hydroxy hexanamide) and *N*,*N*′-hexane-1,6-diyl bis (6-hydroxy hexanamide)]. The corresponding chromophores were obtained by the aminolysis of ε-caprolactone by using the diamines, diaminoethane, diaminobutane and diaminohexane, respectively. All the polymers were synthesized according to the symmetry conditions so as to obtain the non-centrosymmetric environment. A series of polyurethanes were synthesized by varying the chiral–chromophore composition. The polyurethanes developed were characterized by optical and thermal methods.

Introduction

A novel and facile way to attain a non-centrosymmetric medium is to incorporate chiral units and donor acceptor building blocks in the main chain of polymers. The chiral building blocks can induce a helical conformation in the macromolecular chain. The centre of symmetry is necessarily broken when preferred helicity is achieved in supramolecular organization. Polymers of such organized geometry are very interesting since they can supplement the directional order of donor–acceptor π-electron system and the dipole units are tilted in one direction along the polymer axis which leads to high second harmonic generation ability [1–4]. Optically pure materials which have only left handed/right handed symmetry are inherently non-centrosymmetric [5–7]. Such compounds are in fact readily available in nature (amino acids, sugars and alkaloids are well known examples existing only in single enantiomer), which are expected to be NLO active. The dianhydrohexitols are the important by products of biomass obtained in the sugar industry by the double dehydration of starch. These chiral compounds exist as three stereoisomers according to the relative configuration of their two hydroxyl functions namely, isosorbide (IS), isomannide and isoidide. These three isomers have been used as the monomers for the preparation of new biodegradable polymers including polyesters and polyurethanes based on natural and renewable raw materials. These polymers obtained by using the above mentioned dianhydrohexitols have shown high glass transition temperatures, excellent thermal stability and interesting physical properties. In the present work, IS was used to induce the chirality in polyurethane chain. IS is the most interesting monomer for polymer synthesis due to the improved accessibility of the two hydroxyl groups lying in exo(pseudoequatorial) positions. Furthermore, on the basis of thermal measurements (DSC) it has been shown that the exo substituent increases the ring thermal stability. The polymers prepared from aliphatic diols such as IS are of great interest to the chemical industry because such aliphatic diols can be produced from renewable resource materials namely sugars rather than from petroleum feed stocks as for most presently used diol monomers.

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Experimental section

Instrumentation

The UV–Visible spectrum was recorded using Spectro UV–Visible Double beam UVD-3500 instrument. FT-IR spectra of the powdered samples were recorded on JASCO 4100 FTIR spectrometer using KBr discs. Optical rotations were measured using Atago AP100 automatic digital polarimeter. The Fluorescence spectrum was recorded using FluroMax-3 instrument. The refractive index measurements were carried out using ABBE Refractometer (ATAGO) using the wavelength of 589 nm. The MALDI-MS analysis was carried out using Shimadzu Biotech Axima instrument. NMR spectra were recorded using Bruker 300 Hz instrument. Spectroscopic grade solvents were used for all measurements. The XRD analysis was carried out using Rigaku X-ray Photometer. The sample was scanned over the range from 10° to 90° angles with an increment of 0.05° angle and with the rotation speed 5 per minute. TG/DTA measurements were performed using Perkin Elmer Pyrex diamond 6 instrument. The weight of the sample was plotted against temperature to get a thermogram. The analysis was done in nitrogen atmosphere using a heating rate of 10 °C/min from room temperature to 600 °C using platinum crucible. The second harmonic generation test for polymers was performed by Kurtz and Perry powder technique using Nd:YAG laser. The conductivity measurements were carried out in Keithley 2400 Sourcemeter by 2 probe method. IR measurements were done at SAIF, CUSAT Cochin, MALDI-MS anaysis were done at NIIST Trivandrum and the NMR analysis at SAIF, IIT Chennai.

Materials used

Toluene diisocyanate (Acros) and isosorbide (Fluka) are commercially available. Extra pure Dimethyl acetamide (s. d.-fine) was used as the solvent for polymer synthesis. The chromophore such as CED, CBD and CHD were synthesized by the ring opening reaction of ε-caprolactone (Alfa Aesar) by 1,2 diamino ethane (s. d-fine), 1,4 diamino butane (Lancaster), 1,6 diamino hexane (Lancaster), respectively. Isopropanol (s. d-fine) was used as the solvent for monomer synthesis and DBTDL (Alfa Aesar) was used as a catalyst for polymer synthesis.

Monomer synthesis (CED, CBD, CHD)

The amido diol chromophores were synthesized according to the reported procedures. Diamine (1 eqv) and lactone (2 eqv) were taken in two separate conical flasks and both were dissolved in 50 mL isopropanol. The lactone solution was added to the diamine solution over a period of 1 h and kept with stirring for 2 h and the solution was heated (100 °C) to reduce the volume and cooled. The crystalline product was filtered and dried. It was further purified by column chromatography using hexane–ethyl acetate solvent system. The chromophores *N*,*N*′-ethane-1,2-diyl bis (6-hydroxy hexanamide) (**CED**), *N*,*N*′-butane-1,4-diyl bis(6-hydroxy hexanamide) (**CBD**) and *N*,*N*′-hexane-1,6-diyl bis(6-hydroxy hexanamide) (**CHD**) were prepared from 1,2 diamino ethane, 1,4 diamino butane, 1,6 diamino hexane, respectively, using the procedure [8–11].

Polymer synthesis

A solution of chromophore (**CED**, **CBD** or **CHD**) in HPLC grade DMAc (50 mL) was stirred in a flame dried R.B flask of 500 mL capacity equipped with a magnetic stirring bar, nitrogen inlet, a thermometer and a reflux condenser with a $CaCl_2$ guard-tube. To this, a slight excess of the solution of toluene diisocyanate (**TDI**) in 10 mL DMAc and four drops of DBTDL were added with vigorous stirring. To this solution, appropriate mole percentage of chiral diol isosorbide (**IS**) was added. The stirring was continued at room temperature for 10 min and the mixture was heated at 70 °C for 24 h and cooled to room temperature. The viscous reaction mixture obtained was poured into 500 mL of water with stirring. The solid polymer was separated and washed with methanol. The polymer was dried under vacuum for 2 h [12].

Different polymers with varying chiral–chromophore composition were synthesized as the above mentioned procedure. The polymer **PuB1** is the one which is having only chiral unit in polymer chain and considered as the mother polymer in the series. For **PuB1**, the ratio of **TDI** and **IS** were taken as 1:1. **PuB2**, **PuB3**, **PuB4** and **PuB5** were the polyurethanes with **CED** chromophore having the **TDI**:**IS**:**CED** ratio as 1:0.75:0.25(**PuB2**), 1:0.5:0.5(**PuB3**), 1:0.25:0.75 (**PuB4**), 1:0:1(**PuB5**), respectively. **PuB6**, **PuB7**, **PuB8** and **PuB9** were the polyurethanes with **CBD** chromophores in which **TC**:**IS**:**CBD** ratio is maintained as 1:0.75:0.25 (**PuB6**), 1:0.5:0.5(**PuB7**), 1:0.25:0.75(**PuB8**), 1:0:1(**PuB9**), respectively. **PuB10**, **PuB11**, **PuB12** and **PuB13** were the polyurethanes with **CHD** chromophore having the ratio of **TDI**:**IS**:**CHD** as 1:0.75:0.25(**PuB10**), 1:0.5:0.5(**PuB11**), 1:0.25:0.75(**PuB12**), 1:0:1(**PuB13**), respectively.

IR (cm^{-1})

For **PuB1**, 3290 cm^{-1} (–NH stretching of urethanes), 3000–2850 cm^{-1} (sp^3 C–H stretching in isosorbide unit), 1715 cm^{-1} (C=O stretching in urethane formed by isosorbide); 1451 cm^{-1} (C–H bend of $-CH_2$ group in isosorbide), 1415(–CN stretching of urethane) 1230 cm^{-1} due to (C–O stretching of isosorbide unit), 1055–1125(C–O stretching vibrations of urethanes attached to phenyl group). For **PuB2–PuB4**, there is no change in functional groups so similar spectra were obtained for the different chiral chromophore compositions. Similar trends were also observed in the case of polyurethanes from **PuB6** to **PuB8** and **PuB10–PuB12.** Hence, they show similar frequency ranges. 3250–3300 cm^{-1} (–NH stretching of both urethane and chromophoric unit), 3000–2900 cm^{-1} (C–H stretching of –CH_2– in both isosorbide and chromophoric unit), 1740–1750 cm^{-1} (C=O stretching in urethane formed by chromophore), 1720–1725 cm^{-1} (C=O stretching in urethane formed by isosorbide); 1650–1680 cm^{-1} (C=O stretching of –CONH group in chromophore), 1530–1550 cm^{-1} (NH bending in chromophore), 1455–1460 cm^{-1} (C–H bend of CH_2 groups), 1415–1420 cm^{-1} (–C–N stretching in chromophore), 1260–1280 cm^{-1} (interaction between urethane carbonyl with amide of chromophore), 1220–1225 cm^{-1} due to (C–O stretching of isosorbide unit) 1075–1135 cm^{-1} (C–C–O stretching of ester attached to aliphatic group). For **PuB5**, **PuB9**, **PuB13**, where having only chromophoric unit with same functional groups and hence results in the similar spectral pattern. 3280–3300 cm^{-1} (–NH stretching of both chromophoric and urethane unit), 1712–1728 cm^{-1}(C=O stretching in urethanes formed by chromophore), 1640–1650 cm^{-1} (C=O stretching in chromophore), 1541 cm^{-1} (–NH bending in chromophore), 1410–1420 cm^{-1} (–CN stretching in chromophore), 1260–1280 cm^{-1} (interaction between urethane carbonyl with amide of chromophore), 1130–1180 cm^{-1} (C–C–O stretching of ester attached to aliphatic group).

^{1}H NMR (DMSO-d6)

For **PuB1**, the protons resonated at 2.4–2.5 ppm (*s*, –CH_3 of TDI), 4.1 ppm (*q*, –CH_2 in isosorbide unit), 4.3–4.5 ppm (*t*, –CH– bridge protons of isosorbide unit), 5.1 ppm (*m*, –CH in isosorbide unit), 7.5–8.2 ppm (*m*, aromatic protons of TDI), 9.8 ppm (*s*, –CONH– ortho to the –CH3 of TDI), 10.5 ppm (*s*, –CONH– para to the –CH3 of TDI). For **PuB2**, **PuB3**, **PuB4** 1.2–3.4 ppm (*m*, CH_2 of chromophoric unit), 2.4–2.5 ppm (*s*, –CH_3 of TDI), 4.1 (*q*, –CH_2 in isosorbide unit), 4.3–4.5 ppm (*t*, –CH– bridge protons of isosorbide unit), 4.9–5.1 ppm (*m*, –CH in isosorbide unit), 6.7–7.8 ppm (*m*, aromatic protons of TDI), 8.9 ppm (*s*, –CONH– ortho to the –CH_3 of TDI), 9.9 ppm (*s*, –CONH– para to the –CH_3 of TDI). For **PuB6**, **PuB7**, **PuB8** 1.2–3.4 (*m*, –CH_2 of chromophoric unit), 2.5 ppm (*s*, –CH_3 of TDI), 4.02 (*q*, –CH_2 in isosorbide unit), 4.4 ppm (*t*, –CH– bridge protons of isosorbide unit), 4.8 ppm (*m*, –CH in isosorbide unit), 6.5–7.98 ppm (*m*, aromatic protons of TDI), 8.75 ppm (*s*, –CONH– ortho to the –CH_3 of TDI), 9.45 ppm (*s*, –CONH– para to the –CH_3 of TDI). For **PuB10**, **PuB11**, **PuB12** 1.2–3.3 ppm (*m*, –CH_2 of chromophoric unit), 2.4–2.5 ppm (*s*, –CH_3 of TDI), 4–4.2 (*q*, –CH_2 in isosorbide unit), 4.76 ppm (*t*, –CH– bridge protons of isosorbide unit), 5.1–5.2 ppm (*m*, –CH in isosorbide unit), 6.7–8.7 ppm (*m*, aromatic protons of TDI), 8.87 ppm (*s*, –CONH– ortho to the –CH_3 of TDI), 9.45 ppm (*s*, –CONH– para to the –CH_3 of TDI). In case of **PuB5**, 1.2, 2.3, 2.7, 3.0 (*m*, –CH_2 of chromophoric unit), 2.4–2.5 ppm (*s*, –CH_3 of TDI), 7.8 (*m*, aromatic protons of TDI) 8.9 ppm (*s*, –CONH– ortho to the –CH_3 of TDI), 9.3 ppm (*s*, –CONH– para to the -CH_3 of TDI). For **PuB9**, 1.3, 1.7, 2.3, 2.7, 3.2 (*m*, –CH_2 of chromophoric unit), 2.5 ppm (*s*, –CH_3 of TDI), 8 ppm (*m*, aromatic protons of TDI) 8.9 ppm (*s*, –CONH– ortho to the –CH_3 of TDI), 9.5 ppm (*s*, –CONH– para to the –CH_3 of TDI). For **PuB13** 1.2, 1.5, 2.3, 2.8, 3.3 (*m*, –CH_2 of chromophoric unit), 2.5 ppm (*s*, –CH_3 of TDI), 7.2 ppm (*m*, aromatic protons of TDI), 8.2 ppm (*s*, –CONH– ortho to the –CH_3 of TDI), 8.9 ppm (*s*, –CONH– para to the –CH_3 of TDI).

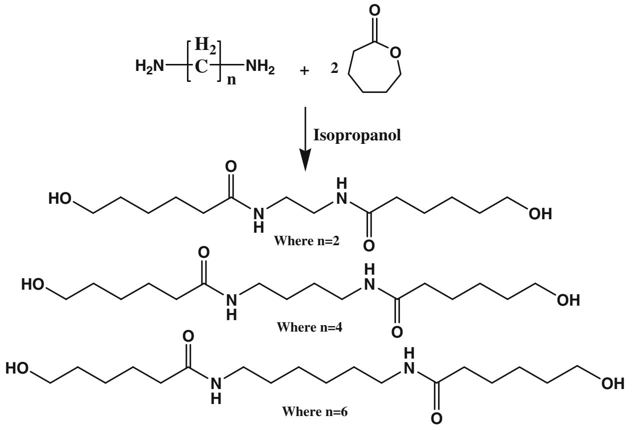
^{13}C NMR (DMSO-d6)

In **PuB1**, the carbon peaks resonated at, 170–175 ppm (ester carbonyl in –OCONH– of urethane ortho and para to the –CH_3 of TDI), 130–160 ppm (aromatic ring carbons), 80–82 ppm (–CH– bridge of isosorbide unit), 75–78 ppm (–CH– of isosorbide unit), 70–72 ppm (–CH_2– isosorbide unit), 18 ppm (–CH_3 of TDI). In **PuB2–PuB4**, **PuB6–PuB8** and **PuB10–PuB12** the extra monomer amido diols, **CED**, **CBD** and **CHD** were incorporated, respectively. They were resonating at 60–67 ppm (–CH_2O–), 43 ppm (–CH_2NH–), 31–36 ppm (–CO–NH–CH_2–$\underline{C}H_2$–), 25–28 ppm (–CO–CH_2–$\underline{C}H_2$–). For **PuB5**, **PuB9**, **PuB13**, where having only chromophoric unit, so they will resonate at the 175 ppm, 136–160 ppm, 60–65 ppm, 39–42 ppm, 32–36 ppm, 28–30 ppm, 16–18 ppm which corresponds to the same above mentioned carbons. The detailed characterization data were given as supporting information.

Results and discussion

Different varieties of amido diol monomers were synthesized by the aminolysis of ε-caprolactone which are shown in Scheme 1. The aminolysis of lactone with diamines in isopropanol medium gave amido diols in good yield and high purity according to the reported procedures [8–11].

Amido diols prepared by the above method were shining crystals and had melting point around 100–130 °C. The amido diols were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, FT-IR etc. IR (KBr, cm^{-1}): 1413 (C–N stretching in chromophore), 1556 (N–H bending), 1639 (C=O group of chromophore), 3270 (N–H stretching), 3450 (–OH stretching in chromophore). The amido diol



Scheme 1 Chromophore synthesis

monomers showed resonance signals at 4.5 ppm corresponding to the proton of the hydroxyl group of –CH_2OH. The proton of –CH_2 of –CH_2OH resonated at 3.4–3.5 ppm. The signals at 2.7–2.9 ppm corresponds to –CH_2 nearer to –C=O group. The signals between 1.3 and 2.1 ppm corresponds to –CH_2 protons of the chromophore. In the case of the ^{13}C NMR, the chemical shift values of the amide carbon appeared in the range from 174 to 178 ppm and the aldol carbon resonated at 67–68 ppm and alkyl carbons gave signals at 24 ppm and for –CH_2NH– appeared around 32 ppm.

A series of polyurethanes were synthesized [12] by the polyaddition reaction between chromophores (**CED**, **CBD** and **CHD**) and chiral diols, IS with the diisocyanate, toluene diisocyanate (TDI) in dimethyl acetamide solvent medium. The scheme of polymer synthesis are shown in Scheme 2.

To analyze the presence of functional groups in the polymers the FT-IR spectra were recorded in the range from 400 to 4000 cm^{-1} using JASCO 4100 FTIR spectrometer.

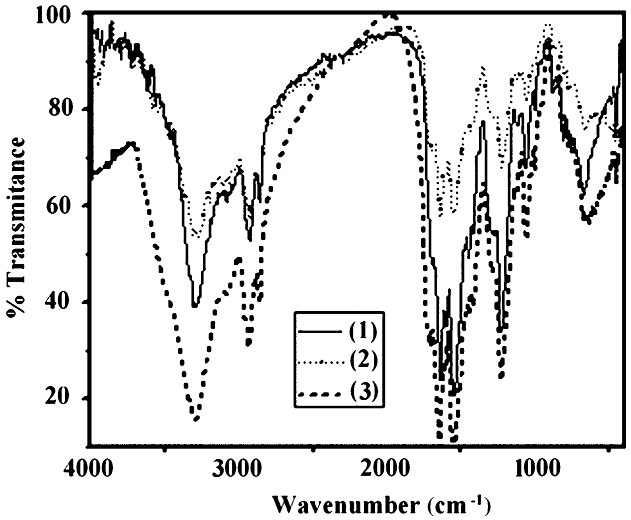


Fig. 1 IR spectrum of polyurethanes

For **PuB2**, **PuB3**, **PuB4** (represented as (**1**) in the Fig. 1) there is only a change in % of chirality and no change in functional groups so similar spectra were obtained for the different chiral chromophore compositions. Similar trends were also observed in the case of polyurethanes from **PuB6–PuB8** (represented as (**2**) in the Fig. 1) and **PuB10–PuB12** (represented as (**3**) in the Fig. 1)**.** The IR spectra for the polyurethanes (**PuB5**, **PuB9**, **PuB13**) with different chromophores **CED**, **CBD**, **CHD** are also having similar functional groups. Hence they show similar frequency ranges. The IR spectra of the polyurethanes showed a broad peak in the range from 3350 to 3050 cm^{-1} which is the characteristic peak of hydrogen bonded –NH groups. The existence of broad band with overlaying shoulders between 3400 and 3300 cm^{-1} indicates the various types of hydrogen bonds with different bond distances for N–H groups present. The absorption bands in the region from 1800 to

Scheme 2 Polymer synthesis (**PuB1–PuB13**)

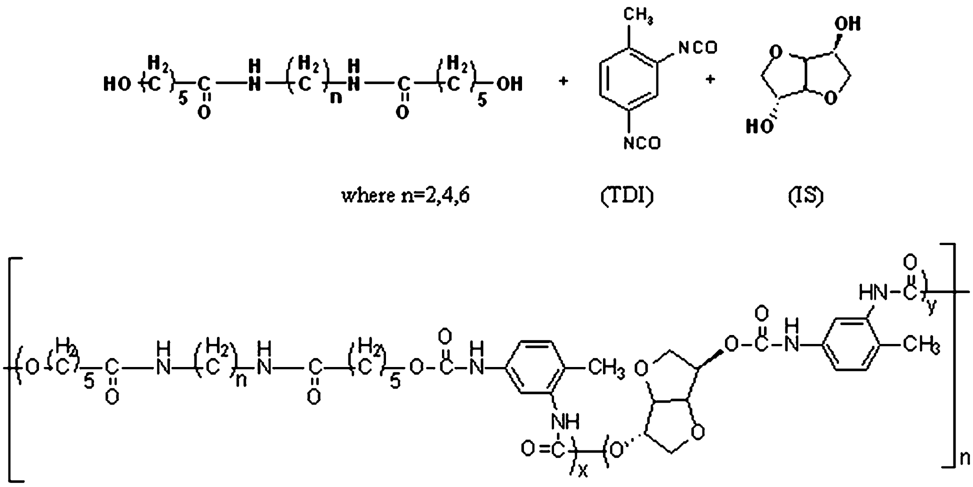


Table 1 Optical and thermal properties of polyurethanes

Polymer	Chirality%	Specific rotation ($[\alpha]_D$°)	Refractive index	Absorption λ_{max} (nm)	Emission λ_{max} (nm)	IDT (°C)	T_g (°C)
PuB1	100	43	1.5302	270	403	190	105
PuB2	75	38	1.5569	268	402	210	115
PuB3	50	27	1.5287	268	404	250	108
PuB4	25	22	1.5230	269	401	280	120
PuB5	0	0	1.4219	268	402	190	60
PuB6	75	35	1.5499	269	404	280	114
PuB7	50	31	1.5928	268	404	278	105
PuB8	25	25	1.6087	269	402	200	98
PuB9	0	0	1.5876	269	405	195	82
PuB10	75	39	1.6176	268	407	280	102
PuB11	50	29	1.5582	269	402	220	118
PuB12	25	23	1.6079	268	406	230	97
PuB13	0	0	1.4697	268	403	190	78

1500 cm^{-1} are associated with the amide bands (two –CONH– groups from chromophores and two –OCONH– from urethanes linkages). Broader shoulder peaks were observed in the above mentioned region. The shoulder peaks observed at 1260–1280 cm^{-1} can be assigned to the H-bonding of urethane carbonyl with –NH– hydrogen of amide linkage or vice versa. The low value of the –C–O stretching vibration is due to the amide carbonyl groups involved in hydrogen bonding.

From the MALDI-MS analysis it was found that the molecular weight of the polyurethanes synthesized were in the range 17,000–20,000 (the molecular weight of one repeating unit ≈500–600) which confirmed the proposed structure consisting of almost 30–35 repeating units (the MALDI-MS spectrum of polyurethanes is given as supporting information).

Absorption and emission spectrum

The UV–Vis spectrum was recorded using Spectro UV–Visible Double beam UVD-3500 Instrument operating in a wavelength range of 200–900 nm. The spectra of polyurethanes were taken in DMSO solvent. All the polymers showed two absorbance peaks at 260–270 nm range (λ_{max}) and 290–300 nm range. The absorption in the region 250–360 nm without any major absorption at shorter wavelengths (200–250 nm) usually indicates the $n \rightarrow \pi^*$ transition in the chromophore containing a hetero atom. This type of transition includes the presence of –C=O, –COOR, –CONH$_2$ etc. The polyurethanes with amido chromophores containing both π bonds and unshared electron pairs exhibits two absorptions, a low intensity shoulder like $n \rightarrow \pi^*$ transition at longer wavelength ~300 nm and a high intensity $\pi \rightarrow \pi^*$ band at a shorter wavelength of ~270 nm. The details are shown in Table 1 and Fig. 2. The band gaps of the synthesized polymeric systems were determined from the $(\alpha h\nu)^2$ versus hν plot. Where α is the absorption coefficient which is calculated by the equation, $\alpha = \lambda_{max}/t$, t is the pathlength of sample. The band gap of each polymer was calculated by extrapolating all the values and all the polymers were found to be having a band gap of approximately 4.6 eV, which accounts for the insulating character of the polymers.

Emission spectrum is particularly an interesting tool to probe the rigidity of the polymer backbone. The broadness of the fluorescence peak decrease with increasing rigidity. The fluorescence spectrum was recorded using FluroMax-3 instrument. The excitation wavelengths were shown in the range of 300–310 nm and emission spectra in the range of 400–410 nm. For all the samples the excitation wavelengths and emission wavelengths were recorded in the fluorimeter by inputting the proper absorbance wavelengths and excitation wavelengths. The emission λ_{max} values were reported in Table 1 and spectra were shown in Fig. 2.

Specific rotation and refractive index

The molecular level chirality of the polymers can be studied by the polarimetric techniques. The polyurethanes synthesized were having optically active monomers. The optical activity of polymers increased when isosorbide molecules were incorporated. The specific rotation $[\alpha]_D$ values measured for polymers varied from 0° to 43°. The $[\alpha]_D$ value increased with increase in the % of chiral component. Low value of $[\alpha]_D$ is due to the low % incorporation of chiral diol. The polyurethanes without chiral molecule possess zero specific rotation. The specific rotations of the polyurethanes are shown in Table 1. Relatively

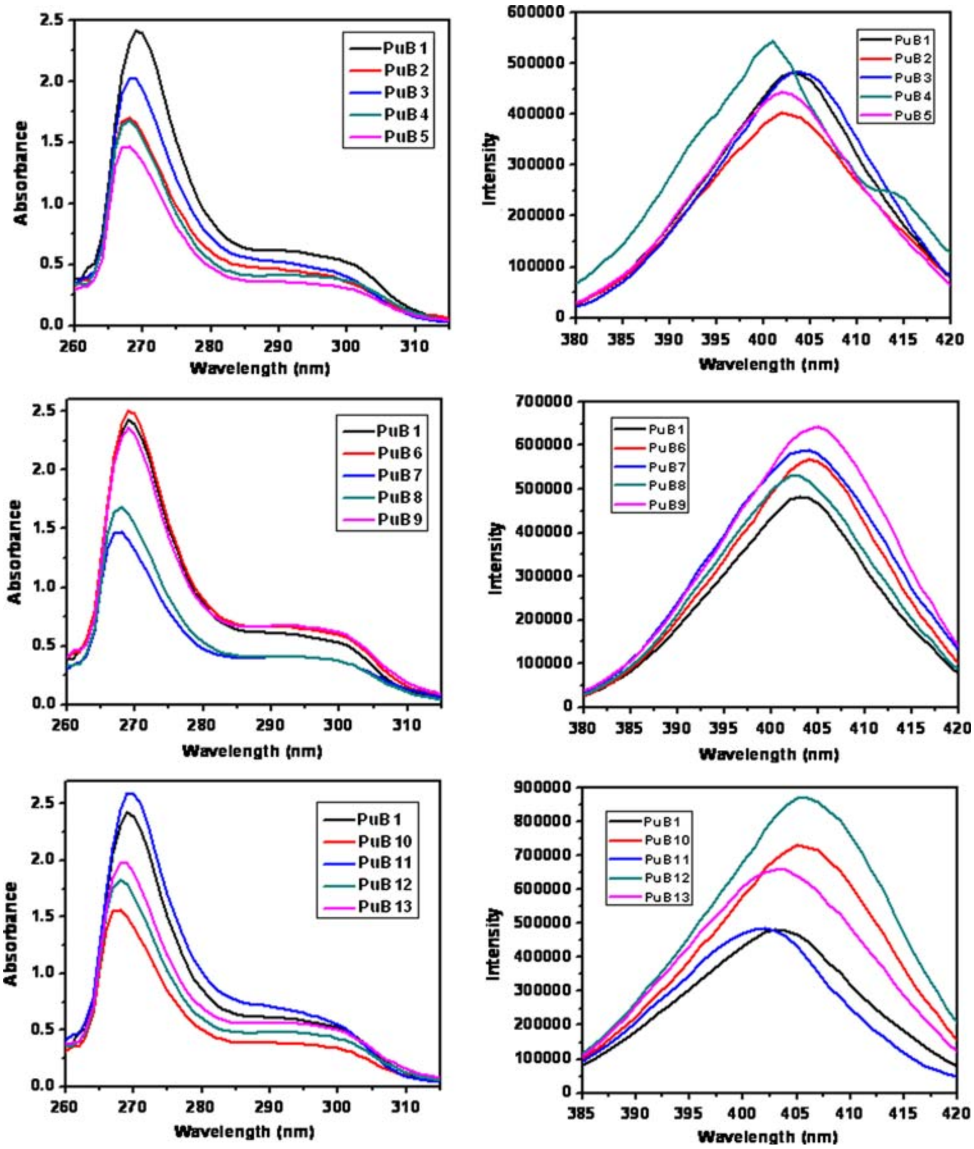


Fig. 2 Absorption and emission spectra of polyurethanes (**PuB1**–**PuB13**)

high values of specific rotation near to the specific rotation of optically active monomers were obtained which indicate that there is no extensive racemization occurred during the polymerization stage.

To determine the refractive indices of the polymer samples, the well-known prism method was used. The measurements were carried out using ABBE Refractometer (ATAGO) DR M2 using the wavelength of 589 nm. Distilled water was taken as the reference which was having the refractive index of 1.33. The specific rotation and refractive index of the polymer samples are shown in Table 1.

NLO measurements (Kurtz–Perry method)

The effective second order susceptibility was evaluated using Kurtz–Perry powder technique [13], which is considered to be a valuable technique for initial screening of materials for second harmonic generation. Particles were graded using standard sieves; sizes ranging from 40 to 300 μm were studied. Samples were loaded in glass capillaries having an inner diameter of 600 μm. The fundamental beam (1064 nm) of a Q-switched nanosecond-pulsed (6 ns, 10 Hz) Nd:YAG laser (Spectra Physics model INDI-40) was used. The second harmonic signal was collected using appropriate optics and detected using a monochromator, photomultiplier tube and oscilloscope (Tektronix model TDS 210, 60 MHz). Filters were used to bring the signals from all the samples into the same range. Urea with particle size of ~150 μm was used as the reference. The second harmonic signal generated by the polymer was confirmed by the emission of green radiation from the polymer.

Conductivity

The conductivity of the samples was measured by using Keithley 2400 Sourcemeter by 2 probe method. The polymer materials studied were pelletized to measure the conductivity. The source meter was interfaced to a computer in which the measurements were done using a program developed in LABVIEW. The measured conductivity was found to be of the order of 10^{-9} S/cm, which accounts for the high insulating character of the material, which also confirms the band gap studies that was already discussed.

Solubility studies

Solubility studies of polyurethanes were performed with solvents having different polarity. A number of solvents were used to check the solubility of polyurethanes. Most of the polyurethanes synthesized were soluble in polar solvents like DMAc, DMSO, DMF etc. and not soluble in non-polar solvents like benzene, toluene, CCl_4, petroleum ether, ethyl acetate, chloroform etc. The polymers were found to be insoluble because of the polarity and rigidity due to hydrogen bonding.

Thermal properties

While designing polymers for second harmonic generation, optimization of thermal properties like glass transition temperature and thermal stability must also be done. The T_g values were derived from DTA analysis and initial decomposition temperature (IDT) from thermogravimetric measurements. The T_g of a polymer depends largely on the thermal energy required to create internal segmental motion in the polymer chain. The stereochemical dependence of the polymers towards polar order can be proved from the T_g values of the polymeric systems. It is reported that isosorbide based polymers has shown very low T_g values compared to isomannide based polymeric systems [14]. The polymers based on isosorbide and isomannide differ from each other only by the stereochemistry of isosorbide and isomannide units. The stereochemistry has played a major role in glass transition temperature through polar ordering. Usually the system with *trans* form shows lower T_g value than gauche form due to the flexibility of the *trans*. Also the molecule with symmetrically ordered polar groups has low T_g value than the one with asymmetrically placed polar group [15]. In isosorbide, the –OH groups are more symmetrically placed than isomannide, hence the polymer containing isosorbide was found to be having low T_g values compared to isomannide. From the structures of polymer

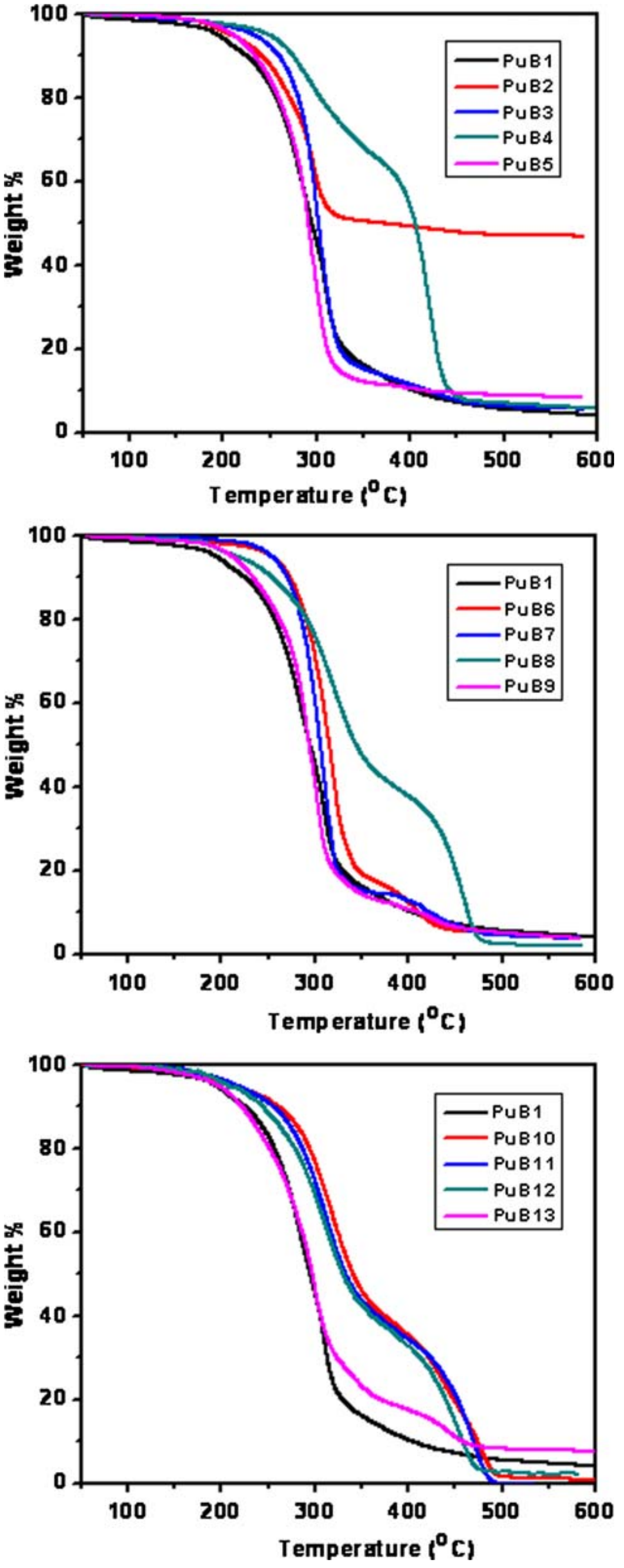


Fig. 3 TG curve of polymers (**PuB1**–**PuB13**) showing the wt% of samples at different temperatures

containing isosorbide it can be seen that the uniform stacking of isosorbide polymer is very difficult due to oppositely oriented –OH groups, hence reduce the polar order which causes the reduction in T_g values. All the samples were thermally stable up to the temperature around 190 °C.

As the IDT values of polymer increases, thermal stability also increases. The observed IDT values of polyurethanes ranges from 190 to 280 °C which are shown in Fig. 3. It is clear that IDT values of polyurethanes with both chromophore and chiral incorporation is found to be having more stability (~250 °C) and such polymers exhibit high SHG efficiency. It has been seen that the T_g values range from 60 to 120 °C. The higher the value of T_g higher will be the degree of polar order. Polymers with both chiral diol and chromophoric diols results in high T_g values compared to the polymers without chiral molecules.

A careful examination of DTA thermograms of all the polymers reveal endothermic peaks at around 280–380 °C, which corresponds to a wt% of 40–50% of the sample in TGA, which confirms that the decomposition of the sample is more at the above mentioned temperature range. For most of the polymers very sharp endothermic peaks were observed in DTA and are shown in Fig. 4. Hence the polymer material may be useful for making the NLO devices below its melting point. The thermal characterization of polymers was given in Table 1. The data obtained by thermal analysis showed that the polyurethanes were having good thermal stability due to the presence of hydrogen bonding and the presence of aromatic backbone in the polymer chain.

Powder X-ray diffraction studies

The X-ray diffraction profiles of the polymers were used to analyze the crystalline nature of polymers. The crystallinity of the prepared polymers was evaluated and the strong reflection peaks between the 2θ range 10° and 40° were observed. Since the peaks were found to be broad, the polymeric system was considered to be amorphous in nature. The diffraction patterns of the polymers are shown in the Fig. 5, the XRD pattern shows a broad peak at 10–30°. There is no prominent shift observed for the polymeric materials. From the scattering angle, the layer spacing d can be evaluated using the Braggs equation, $n\lambda = 2d \sin\theta$. For polymers this distance is often referred to as the intersegmental distance [16]. Larger the d-spacing a more disruptive packing of the polymer chain is expected. The polyurethanes with isosorbide chiral moiety possess amorphous character.

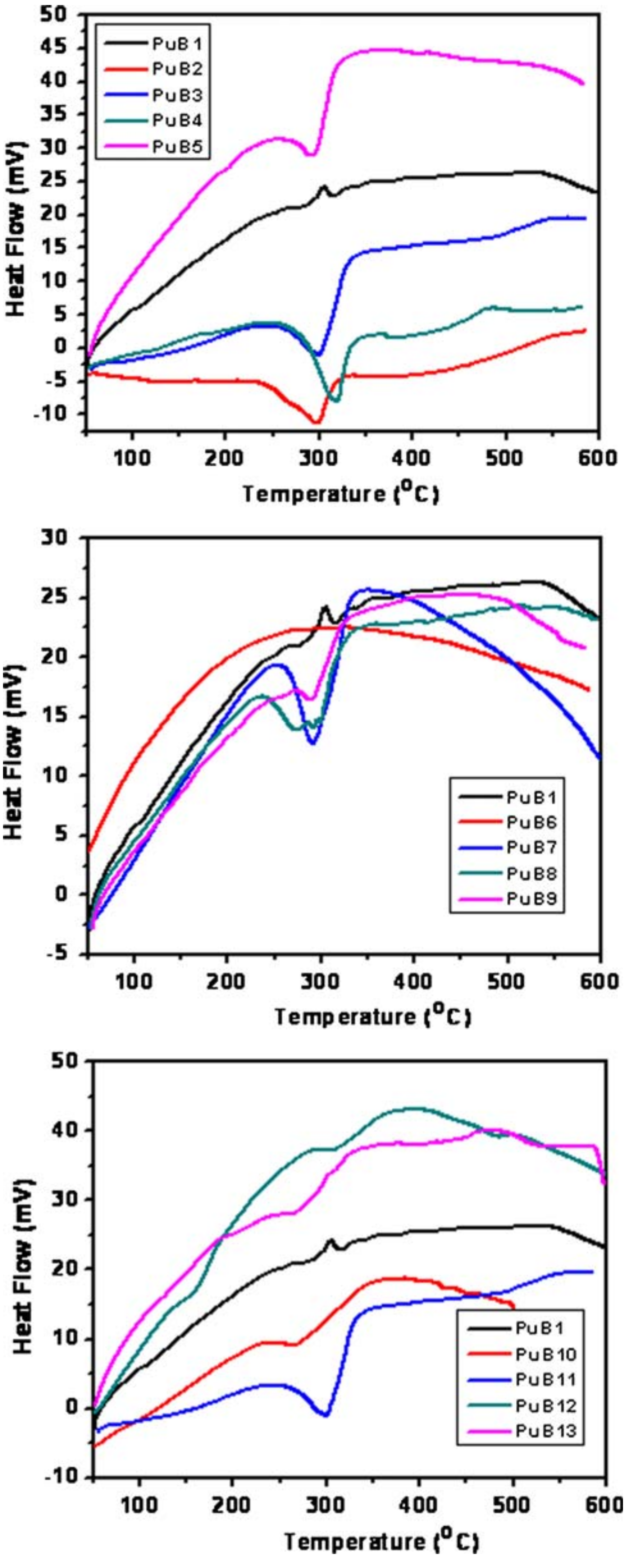


Fig. 4 DTA curve for polyurethanes (**PuB1–PuB13**)

Conclusions

A series of polyurethanes were synthesized by incorporating the isosorbide chiral moiety and amido diol chromophores in the main chain. All the polymers showed absorption bands in ultraviolet region from 260 to 300 nm in which λ_{max} values were in between 260 and 270.

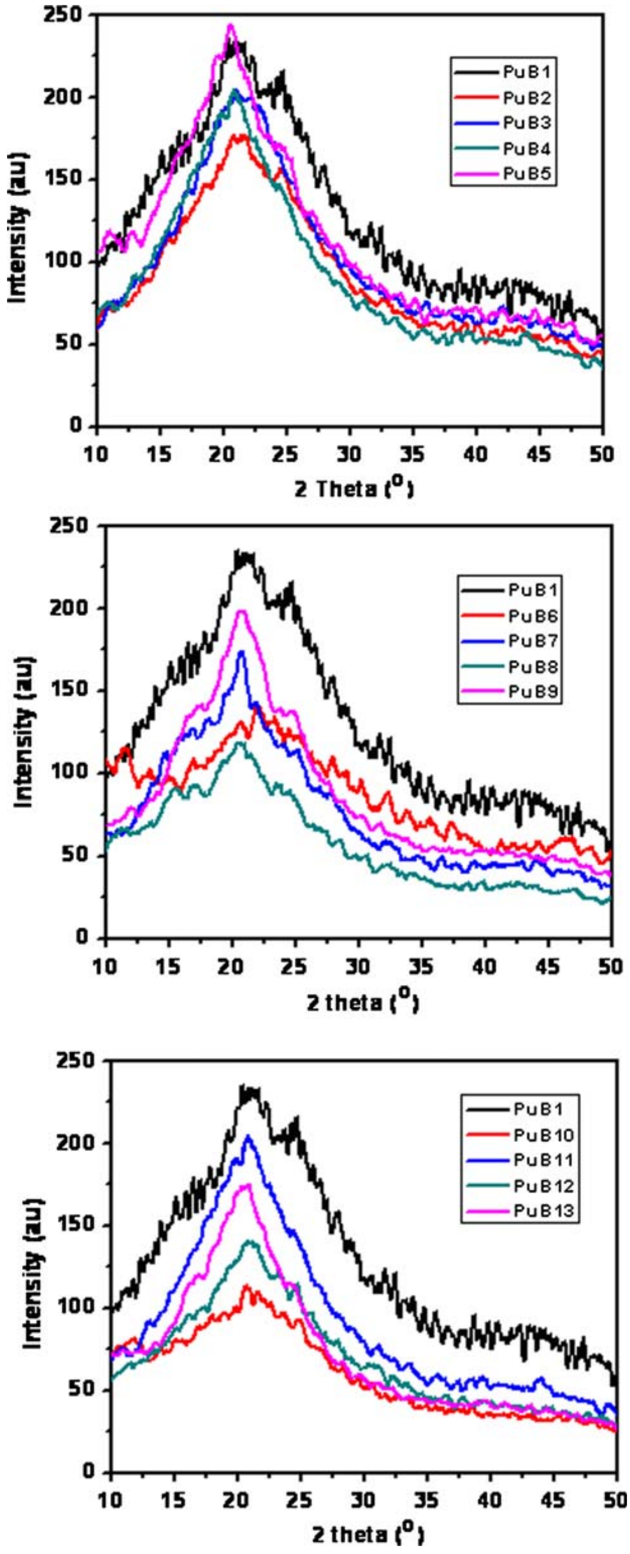


Fig. 5 XRD pattern of polyurethanes (**PuB1**–**PuB13**)

The electronic excitation occurs at a wavelength of 300–310 nm and the emission observed at 400–410 nm. From the polarimetric measurements, the specific rotation of the polymers is found to be increased with increase in percentage of isosorbide moiety. The NLO studies showed that the efficiency of the polymers is comparable with that of the standard and hence the polymers can be used for nonlinear optical applications. The polymers were found to exhibit T_g in the range of 60–120 °C. The high glass transition temperature assures a better stability of the induced polar order and the increase in polar order results in better temporal stability. From the thermal measurement we found that the polymer is stable up to 190 °C and hence can be useful for SHG applications below its melting point. The amorphous nature of polymers were confirmed by the XRD studies and insulating behaviour by conductivity studies. The thermal characteristics and optical non-linear activities clearly demonstrated that these polyurethanes are useful in device applications.

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