

Optical and Thermal Properties of Diethyl-(2R, 3R) (+)-tartrate Based Chiral Polyurethanes with Main Chain Amido Chromophores

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ABSTRACT: The toluene diisocyanate based optically active chiral polyurethanes were synthesized according to the symmetry conditions. The noncentrosymmetric (both charge asymmetry and spatial asymmetry) environment were attained by the incorporation of the chiral units (diethyl-(2R,3R)(+)-tartrate) and donor-acceptor building blocks in the main chain which induce a helical conformation in the macromolecular chain. A series of optically active polyurethanes containing chiral linkages in the polymer back bone have been synthesized by using DBTDL catalyst by incorporating the amido diols which were obtained by the aminolysis of ϵ -caprolactone by

using the diamines, diaminoethane, diaminobutane, and diaminoethane respectively. The effect of incorporation of the chiral molecule diethyl-(2R,3R)(+)-tartrate on the properties of polyurethanes was studied by changing the chromophores and also by varying the chiral-chromophore composition. Various properties of polyurethanes were investigated by UV, Fluorescence, TG/DTA, XRD, polarimetric techniques, Kurtz-Perry powder techniques, etc. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 111–119, 2011

Key words: thermal properties; amorphous; polyurethanes; optics; NLO

INTRODUCTION

In the past few years there has been a growing research interest in developing materials, which exhibits nonlinear optical (NLO) properties, for the applications, such as optical devices, optical signal processing, and information storage.^{1,2} Although the second order NLO polymers hold promising applications in electro-optic devices, a number of issues have to be addressed thoroughly before they possess commercial value. The main crucial issues are the high thermal stability of the dipole orientation and large optical nonlinearity.³ Many organic molecules and polymers which can exhibit high second harmonic generation activity require special techniques like poling under an electric field to remove the center of symmetry and orient themselves in a directional fashion so that they are practically applicable for device fabrication.^{4,5} A facile way to synthesize chiral main-chain NLO polymers involves the polycondensation of chiral units and donor-acceptor chromophores. The incorporation of donor-acceptor systems provides a pathway for redistribution of electronic charges across the entire length or parts or segments of the polymer molecule under the influence of an electric field (optical or electric). The use of chiral

building blocks tends to crystallize the polymer into a chiral supramolecular organization. Additionally, cooperative chiral order plays a vital role in the self-assembly of ordered supramolecular structures. Chiral order in a polymer material always exists in parallel with its optical activity. The chiral molecules possess electric-dipole allowed second order and higher order nonlinearity due to the absence of center of symmetry.^{6–8}

In this work diethyl-(2R,3R)(+)-tartrate was used to induce the chirality in the polyurethane chain. Three different sets of polyurethanes containing the chromophore and chiral building block in the main chain were synthesized by varying the composition of chiral diol and chromophoric diols. One set of polyurethane consist of *N,N'*-ethane-1,2-diyl bis (6-hydroxy hexanamide) (CED) as amido diol, another set consists of *N,N'*-butane-1,4-diyl bis (6-hydroxy hexanamide) (CBD), and the third set consists of *N,N'*-hexane-1,6-diyl bis (6-hydroxy hexanamide) (CHD) as chromophoric units. It is reported that the polymers that are synthesized from amido diols obtained by the aminolysis of lactones are highly stable.^{9–12} The stability is explained mainly due to the contributions from the extensive H-bonding between the amide-amide and amide-urethane linkages.

Additional Supporting Information may be found in the online version of this article.

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EXPERIMENTAL

Instrumentation

The UV-Visible spectrum was recorded using Spectro UV-Visible Double beam UVD- 3500 instrument.

FTIR spectra of the powdered samples were recorded on JASCO 4100 FTIR spectrometer using KBr discs. The MALDI-MS analysis was carried out using Shimadzu Biotech Axima instrument. 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. 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 of 10°–90° angles with an increment of 0.05° angle and with the rotation speed 5°/min. 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/minute 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 insolubility of the polymer in common organic solvents limited the determination of molecular weights. IR measurements were done at SAIF, CUSAT, MALDI-MS analysis at NIIST, Trivandrum and the NMR analysis at SAIF, IIT Chennai.

Materials used

Toluene diisocyanate (Acros) and Diethyl L (+) tartrate (Aldrich) 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. DBTDL (Alfa Aesar) was used as a catalyst for the polyurethane synthesis.

Monomer synthesis (CED, CBD, CHD)

The amido diol chromophores were synthesized according to reported procedures.^{9–12} 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 white 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 synthesized from 1,2-diamino ethane, 1,4-diamino butane, 1,6-diamino hexane, respectively.

Polymer synthesis

A solution of chromophore (CED, CBD, or CHD) in HPLC grade DMAc (50 mL) was stirred in a flame dried round-bottom flask of 500 mL capacity equipped with a magnetic stirring bar, nitrogen inlet, a thermometer, and a reflux condenser with a CaCl₂ 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 diethyl-(2R,3R)(+)-tartrate (DT) 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.¹³ Different polymers with varying chiral-chromophore composition were synthesized using the above mentioned procedure.

The polymer **PuD1** was the one which has only the chiral diol in the polymer chain and the ratio of TDI and DT were taken as 1 : 1. **PuD2**, **PuD3**, **PuD4**, **PuD5** were the polyurethanes with CED chromophore having the TDI : DT : CED ratio as 1 : 0.75 : 0.25 (**PuD2**), 1 : 0.5 : 0.5 (**PuD3**), 1 : 0.25 : 0.75 (**PuD4**), 1 : 0 : 1 (**PuD5**), respectively. **PuD6**, **PuD7**, **PuD8**, **PuD9** were the polyurethanes with CBD chromophore in which TDI : DT : CBD ratio was maintained as 1 : 0.75 : 0.25 (**PuD6**), 1 : 0.5 : 0.5 (**PuD7**), 1 : 0.25 : 0.75 (**PuD8**), 1 : 0 : 1 (**PuD9**), respectively. **PuD10**, **PuD11**, **PuD12**, **PuD13** were the polyurethanes with CHD chromophore having the ratio of TDI : DT : CHD as 1 : 0.75 : 0.25 (**PuD10**), 1 : 0.5 : 0.5 (**PuD11**), 1 : 0.25 : 0.75 (**PuD12**), 1 : 0 : 1 (**PuD13**), respectively.

PuD1: IR (cm⁻¹) 3270–3300 (NH str.), 3000–2890 (sp³ CH str.), 1736–1740, 1720–1725 (C=O str.), 1537 (NH bend), 1468, 1380 (–CH bend), 1055–1125 (C–O str. of urethane). ¹H NMR (DMSO-d₆) (ppm): 1.2 (t, CH₃), 2.5 (s, CH₃), 4.1–4.3 (q, CH₂), 4.8 (s, CH), 7.2–7.6 (m, aromatic), 8.4 (s, CONH), 9.2 (s, CONH). ¹³C NMR (DMSO-d₆) (ppm): 170–175 (–CONH of urethane), 168 (C=O ester), 135 (aromatic), 68 (CH), 32 (CH₂), 18 (CH₃).

PuD2, **PuD3**, **PuD4**: IR (cm⁻¹) 3250–3300 (–NH str.), 3000–2900 (sp³ C–H str.), 1740–1750, 1720–1725,

1700–1710, 1640–1665 (C=O str.), 1530–1550 (NH bend), 1455–1460 (–CH bend), 1415–1420 (CN str.), 1220–1230 (interaction between C=O and NH), 1075–1116 (C–O str.). $^1\text{H NMR}$ (DMSO- d_6) (ppm): 0.9 (t, CH_3 of tartrate), 1.2, 1.6, 2.2, 3.2 (m, CH_2), 2.5 (s, CH_3), 4.1–4.3 (q, CH_2), 4.8 (s, CH), 7.1–8 (m, aromatic), 8.8 (s, CONH), 9.4 (s, CONH). $^{13}\text{C NMR}$ (DMSO- d_6) (ppm): 175 (–OCONH of urethane), 170 (C=O amide), 165 (C=O ester), 138 (aromatic), 62 (CH), 33–39, 29–31, 24–28 (CH_2), 19, 15 (CH_3).

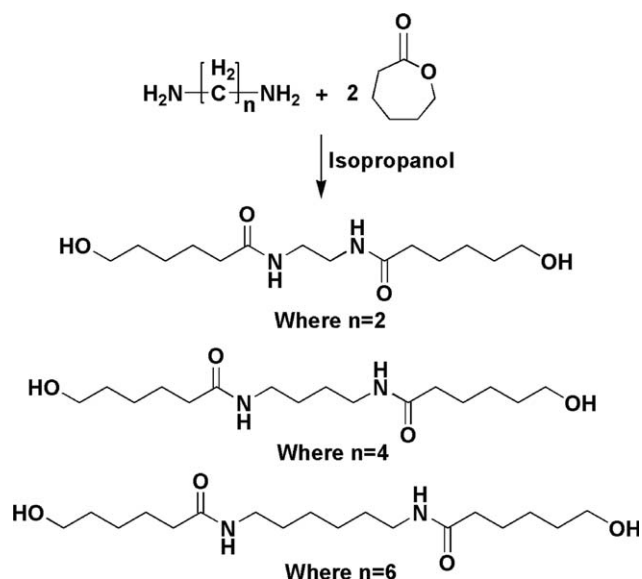
PuD5: IR (cm^{-1}): 3280–3300 (–NH str), 3000–2890 (C–H str.), 1708–1720, 1640–1650 (C=O str.), 1548 (NH bend), 1410–1420 (CN str.), 1260–1280 (interaction between C=O and NH), 1050–1060 (C–O str. in chromophore). $^1\text{H NMR}$ (DMSO- d_6) (ppm): 1.3, 1.7, 2.2, 3.2 (m, CH_2), 2.5 (s, CH_3), 8.1–8.9 (m, aromatic), 9.4 (s, CONH), 9.9 (s, CONH). $^{13}\text{C NMR}$ (DMSO- d_6) (ppm): 172 (–OCONH of urethane), 164 (C=O amide), 138 (aromatic), 31–36, 23–29 (CH_2), 18 (CH_3).

PuD6, PuD7, PuD8: IR (cm^{-1}): 3250–3300 (–NH str), 3000–2900 (sp^3 C–H str.), 1740–1750, 1720–1725, 1700–1710, 1640–1665 (C=O str.), 1530–1550 (NH bend), 1455–1460 (–CH bend), 1415–1420 (CN str.), 1220–1230 (interaction between C=O and NH), 1075–1116 (C–O str.). $^1\text{H NMR}$ (DMSO- d_6) (ppm): 1.1(t, CH_3) 1.3, 1.9, 2.1, 2.8, 3.4 (m, CH_2), 2.5 (s, CH_3), 4.1(q, CH_2), 5.2(s, CH) 6.5–7.9 (m, aromatic), 8.9 (s, CONH), 9.4 (s, CONH). $^{13}\text{C NMR}$ (DMSO- d_6) (ppm): 173 (–OCONH of urethane), 170 (C=O amide), 168 (C=O ester), 135–155 (aromatic), 62–68 (CH), 36, 32, 28–31, 24–26 (CH_2), 19, 14 (CH_3).

PuD9: IR (cm^{-1}): 3280–3300 (–NH str), 3000–2890 (C–H str.), 1708–1720, 1640–1650 (C=O str.), 1548 (NH bend), 1410–1420 (CN str.), 1260–1280 (interaction between C=O and NH), 1050–1060 (C–O str. in chromophore). $^1\text{H NMR}$ (DMSO- d_6) (ppm): 1.2–1.4, 1.6–1.8, 2–2.2, 3.2 (m, CH_2), 2.5 (s, CH_3), 6.9–7.3 (m, aromatic), 8.9 (s, CONH), 9.8 (s, CONH). $^{13}\text{C NMR}$ (DMSO- d_6) (ppm): 172 (–OCONH of urethane), 168 (C=O of amide) 138 (aromatic), 31–36, 23–29 (CH_2), 17 (CH_3).

PuD10, PuD11, PuD12: IR (cm^{-1}): 3250–3300 (–NH str), 3000–2900 (sp^3 C–H str.), 1740–1750, 1720–1725, 1700–1710, 1640–1665 (C=O str.), 1530–1550 (NH bend), 1455–1460 (–CH bend), 1415–1420 (CN str.), 1220–1230 (interaction between C=O and NH), 1075–1116 (C–O str.) $^1\text{H NMR}$ (DMSO- d_6) (ppm): 0.9 (t, CH_3), 1.2, 1.5, 2.1, 2.7, 3.2 (m, CH_2), 2.5 (s, CH_3), 4(q, CH_2), 5.3(s, CH), 6.7–8.7 (m, aromatic), 8.9 (s, CONH), 9.8 (s, CONH). $^{13}\text{C NMR}$ (DMSO- d_6) (ppm): 173–175 (–OCONH of urethane), 168 (C=O ester), 132–150 (aromatic), 60–65 (CH), 33–39, 30–31, 24–28 (CH_2), 19, 14 (CH_3).

PuD13: IR (cm^{-1}): 3280–3300 (–NH str), 3000–2890 (C–H str.), 1708–1720, 1640–1650 (C=O str.), 1548 (NH bend), 1410–1420 (CN str.), 1260–1280 (interaction between C=O and NH), 1050–1060 (C–O str. in chromophore). $^1\text{H NMR}$ (DMSO- d_6) (ppm): 1.2, 1.8, 2.2, 3.2 (m, CH_2), 2.5 (s, CH_3), 8.3–8.9 (m, aromatic), 9.5 (s,



Scheme 1 Chromophore synthesis.

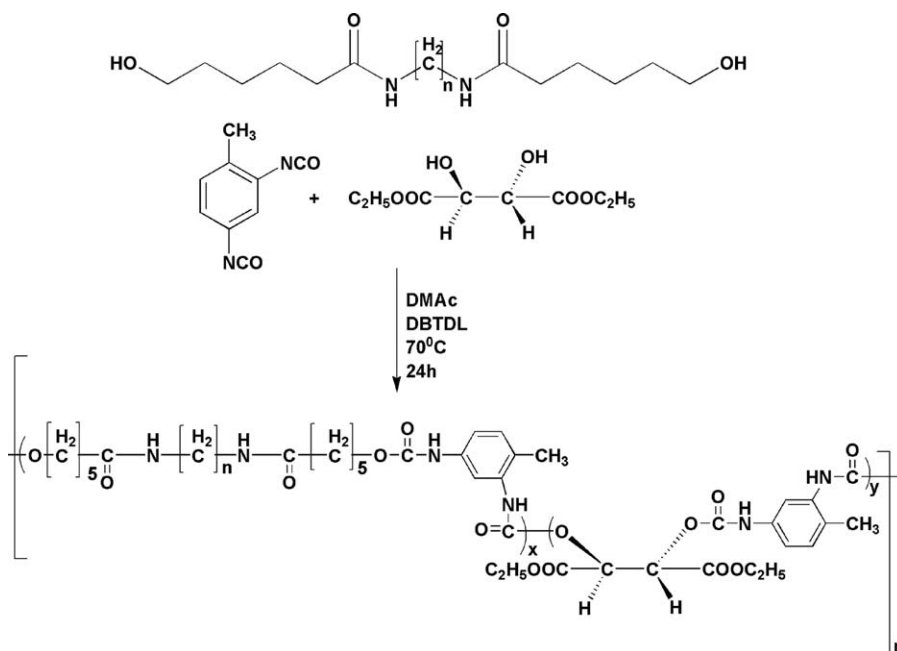
CONH), 9.9 (s, CONH). $^{13}\text{C NMR}$ (DMSO- d_6) (ppm): 172–177 (–OCONH of urethane), 133–158 (aromatic), 62–68, 42–45, 31–36, 23–29 (CH_2), 17(CH_3).

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.^{9–12}

The amido diols synthesized were shining crystals and had melting points around 100–130°C. The amido diols were characterized by elemental analysis, $^1\text{H NMR}$, $^{13}\text{CNMR}$, FTIR, 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 str.in chromophore). The amido diol monomers showed resonance signals at 4.5 ppm corresponding to the proton of the hydroxyl group of $-\text{CH}_2\text{OH}$. The proton of $-\text{CH}_2\text{OH}$ resonated at 3.4–3.5 ppm. The signals at 2.7–2.9 ppm corresponds to $-\text{CH}_2$ nearer to $-\text{C}=\text{O}$ group. The signals between 1.3 and 2.1 ppm corresponds to $-\text{CH}_2$ protons of the chromophore. In the case of the $^{13}\text{CNMR}$ 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 $-\text{CH}_2\text{NH}-$ appeared around 32 ppm.

A series of polyurethanes were synthesized by the polyaddition reaction between chromophores (CHD, CBD, and CED) and chiral diol (diethyl tartrate, DT) with the diisocyanate (toluene diisocyanate, TDI) in



Scheme 2 Polymer synthesis (PuD1–PuD13).

dimethyl acetamide solvent medium. Different polymers were synthesized by varying the chiral-chromophore composition using the above mentioned procedure. The scheme of polymer synthesis is shown in Scheme 2.¹³ The polymer **PuD1** is the one which is having only chiral unit in polymer chain and considered as the mother polymer in the series.

For **PuD2**, **PuD3**, **PuD4** polyurethanes [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 **PuD6–PuD8** [represented as (2) in the Fig. 1] and **PuD10–PuD12** [represented as (3) in the Fig. 1]. The IR spectra for the polyurethanes (**PuD5**, **PuD9**, **PuD13**) with different chromophores **CED**, **CBD**, **CHD** are also having similar functional groups. Hence they also show similar frequency ranges.

The IR spectra of the polyurethanes showed a broad peak in the range of 3350 to 3050 cm^{-1} which is the characteristic peak of hydrogen bonded —NH— groups. The existence of broad band with overlaying shoulders between 3400–3300 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 1800–1500 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 18,000–20,000 which confirmed the proposed structure consisting of almost 28–33 repeating units (The MALDI spectrum is given as supporting information).

Absorption spectrum

The UV-Vis spectrum was recorded using Spectro UV-Visible Double beam UVD-3500 Instrument

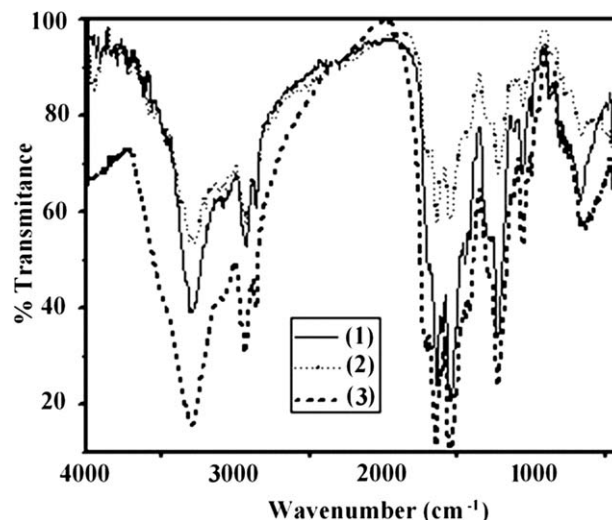


Figure 1 IR spectrum of polyurethanes.

TABLE I
Optical and Thermal Properties of Polyurethanes (PuD1–PuD13)

Polymer	Chirality (%)	Absorption λ_{\max} (nm)	Emission λ_{\max} (nm)	Specific rotation ($[\alpha]_D^0$)	Refractive index	IDT (°C)	T_g (°C)
PuD1	100	272	346	43	1.5257	190	101
PuD2	75	270	345	35	1.5107	180	158
PuD3	50	271	347	21	1.5012	185	203
PuD4	25	270	429	12	1.4570	270	210
PuD5	0	270	415	0	1.4219	185	98
PuD6	75	272	400	38	1.4725	280	108
PuD7	50	267	346	31	1.5152	260	180
PuD8	25	268	345	24	1.5211	250	197
PuD9	0	270	417	0	1.5876	190	82
PuD10	75	267	413	31	1.4771	240	106
PuD11	50	272	386	26	1.4910	185	118
PuD12	25	270	388	16	1.5151	230	205
PuD13	0	269	414	0	1.4697	186	128

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 267–272 nm range (λ_{\max}) and 290–300 nm range. Some of the polymers with both chiral and chromophoric units showed splitting patterns at the λ_{\max} . The absorption in the region 260–350 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 $-\text{C}=\text{O}$, $-\text{COOR}$, $-\text{CONH}_2$, 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 ~ 267 – 272 nm. The λ_{\max} values of polyurethanes are shown in Table I. The band gaps of the synthesized polymeric systems were determined from the $(\alpha h\nu)^2$ versus $h\nu$ plot. Where α is the absorption coefficient which is calculated by the equation, $\alpha = \lambda/t$, where t is the path length of sample. The band gap of each polymer was calculated by extrapolating all the values and all the polymers were found to be of band gap of ~ 4.43 to 4.68 eV, which accounts for the insulating character of the polymer. The absorption λ_{\max} values are given in Table I and the emission spectra are shown in Figure 2.

Emission spectrum

Fluorescence spectroscopy is a type of electromagnetic spectroscopy, which uses a beam of light, usually ultraviolet light, that excites the electrons in molecules of certain compounds and causes them to emit light of a lower energy, typically, but not necessarily, visible light. In fluorescence spectroscopy, the species is first excited, by absorbing a photon, from its ground electronic state to one of the various vibrational states in the excited electronic state. The molecule then drops

down to one of the various vibrational levels of the ground electronic state by emitting a photon in the process. As molecules may drop down into any of several vibrational levels in the ground state, the emitted photons will have different energies, and hence different frequencies. Therefore, by analyzing the different frequencies of light emitted in fluorescent spectroscopy, along with their relative intensities, give the emission spectrum of polymers. Fluorescence 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. For all the samples the excitation wavelengths and emission wavelengths were recorded in the fluorescence spectrum by inputting the proper absorbance wavelengths and excitation wavelengths. The emission λ_{\max} values were shown in Table I and the emission spectra were shown in Figure 3. The excitation spectra of all the polymers exhibits a wavelength of maximum around 300–315 nm. The emission spectra of the polymers PuD4, PuD5, PuD6, PuD9, PuD10, PuD11, PuD12, and PuD13 displays a broad band in between 360–480 nm with a maximum around 385–430 nm (Table I) when excited in the 310 nm wavelength. PuD1, PuD2, PuD3, PuD7, and PuD8 exhibits the characteristically sharp band emissions of λ_{\max} in between 345–350 nm. For the polymers PuD10, PuD11, and PuD12 shoulder peaks were observed in the range of 425–490 nm and a bright green emission was observed in the chamber.

Specific rotation and refractive index

The specific rotation value is equivalent to the angle of rotation obtained by a measurement using a solution of 100% concentration in a 100 mm observation tube. The angle of rotation depends upon the concentration of the solution, the length of the tube, temperature, and measurement wavelength which was taken as 589 nm. The polyurethanes synthesized

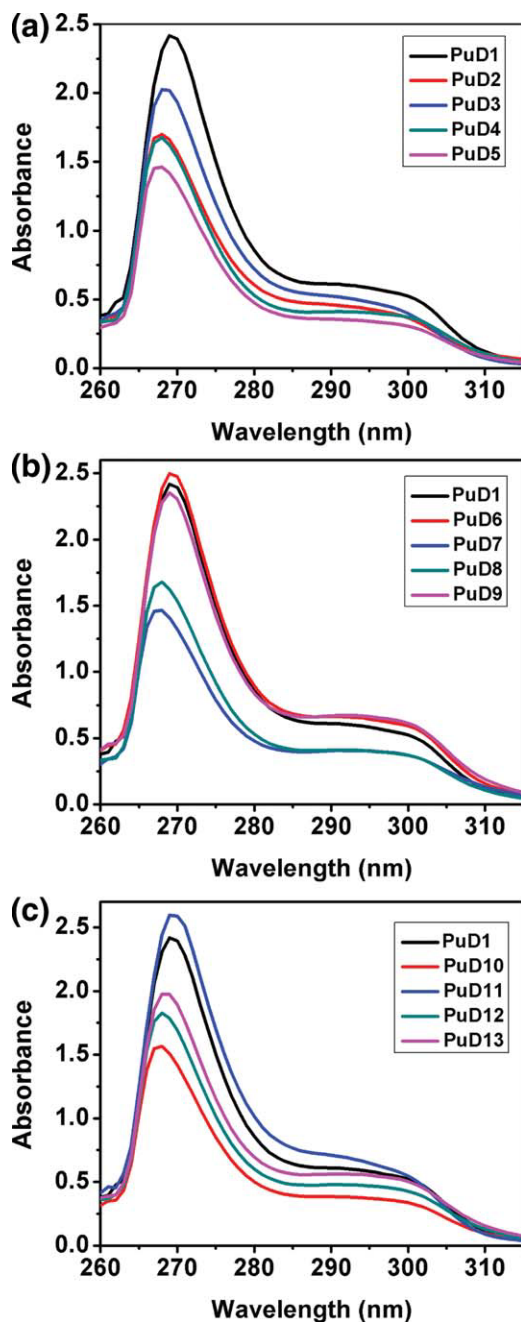


Figure 2 Absorption spectra of polyurethanes (PuD1–PuD13). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were having optically active monomers. The optical activity of polymers increased when chiral 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 I. 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 = 1.33. The refractive indices of the polymer samples are shown in Table I.

NLO measurements (Kurtz-Perry method)

The effective second order susceptibility was evaluated using Kurtz-Perry powder technique which is

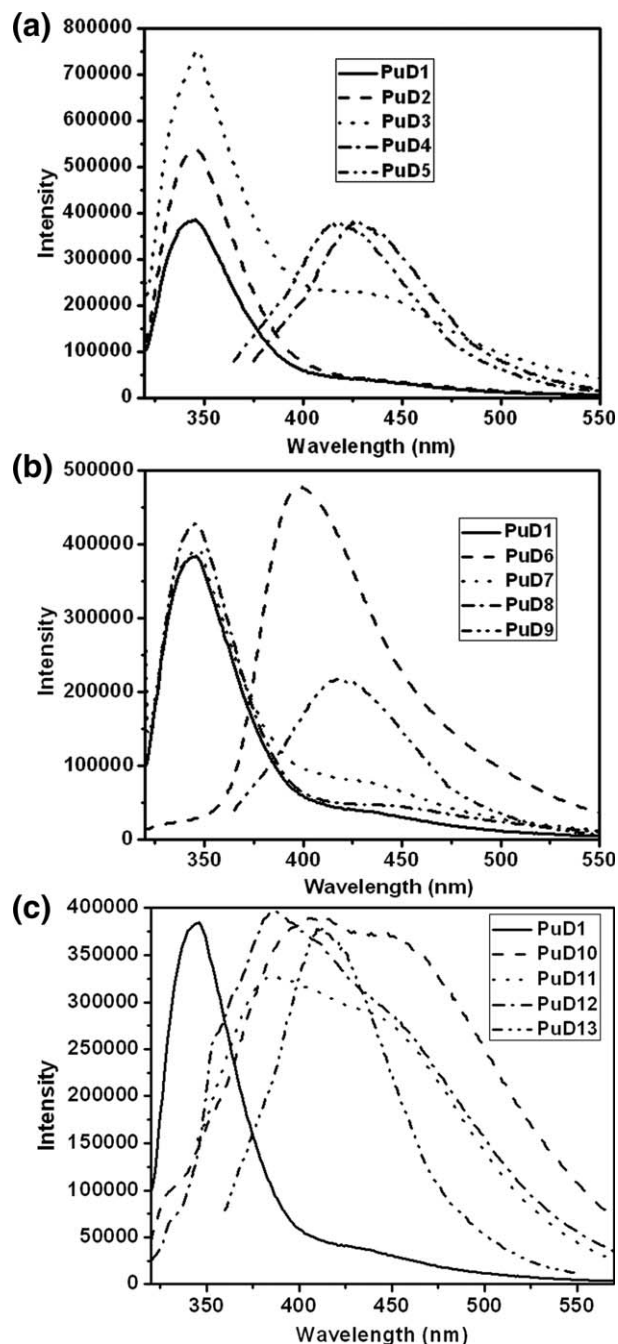


Figure 3 Emission spectra of polyurethanes (PuD1–PuD13).

considered to be a valuable technique for initial screening of materials for second harmonic generation.¹⁴ 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. Urea with particle size of $\sim 150 \mu\text{m}$ was used as the reference. The results obtained were found to be comparable with the results of urea (72 mV). According to the measurements, it is found that the polymers possess good Second Harmonic Generation Efficiency.

Conductivity

The conductivity of the sample were measured by using Keithley 2400 Sourcemeter by two probe method. The polymer materials studied were pelletised to analyze the conductivity. The source meter was interfaced to a computer in which the measurements were done by 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.

Crystallinity

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 30° were observed. Since the peaks were found to be broad the polymeric system were considered to be amorphous in character. The diffraction patterns of the polymers are shown in the Figure 4, the XRD pattern shows broad peaks at $10\text{--}30$ degrees. There is no prominent shift is 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 inter-segmental distance. Larger the d spacing a more disruptive packing of the polymer chain is expected.^{15–17} The increase in scattering angles with an increase in mole percentage of the chiral component means that the layer distance shrinks and the shrinking is parallel to the mole fraction of the chiral unit or with the increase in % of chiral unit the packing order in the polymers was increased. The polymer with diethyl tartrate chiral moiety shows amorphous character.

Solubility

Solubility studies of polyurethanes were performed with solvents having different polarity. A number of solvents were used to check the solubility of polyur-

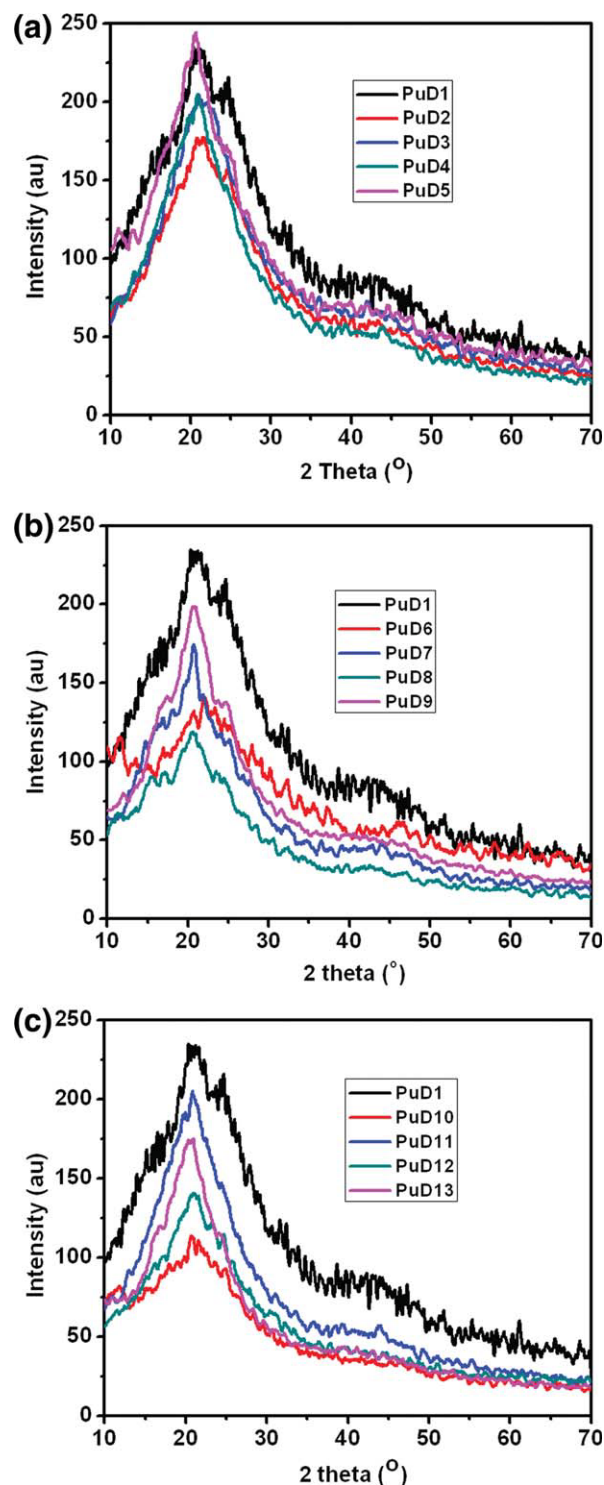


Figure 4 XRD pattern of polyurethanes (PuD1–PuD13). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ethanes. Most of the polyurethanes synthesized were soluble in polar solvents like DMAc, DMSO, DMF, etc. and not soluble in nonpolar 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 stability

Thermal properties of the polyurethanes were examined by TG/DTA measurements. High thermal stability is an important feature for a material to be usable in nonlinear optical applications. The T_g values were obtained from DTA analysis and initial decomposition temperature (IDT) from thermogravimetric measurements.^{15–17} The T_g of a polymer depends largely on the thermal energy required to create internal segmental motion in the polymer chain. A transition from rigid to flexible structures is indicated by the glass transition (T_g) temperatures for the polymer and a flexible working behavior of the polymer is found to be decreased below its T_g . The glass transition effects are relatively small in magnitude compared to the melting point. Higher the thermal energy and degree of polar order, higher will be the values of T_g . For all the polymers some sort of similarities in thermal stability were observed. All the samples were thermally stable upto the temperature around 180–280°C. In all the polymeric systems one major thermal decomposition was observed. From the wt % graph of TGA (Fig. 5), the temperature for different weight loss (% weight loss) can be determined.

As the IDT values of polymer increases, thermal stability also increases. The IDT values observed for the polyurethanes ranges from 180 to 280°C. It is clear that IDT values of polyurethanes with both chromophore and chiral incorporation is found to be having more stability ($\sim 200^\circ\text{C}$) and such polymers found to exhibit high SHG efficiency. It has been seen that the T_g values range from 80 to 210°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. From the DTA traces it is observed that no thermal transitions were noticed between 50–250°C, which confirms the stability of the material upto 250°C.

A careful examination of DTA curves of all the polymers reveal endothermic peaks at around 250–350°C, which corresponds to a wt % of 60–20% 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 broad endothermic peaks were observed in DTA graph shown in Figure 6. The endothermic peaks in DTA are assigned to be the melting point of the polymer samples and it's found to be in between 300–350°C. Hence it is found that the polymer materials may be useful for making the NLO devices

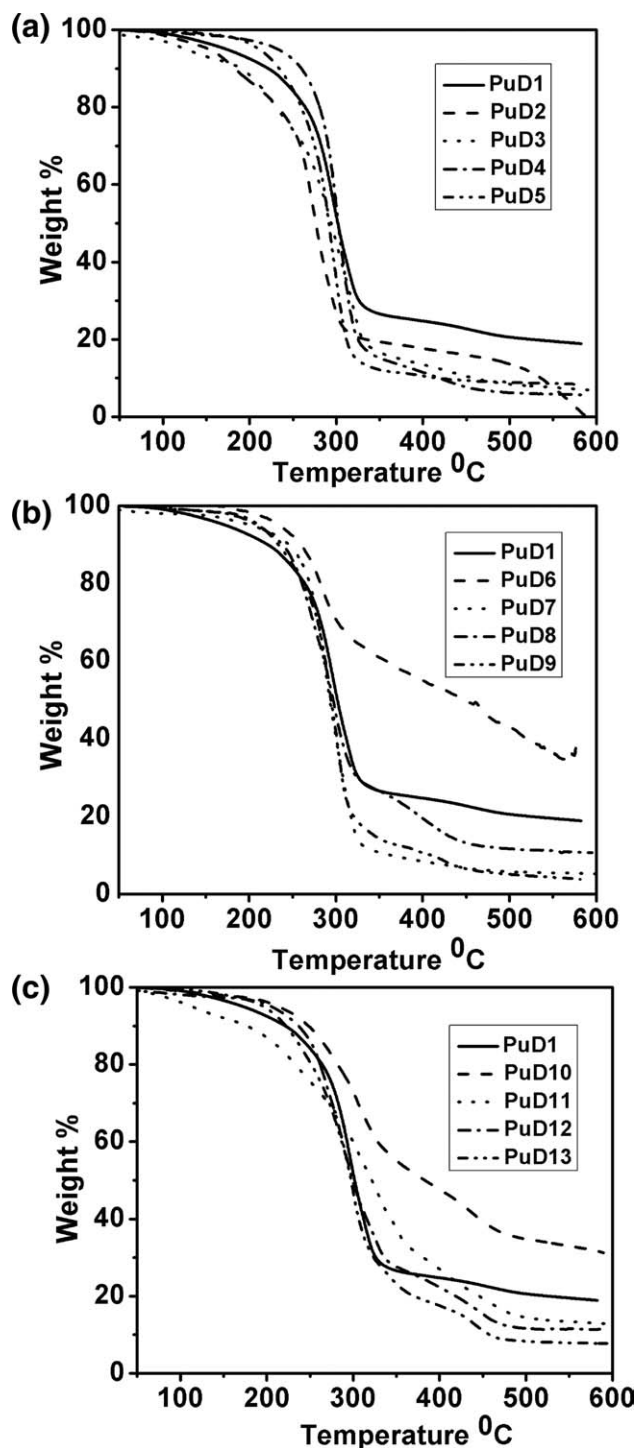


Figure 5 TG curve of polymers (PuD1–PuD13) showing the wt % of samples at different temperatures (heating rate of 10°C per minute under nitrogen atmosphere).

below its melting point. The thermal characterization data of polymers are given in Table I.

The data obtained by thermal analysis showed that the polyurethanes were having good thermal stability due to the presence of hydrogen bonding

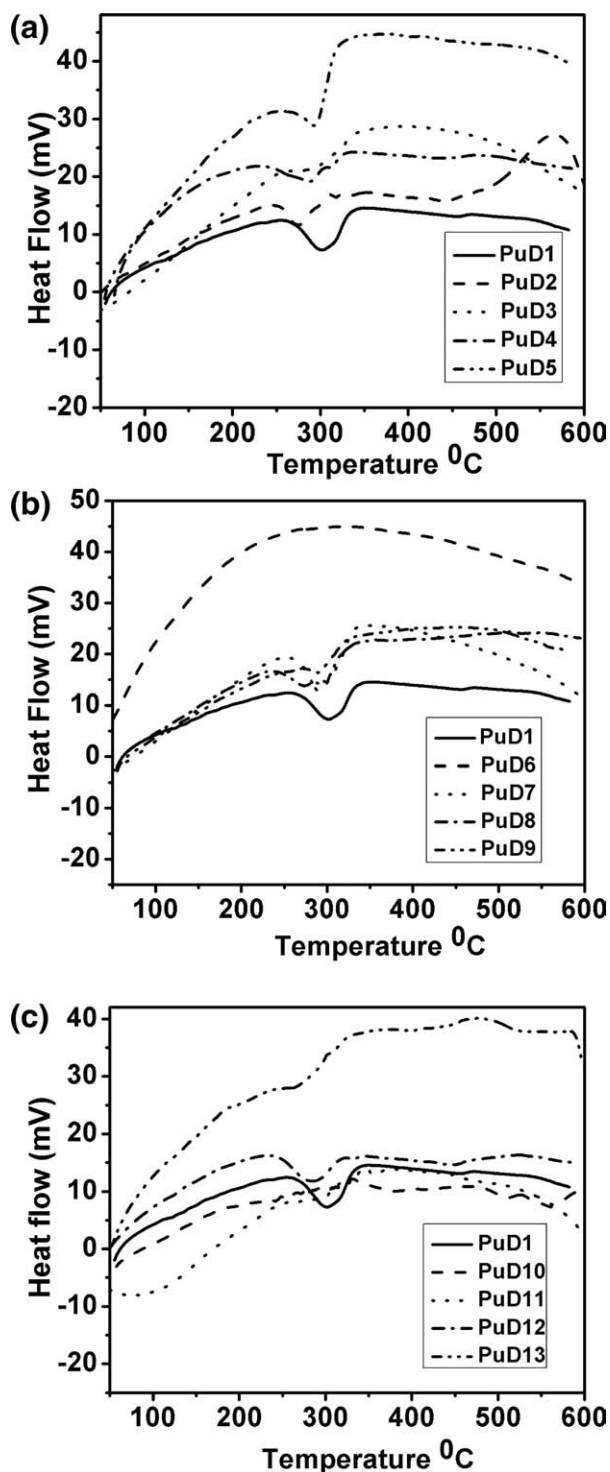


Figure 6 DTA curve for Polyurethanes (PuD1–PuD13) (heating rate of 10°C per minute under nitrogen atmosphere).

and the presence of aromatic backbone in the polyurethane chain

CONCLUSIONS

A series of optically active polyurethanes with diethyl-(2R, 3R) (+)-tartrate as chiral moiety in the main chain

were successfully synthesized. The amido diol chromophores were synthesized by the aminolysis of ϵ -caprolactone. All the polymers showed the absorption maximum at UV region from 267–272 nm. The band gap calculated for the polymeric systems is in between 4.43 to 4.68 eV. The emission of polyurethanes are observed at 345–430 nm. From the polarimetric measurements the specific rotation of the polymers is found to be increased with increase in percentage of chirality. From the conductivity measurements it is concluded that the polymers possess high insulating character. The XRD studies showed that the polymers synthesized were amorphous in nature. The polymers were found to exhibit T_g in the range of 80–210°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 200°C and hence can be useful for SHG applications below its melting point. We also predict the liquid crystalline behavior for the corresponding systems, because of the presence of amido groups and the rigidity due to the double bond character of the amide group coupled with extensive hydrogen bonding. The thermal characteristics and optical nonlinear activities clearly demonstrated that these polyurethanes are useful in device applications.

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