Polymer 51 (2010) 5392–5399

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and characterization of polyesters based on tartaric acid derivatives

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ARTICLE INFO

Article history:
Received 12 July 2010
Received in revised form
10 September 2010
Accepted 14 September 2010
Available online 21 September 2010

Keywords:
Aliphatic polyesters
Hydroxyl functionalized polyesters
L-tartaric acid

ABSTRACT

A series of aliphatic polyesters based on tartaric acid and its derivatives were synthesized starting from naturally occurring L-tartaric acid. The hydroxyl groups of the tartaric acid derivatives were first protected and the polyesters were synthesized by bulk and solution polycondensation methods. Two classes of polyesters were synthesized and characterized, the first by polycondensation of dimethyl 2,3-*O*-isopropylidene-L-tartrate with various alkanediols, and the second by reaction of 2,3-*O*-isopropylidene-L-threitol with various diacid chlorides. Acid catalyzed deprotection of isopropylidene groups gave well-defined polyesters having pendant hydroxyl functional groups regularly distributed along the polymer chain. The number average molecular weights (M_n) of the polymers were found to vary in the range of 2.3–15.7 $\times$ 10^3 g mol^{-1}. Differential scanning calorimetry (DSC) analysis showed the glass transition temperatures (T_g) of the polyesters varied from −36.1 °C to 17.9 °C on varying the chain length.

1. Introduction

Aliphatic polyesters are an interesting class of materials in that they hold great promise in biomedical and pharmaceutical applications. Aliphatic polyesters are known to be the most promising category of biodegradable polymers and environmentally benign materials [1–3]. For example, aliphatic polyesters, like poly(lactide) (PLA), poly(ϵ-caprolactone) (PCL), poly(glycolide) (PGA), and poly (β-hydroxy butyrate) (PHB) have shown the highest potential as biodegradable and biocompatible polymers [3–5]. PLA has been used in the field of tissue engineering as a scaffold material to support cell and tissue growth [6]. However, most of the aliphatic polyesters in existence are highly hydrophobic, thus practically leading to limitation in their biomedical applications due to the lack of desirable hydrophilicity and reactive pendant functional groups.[7] The presence of pendant groups such as carboxylic acid or hydroxyl functionalities impart attractive characteristics to the polymer including increased hydrophilicity, that are lacking in their unsubstituted analogues. Therefore, new functional biodegradable polyesters bearing hydrophilic reactive pendant groups such as hydroxyl, carboxyl, amino and so forth are desirable [8–12]. The combination of partial or complete water solubility, reactive functional groups and tunable biodegradability can enable these functional polyesters to be new biomaterials useful in the construction of novel controlled drug delivery systems and functional vectors as well as in related biomedical applications [13]. Furthermore, these functional polymers bearing reactive pendant groups could be applied to prepare novel comb, graft, or network polymers through post-polymer modification [14].

Tartaric acid is an attractive monomer or comonomer for synthesis of functional polymers. L-Tartaric acid, a widely available and relatively inexpensive natural resource from a large variety of fruits, has been used in the synthesis of polyamides, [15,16] poly(ester amide)s [17,18] and polycarbonates [19,20] etc. Tartaric acid based polyesters [21,22] have also been synthesized, however these polyesters were low molecular weight and mostly insoluble because pendant hydroxyl groups participate in the polycondensation that led to crosslinked polymers. Kimura et al. [23] synthesized polyesters having dioxolane ring from tartaric acid but hydroxyl deprotection was not attempted in these polyesters. Tartaric acid based polyesters have the potential to be used as vectors or drug carriers or controlled release agents in drug delivery [24,25].

In this study, aliphatic polyesters were synthesized from protected and naturally occurring L-tartaric acid derivatives using bulk and solution polycondensation methods by systematically varying the chain length of either the diol or the diacid. The acetal protecting groups in the polyesters were then selectively hydrolyzed to generate polyesters with pendant hydroxyl groups. The synthesized polyesters were characterized by ^{1}H NMR, ^{13}C NMR, gel permeation chromatography (GPC), FT-IR, optical polarimetry, hydroxyl titration, DSC, and TGA.

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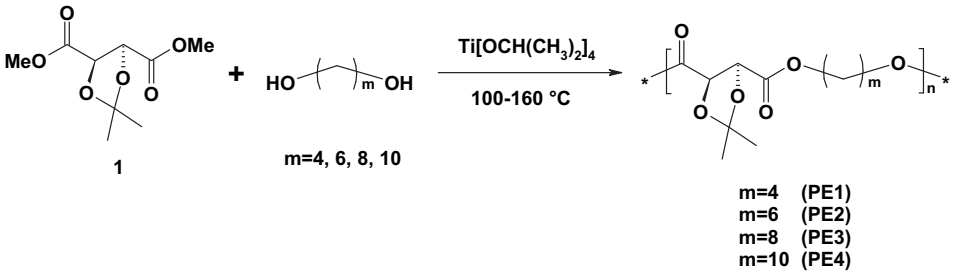
doi:10.1016/j.polymer.2010.09.034



Scheme 1. Synthesis of polyesters PE1-PE4.

2. Experimental section

2.1. Materials

L-Tartaric acid, *p*-toluenesulfonic acid, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol, 2,2-dimethoxypropane, adipoyl chloride, thionyl chloride, and pyridine were purchased from Spectrochem Chemicals and used as received. Titanium tetraisopropoxide, lithium aluminium hydride, and succinoyl chloride were purchased from Aldrich. Pyridine (AR grade) was dried with potassium hydroxide overnight and was further purified by distillation. Solvents were dried and purified, when necessary, by appropriate standard procedures.

2.2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 25 °C operating at 300 and 75.5 MHz, respectively. Polyesters were dissolved in deuterated chloroform, and spectra were internally referenced to tetramethylsilane (TMS). IR spectra were recorded on a Thermo Nicolet IR 200 spectrometer using KBr disks. Optical rotations were measured at 25 ± 0.5 °C (1 cm cell). Inherent viscosity was measured using an Ubbelohde viscometer at a concentration of 0.5 g/dL in chloroform at 30 °C. Gel permeation chromatography (GPC) was carried out using tetrahydrofuran (THF) as the mobile phase at 30 °C. GPC analysis was performed on a Perkin–Elmer, Series 200, USA GPC system equipped with a refractive index detector. Molecular weights were calculated against monodisperse polystyrene standards using the Totalchrom software. The thermal behaviour of the polyesters was examined by differential scanning calorimetry (DSC) using a DSC Q 200 calibrated with indium. DSC data were obtained from samples of 4–6 mg at heating/cooling rates of 10 or 20 °C min^{-1} under nitrogen. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer Pyris-6 TGA thermobalance at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. The water contact angles of the polyester films were measured at room temperature using a Rame-hart, CA goniometer, USA. The volume of the water for each measurement was kept at 2 μL. Three specimens per sample were used, and three measurements were performed with each specimen. The contact angle data for each sample are averages of nine individual measurements.

2.3. Hydroxyl titration

To determine the hydroxyl content in the synthesized polyesters, a non-aqueous titration method was employed.[26,27] In general, 100 mg of polyester was added to 4.0 mL of pyridine/acetic anhydride (3:1 v/v) solution, and then heated in an oil bath at 100 °C for 1 h. Subsequently, 2.0 mL of distilled water was added into the reaction mixture. After 0.5 h, a methanolic KOH solution (83 mM) was used to titrate the polyester solution in triplicate with thymol blue as the indicator. Similarly, a blank titration was also conducted.

2.4. Intrinsic viscosity measurements

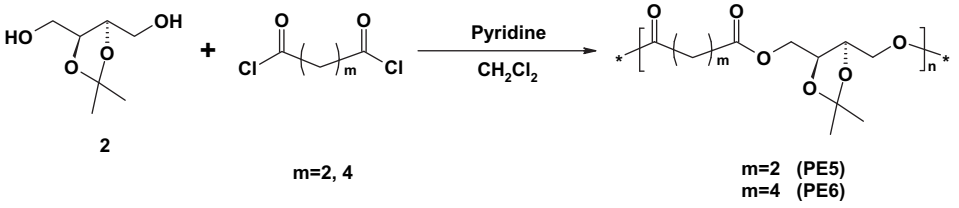
Solution viscosities of polyesters were carried out with an Ubbelohde viscometer at 30 °C. Purified polyester samples of concentration 0.5 g/dL were prepared in chloroform and the flow time for solvent and polymer solutions were measured. Similarly, by the dilution of the polymer solution five different solution concentrations were prepared and the flow time for each was determined. A graph between the reduced viscosity and concentration was plotted and the intrinsic viscosity $[\eta]_D$ was determined by extrapolation of reduced viscosity to zero concentration.

2.5. Synthesis

The polyesters were synthesized by either bulk or solution polycondensation.

2.5.1. General procedure for bulk polycondensation method (PE1-PE4)

Dimethyl 2,3-*O*-isopropylidene-L-tartarate and 10% molar excess of alkanediol were taken in a Schlenk tube under nitrogen atmosphere, equipped with a Dean Stark apparatus and condenser. The reactants were stirred to a homogeneous mixture and 0.5 mol% of titanium tetraisopropoxide was added as catalyst. In the first step (esterification), the reaction mixture was heated at 90–120 °C for 6–8 h, till almost the theoretical amount of methanol was collected. In the second step (polycondensation), a vacuum (0.5–1 mm Hg) was applied and the reaction mixture was heated at 100–160 °C for 10–15 h till the stirring ceased. The cooled reaction



Scheme 2. Synthesis of polyesters PE5 and PE6.

Table 1
Characterization data for polyesters PE1-PE6.

Polyester	Yield (%)	$[\alpha]_D$ (deg)[a]	$[\eta]_D$ (dL/g)[b]	M_n[c] × 10^3	M_w/M_n[c]	T_g (°C)[d]	T_d (°C)[e]
PE1	73	−84.2	0.12	3.8	1.7	−9.2	298.1
PE2	88	−84.4	0.25	15.7	2.1	−22.5	349.9
PE3	86	−82.6	0.17	6.4	1.8	−29.6	336.2
PE4	83	−80.8	0.17	6.9	2.3	−36.1	347.5
PE5	74	+72.6	0.14	5.4	1.9	−7.8	397.6
PE6	82	+71.8	0.19	8.8	1.8	−14.6	415.2

[a] *c* 1.0, dichloromethane, at 25 °C.
[b] In chloroform at 30 ± 0.5 °C.
[c] By GPC against polystyrene standards, using THF as a mobile phase.
[d] Glass transition temperature measured by DSC.
[e] The thermal degradation temperature for maximum derivative weight loss, measured by TGA.

mixture was then dissolved in minimum amount of chloroform and poured into ten fold amount of methanol to precipitate the polymer.

2.5.1.1. Poly(butylene 2,3-O-isopropylidene tartarate) (PE1). Dimethyl 2,3-*O*-isopropylidene-L-tartarate (4 g, 18.34 mmol), 1,4-butanediol (1.82 g 20.19 mmol) and titanium tetraisopropoxide (30 μL) were mixed, and the reaction mixture was heated at 90 °C for 8 h in the esterification step and was heated at 100 °C for 15 h in the polycondensation step (Yield 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.69 (s, 2H), 4.17 (s, 4H), 1.70 (s, 4H), 1.40 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.5, 113.8, 77.0, 65.0, 26.2, 24.9; FT-IR (KBr disk, cm^{-1}) 2935 (υ_{C-H}), 1751 ($\upsilon_{C=O}$), 1208 and 1108 (υ_{C-O-C}).

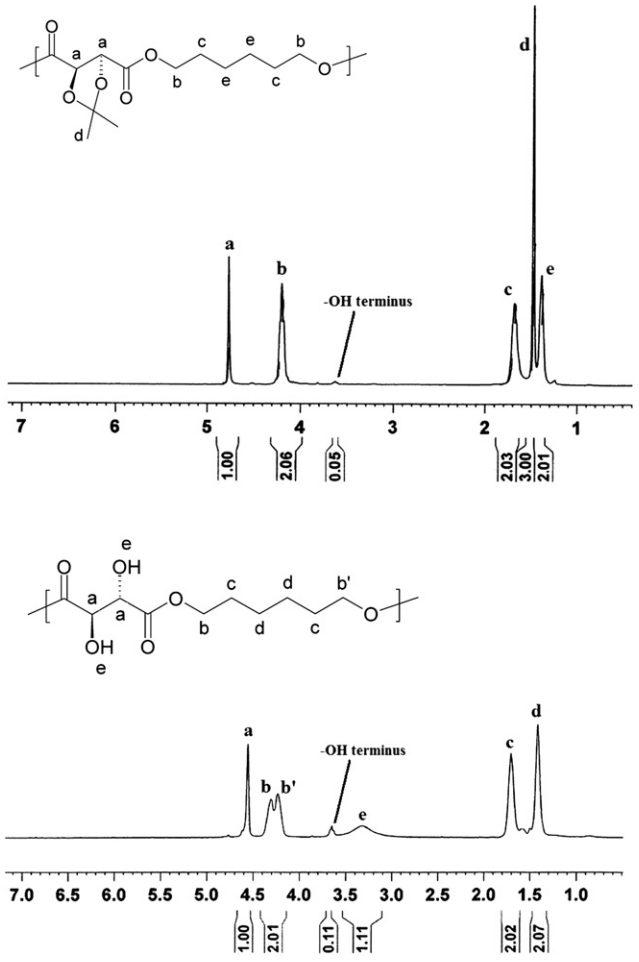


Fig. 1. ^{1}H NMR spectra of polyesters PE2 and PE8.

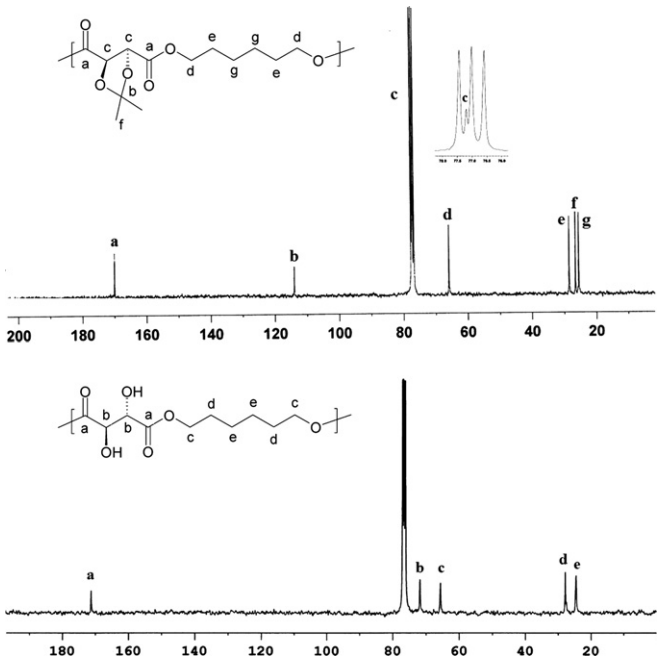


Fig. 2. ^{13}C NMR spectra of polyesters PE2 and PE8.

2.5.1.2. Poly(hexamethylene 2,3-O-isopropylidene tartarate) (PE2). Dimethyl 2,3-*O*-isopropylidene-L-tartarate (6 g, 27.52 mmol), 1,6-hexanediol (3.54 g 29.97 mmol) and titanium tetraisopropoxide (42 μL) were mixed, and the reaction mixture was heated at 100 °C for 8 h in the esterification step and was heated at 160 °C for 10 h in the polycondensation step when the stirring totally ceased (Yield 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.77 (s, 2H), 4.20 (m, 4H), 1.69 (m,

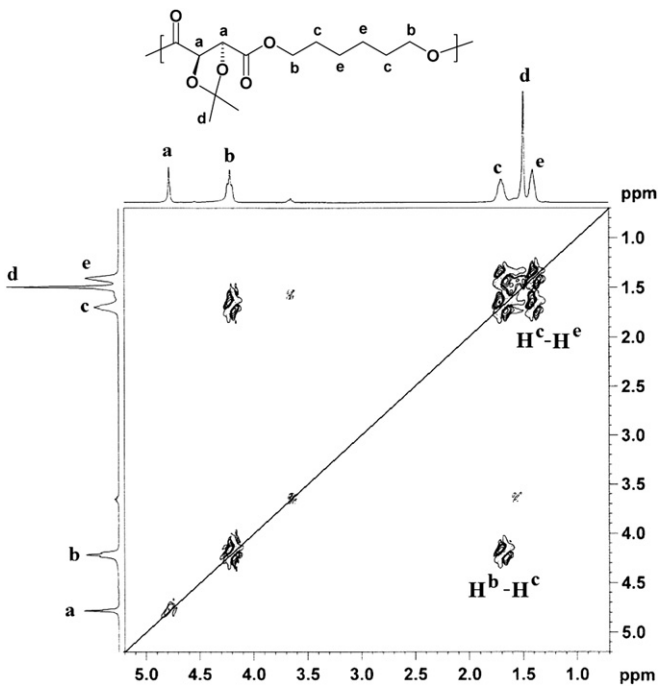


Fig. 3. ^{1}H–^{1}H COSY (300 MHz) spectrum of polyester PE2.

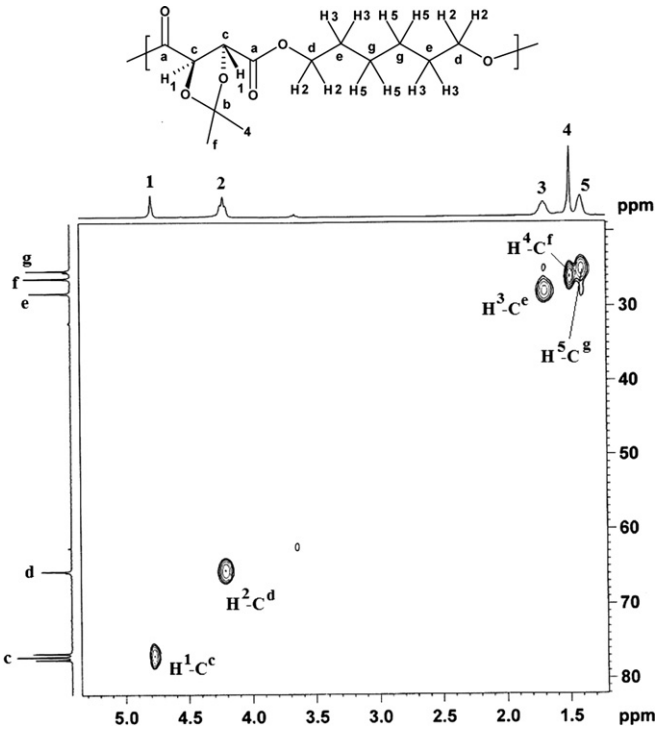


Fig. 4. $^{1}H-^{13}C$ HMQC (300 MHz) spectrum of polyester PE2.

4H), 1.48 (s, 6H), 1.40 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.8, 113.8, 77.2, 65.7, 28.3, 26.4, 25.3; FT-IR (KBr disk, cm^{-1}) 2924 (υ_{C-H}), 1739 ($\upsilon_{C=O}$), 1216 and 1168 (υ_{C-O-C}).

2.5.1.3. Poly(octamethylene 2,3-O-isopropylidene tartarate) (PE3). Dimethyl 2,3-*O*-isopropylidene-L-tartarate (2.83 g, 12.98 mmol), 1,8-octanediol (2.1 g 14.36 mmol) and titanium tetraisopropoxide (20 μL) were mixed, and the reaction mixture was heated at 120 °C for 6 h in the esterification step and was heated at 160 °C for 10 h in the polycondensation step till the stirring ceased (Yield 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.77 (s, 2H), 4.20 (t, $J = 6.3$ Hz, 4H), 1.67 (m, 4H), 1.49 (s, 6H), 1.33 (s, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.7, 113.7, 77.2, 65.8, 29.0, 28.4, 26.3, 25.6; FT-IR (KBr disk, cm^{-1}) 2929 (υ_{C-H}), 1750 ($\upsilon_{C=O}$), 1208 and 1106 (υ_{C-O-C}).

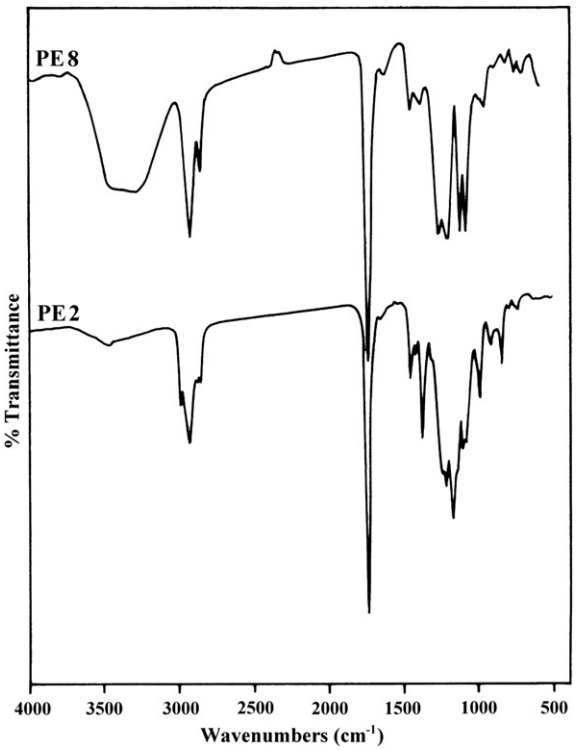


Fig. 5. FT-IR spectra of polyesters PE2 and PE8.

Table 2
Water contact angles for polyesters PE1-PE6.

Polyester	Water contact angle (deg)
PE1	61
PE2	64
PE3	66
PE4	70
PE5	59
PE6	61

2.5.1.4. Poly(decamethylene 2,3-O-isopropylidene tartarate) (PE4). Dimethyl 2,3-*O*-isopropylidene-L-tartarate (3 g, 13.76 mmol), 1,10-decanediol (2.63 g 15.09 mmol) and titanium tetraisopropoxide (20 μL) were mixed and the reaction mixture was heated at 120 °C for 6 h in the esterification step and was heated at 160 °C for 10 h in the polycondensation step till the stirring ceased (Yield 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.79 (s, 2H), 4.22 (t, $J = 6.6$ Hz, 4H), 1.69 (m, 4H), 1.51 (s, 6H), 1.31 (s, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 169.7, 113.7, 77.2, 65.9, 29.3, 29.1, 28.4, 26.4, 25.7; FT-IR (KBr disk, cm^{-1}) 2932 (υ_{C-H}), 1750 ($\upsilon_{C=O}$), 1207 and 1108 (υ_{C-O-C}).

2.5.2. General procedure for solution polycondensation method (PE5 and PE6)

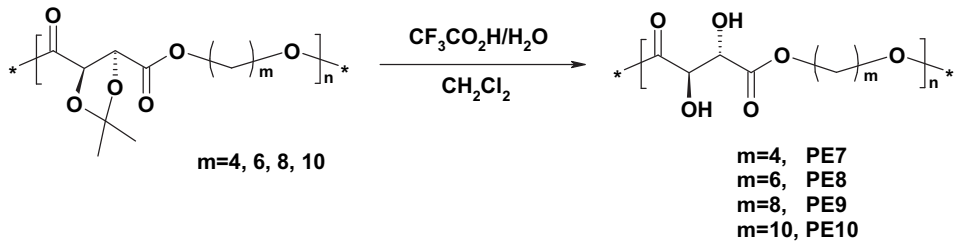
2,3-*O*-Isopropylidene-L-threitol was dissolved in dry dichloromethane (keeping 1.0 M concentration) in a Schlenk tube under nitrogen atmosphere and 3 M equivalents of dry pyridine was added as a proton trap. Diacid chloride (succinoyl chloride for PE5 and adipoyl chloride for PE6) was added dropwise over a period of 30 min and the reaction mixture was stirred at room temperature for 48 h. The resulting crude product was diluted with minimum amount of chloroform and poured into ten fold excess of methanol to precipitate the polymer.

2.5.2.1. Poly(2,3-O-isopropyl butylene succinate) (PE5). 2,3-*O*-Isopropylidene-L-threitol (1.05 g, 6.45 mmol), succinoyl chloride (1 g, 6.45 mmol), dry pyridine (1.55 mL, 19.35 mmol) were dissolved in dichloromethane (3 mL) (Yield 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34–4.16 (m, 4H), 4.05 (s, 2H), 2.69 (s, 4H), 1.42 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.8, 110.3, 75.7, 64.0, 28.7, 26.9; FT-IR (KBr disk, cm^{-1}) 2988 (υ_{C-H}), 1740 ($\upsilon_{C=O}$), 1213 and 1160 (υ_{C-O-C}).

2.5.2.2. Poly(2,3-O-isopropyl butylene adipate) (PE6). 2,3-*O*-Isopropylidene-L-threitol (2.66 g, 16.39 mmol), adipoyl chloride (3 g, 16.39 mmol), dry pyridine (3.95 mL, 49.17 mmol) were dissolved in dichloromethane (8 mL) (Yield 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31–4.10 (m, 4H), 4.02 (s, 2H), 2.38 (s, 4H), 1.67 (s, 4H), 1.41 (s, 6H) ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.8, 110.3, 75.8, 63.8, 33.55, 26.9, 24.1; FT-IR (KBr disk, cm^{-1}) 2988 (υ_{C-H}), 1740 ($\upsilon_{C=O}$), 1213 and 1161 (υ_{C-O-C}).

2.5.3. General procedure for the removal of isopropylidene groups (PE7-PE12)

The polymer was first dissolved in dichloromethane and then 10 M equivalents of both trifluoroacetic acid and water were added and the reaction mixture was stirred at room temperature for



Scheme 3. Synthesis of polyesters PE7-PE10.

30 min. After 30 min, the solvents were removed under reduced pressure and the residue was dissolved in minimum amount of methanol and poured into ten fold excess of diethyl ether to precipitate the polymer.

2.5.3.1. Poly(butylene tartarate) (PE7). Polyester (400 mg, 1.63 mmol), trifluoroacetic acid (1.21 mL, 16.3 mmol), and water (0.3 mL, 16.3 mmol) were dissolved in dichloromethane (2.5 mL). (Yield 82%) ^{1}H NMR (300 MHz, CD_3OD) δ 4.63 (s, 2H), 4.28 (s, 4H) 1.83 (s, 4H); ^{13}C NMR (75.5 MHz, CD_3OD) δ 173.1, 73.7, 66.2, 26.0; FT-IR (KBr disk, cm^{-1}) 3357 (υ_{O-H}) 2952 (υ_{C-H}), 1741 ($\upsilon_{C=O}$), 1275 and 1131 (υ_{C-O-C}).

2.5.3.2. Poly(hexamethylene tartarate) (PE8). Polyester (500 mg, 1.83 mmol), trifluoroacetic acid (1.36 mL, 18.3 mmol), and water (0.33 mL, 18.3 mmol) were dissolved in dichloromethane (3 mL). (Yield 85%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.55 (s, 2H), 4.31–4.23 (m, 4H), 3.33 (br, –OH), 1.70 (s, 4H) 1.41 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.6, 72.2, 66.0, 28.2, 24.9; FT-IR (KBr disk, cm^{-1}) 3305 (υ_{O-H}) 2926 (υ_{C-H}), 1741 ($\upsilon_{C=O}$), 1271 and 1130 (υ_{C-O-C}).

2.5.3.3. Poly(octamethylene tartarate) (PE9). Polyester (300 mg, 1 mmol), trifluoroacetic acid (0.74 mL, 10 mmol), and water (0.18 mL, 10 mmol) were dissolved in dichloromethane (2.5 mL). (yield 83%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.54 (s, 2H), 4.27–4.25 (m, 4H), 2.35 (br, –OH), 1.69 (m, 4H) 1.30 (s, 8H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.6, 72.2, 66.3, 28.8, 28.4, 25.4; FT-IR (KBr disk, cm^{-1}) 3449 (υ_{O-H}) 2925 (υ_{C-H}), 1742 ($\upsilon_{C=O}$), 1275 and 1133 (υ_{C-O-C}).

2.5.3.4. Poly(decamethylene tartarate) (PE10). Polyester (400 mg, 1.21 mmol), trifluoroacetic acid (0.9 mL, 12.19 mmol), and water (0.21 mL, 12.19 mmol) were dissolved in dichloromethane (2.5 mL). (Yield 87%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (s, 2H) 4.26–4.24 (m, 4H), 3.11 (br, –OH) 1.68 (m, 4H) 1.29 (s, 12H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 171.6, 72.1, 66.5, 29.2, 29.0, 28.4, 25.6; FT-IR (KBr disk, cm^{-1}) 3443 (υ_{O-H}) 2923 (υ_{C-H}), 1745 ($\upsilon_{C=O}$), 1274 and 1131 (υ_{C-O-C}).

2.5.3.5. Poly(2,3-hydroxyl butylene succinate) (PE11). Polyester (200 mg, 0.82 mmol), trifluoroacetic acid (0.6 mL, 8.2 mmol), and water (0.15 mL, 8.2 mmol) were dissolved in dichloromethane (2 mL). (Yield 81%) ^{1}H NMR (300 MHz, DMSO) δ 4.16–3.97 (m, 4H), 3.92 (s, 2H), 2.50 (s, 4H); ^{13}C NMR δ (75.5 MHz, DMSO) 171.6, 74.9, 63.4, 28.3; FT-IR (KBr disk, cm^{-1}) 3492 (υ_{O-H}) 2928 (υ_{C-H}), 1754 ($\upsilon_{C=O}$), 1208 and 1110 (υ_{C-O-C}).

2.5.3.6. Poly(2,3-hydroxyl butylene adipate) (PE12). Polyester (300 mg, 1.1 mmol), trifluoroacetic acid (0.8 mL, 11 mmol), and water (0.2 mL, 11 mmol) were dissolved in dichloromethane (2.5 mL). (Yield 83%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.33–4.17 (m, 4H), 3.91 (s, 2H), 2.39 (s, 4H), 1.66 (s, 4H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 172.7, 75.8, 63.7, 33.5, 24.1; FT-IR (KBr disk, cm^{-1}) 3415 (υ_{O-H}) 2928 (υ_{C-H}), 1742 ($\upsilon_{C=O}$), 1212 and 1131 (υ_{C-O-C}).

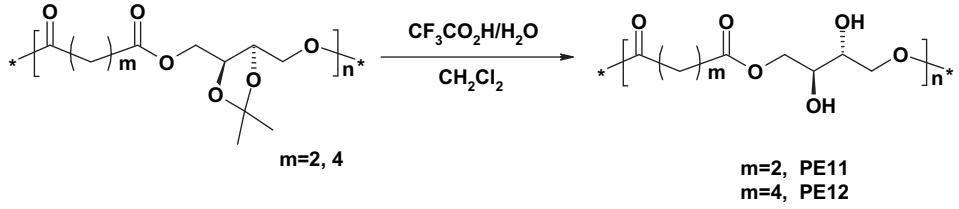
3. Results and discussion

3.1. Synthesis and characterization of polyesters PE1-PE6

The polyesters were synthesized by either bulk or solution polycondensation. The polyesters PE1-PE4, with lateral isopropylidene groups were synthesized by bulk polycondensation of dimethyl 2,3-*O*-isopropylidene-L-tartarate 1 with commercially available alkanediols in the presence of titanium tetraisopropoxide as a catalyst (Scheme 1).

2,3-*O*-isopropylidene-L-tartarate 1 was prepared according to the literature [20]. Synthesis of aliphatic polyesters was performed following a two-stage polycondensation method. In the first step (esterification), oligomers were synthesized without the application of vacuum on the reaction mixture by heating it to 90–120 °C for 6–8 h until the theoretical amount of methanol was collected in the side arm of the Dean Stark apparatus. Then in a second step (polycondensation), the Dean Stark apparatus was removed and a vacuum (0.5–1 mm Hg) was applied slowly over a period of about 30 min to minimize the sublimation of oligomers. PE2, PE3, and PE4 were synthesized at a temperature of 160 °C and pressure of 0.5–1 mm Hg, however, in the case of PE1 temperature was not increased beyond 100 °C, as higher temperature resulted in an insoluble polymer.[23] The polyesters PE5 and PE6, with lateral isopropylidene groups were synthesized by solution polycondensation of 2,3-*O*-isopropylidene-L-threitol 2 with diacid chlorides at room temperature using pyridine as a proton trap (Scheme 2).

2,3-*O*-isopropylidene-L-threitol 2 was prepared according to the literature.[20] Table 1 summarizes the results obtained for polymers PE1-PE6.



Scheme 4. Synthesis of polyesters PE11 and PE12.

Table 3
Characterization data for polyesters PE7-PE12.

Polyester	Yield (%)	$[\alpha]_D$ (deg)[a]	$[\eta]_D$ (dL/g)[b]	M_n[c] × 10^3	M_w/M_n[c]	T_g (°C)[d]	T_d (°C)[e]
PE7	82	−80.1[f]	0.09[g]	2.3[h]	–	6.2	278.1
PE8	85	−76.2	0.15	4.6	1.8	−8.0	305.6
PE9	83	−76.8	0.11	3.2	1.6	−17.8	320.8
PE10	87	−74.1	0.11	2.8	2.0	−18.0	327.3
PE11	81	+68.8[f]	0.10[g]	3.0[h]	–	17.9	342.2
PE12	83	+60.7	0.13	3.5	1.7	8.9	378.7

[a] *c* 1.0, dichloromethane, at 25 °C.
[b] In chloroform at 30 ± 0.5 °C.
[c] By GPC against polystyrene standards, using THF as a mobile phase.
[d] Glass transition temperature measured by DSC.
[e] The thermal degradation temperature for maximum derivative weight loss, measured by TGA.
[f] *c* 1.0, methanol, at 25 °C.
[g] In methanol at 30 ± 0.5 °C.
[h] Molecular weight evaluated by ^{1}H NMR.

Table 4
Solubility of polyesters in various solvents.[a]

Solvent	PE 1	PE2	PE3	PE4	PE5	PE6	PE7	PE8	PE9	PE 10	PE 11	PE 12
H_2O	−	−	−	−	−	−	+	+	±	±	+	+
CH_3OH	−	−	−	−	−	−	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+	+	+	+	+
DMF	+	+	+	+	+	+	+	+	+	+	+	+
CH_2Cl_2	+	+	+	+	+	+	−	+	+	+	−	+
$CHCl_3$	+	+	+	+	+	+	−	+	+	+	−	+
THF	+	+	+	+	+	+	−	+	+	+	−	+
Et_2O	−	−	−	−	−	−	−	−	−	−	−	−
Hexane	−	−	−	−	−	−	−	−	−	−	−	−

[a] Key: (−) insoluble; (+) soluble; (±) partially soluble.

The polymers were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, GPC, DSC, and TGA. ^{1}H and ^{13}C NMR spectra of the polyester PE2 are depicted in Figs. 1 and 2, respectively, and are in good agreement with the chemical structure of the polyester.

^{1}H–^{1}H 2D COSY and ^{1}H–^{13}C 2D HMQC were taken to further confirm the assignments and structure. The ^{1}H–^{1}H 2D COSY spectrum of polyester PE2 is shown in Fig. 3. In PE2 protons b and c are coupled to each other as are protons c and e, as evidenced by the off-diagonal peaks labelled as H^b–H^c and H^c–H^e, respectively. The low intensity peaks stands for the terminal groups of the polymer chain.

The ^{1}H–^{13}C 2D HMQC spectrum of polyester PE2 is depicted in Fig. 4. The protons are labelled with numbers and carbon atoms are labelled with alphabets. The carbon atoms that are not directly linked to protons do not cause any resonance signal in HMQC spectra. There are seven types of carbon atoms in PE2 out of which five are directly attached to protons and give corresponding resonance signals. These resonance signals are labelled in Fig. 4 and the observed ^{1}H–^{13}C correlation again confirms the structure. For example, protons labelled as 1 are correlate with carbon atom labelled as c and is shown as H^1–C^c.

Furthermore, the infrared spectrum of PE2 (Fig. 5) exhibited characteristic absorptions at 1739 cm^{-1} (C=O stretching) confirming the presence of ester bond in the polymer. The molecular weights of the polyesters were determined by gel permeation chromatography (GPC) using THF as a mobile phase. The number average molecular weights (M_n) of the polyesters PE1-PE6 were obtained in the range of 3.8–15.7 × 10^3 g mol^{-1} with a polydispersity index varied in the range of 1.7–2.3. In addition, the results of optical rotation measurements show that the polyesters are optically active with specific rotation $[\alpha]_D$ values from −80.8° to −84.4° for polyesters PE1-PE4, and +71.8° to +72.6° for polyesters PE5 and PE6. The viscosity of the polyesters were measured in chloroform at 30 °C and exhibit intrinsic viscosity $[\eta]_D$ values from 0.12 to 0.25 for polyesters PE1-PE6, which fall in comparable range for aliphatic polyesters with similar molecular weights reported in literature.[28–30] Also, contact angle measurements were made for PE1-PE6 to evaluate the hydrophilicity of the polyesters (Table 2). The contact angles for PE1-PE4 were found to vary between 61° and 70° on increasing the methylene units from 4 to 10 in the diol, consistent with what is expected. For PE5 and PE6, the contact angle values were found to be 59° and 61°, respectively indicating almost similar hydrophilicity values for the two polymers. In comparison, the literature values for PLA [31], and PCL [32] are 83° and 85° respectively, suggesting that PE1-PE6 are relatively more hydrophilic. Similarly, a comparison with PGA (53°)[33], poly (butylene succinate) (PBS) (59°)[34], and polyhydroxy butyrate-polyhydroxy valerate (PHBV) (66°)[34], shows that PE1-PE6 possess comparable hydrophilicity with PGA, PBS and PHBV.

3.2. Synthesis and characterization of hydroxyl functionalized polyesters by selective deprotection (PE7-PE12)

One of the highlights of this work is the ability to introduce hydroxyl functional groups on the polymer backbone by selective

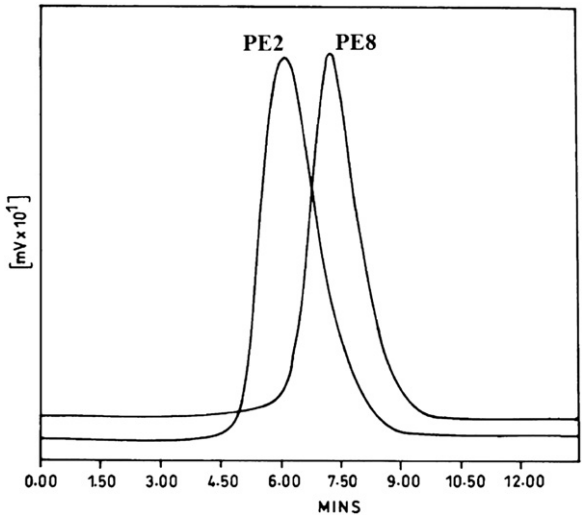


Fig. 6. GPC chromatograms of polyesters PE2 and PE8.

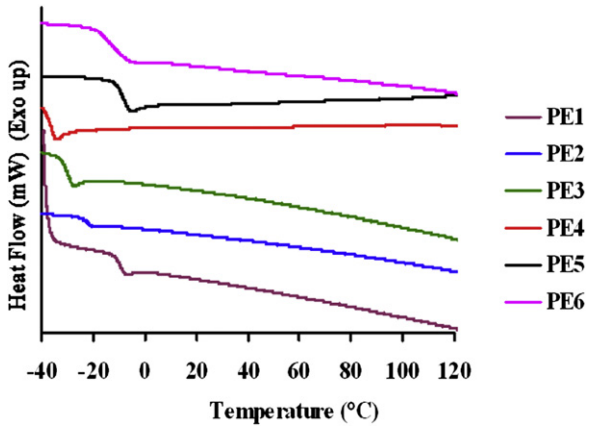


Fig. 7. DSC traces of polyesters PE1-PE6.

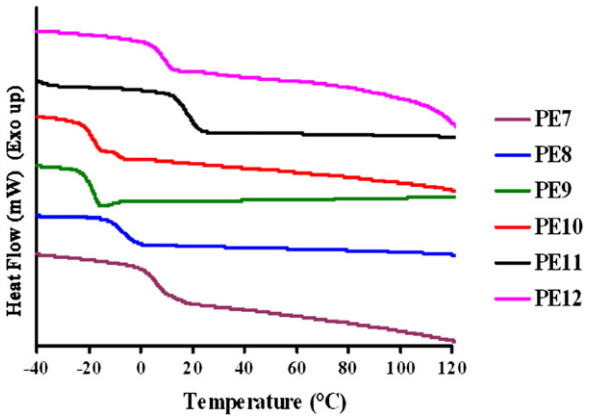


Fig. 8. DSC traces of polyesters PE7-PE12.

hydrolysis and trifluoroacetic acid was used for selective removal of the lateral isopropylidene groups [20, 35] (Schemes 3 and 4).

Trifluoroacetic acid and water, both in 10 M equivalents were used and stirred with the polymer for 30 min at room temperature to completely remove the isopropylidene groups. The resulting polymers were dissolved in methanol and reprecipitated from diethyl ether. Table 3 summarizes the results obtained for polymers PE7-PE12.

^{1}H and ^{13}C NMR spectra of the polyester PE8 are depicted in Figs. 1 and 2, respectively; and are in good agreement with the chemical structure of the polyester.

Comparing the ^{1}H NMR spectrum of PE2 and PE8, it can be clearly seen that the resonance signal at 1.49 ppm, attributed to the isopropylidene groups, completely disappears in the ^{1}H NMR spectrum of PE8, and a new resonance signal at 3.33 ppm appears, corresponding to the hydroxyl groups. Similarly, a comparison of the ^{13}C NMR spectra of PE2 and PE8 shows that the resonance signals at 113.80 ppm and 26.39 ppm, corresponding to the isopropylidene groups, completely disappears in the ^{13}C NMR spectrum of PE8. Furthermore, FT-IR spectra of the polyesters before and after deprotection are depicted in Fig. 5 and the most distinctive feature in PE8 is the appearance of a broad hydroxyl band at 3700–3300 cm^{-1}.

These data suggest complete removal of the isopropylidene groups to provide pendant hydroxyl groups along the polymer backbone. The molecular weights of the polyesters were determined by gel permeation chromatography (GPC) using THF as a mobile phase. The number average molecular weights (M_n) of the polyesters were obtained in the range of 2.3–4.6 $\times$ 10^{3} g mol^{-1} with a polydispersity index of 1.6–2.0. In case of PE7 and PE11 molecular weights were evaluated by ^{1}H NMR because these polyesters were insoluble in THF and chloroform. As an example, the GPC chromatograms of polyesters PE2 and PE8 (before and after deprotection) are depicted in Fig. 6 and clearly show the decrease in molecular weight upon deprotection. The optical rotation measurements show that the polyesters are optically active with specific rotation $[\alpha]_D$ values from -74.1° to -80.1° for polyesters PE7-PE10, and $+60.7^\circ$ to $+68.8^\circ$ for polyesters PE5 and PE6. The viscosity of polyesters PE7-PE12 were measured in chloroform at 30 °C and the intrinsic viscosity $[\eta]_D$ values varied from 0.09 to 0.15, showing that the intrinsic viscosity $[\eta]_D$ decreased on deprotection, in part due to the decrease in molecular weight after deprotection. Furthermore, a quantitative titration of the hydroxyl content was conducted to determine the hydroxyl contents in the polyesters with lateral hydroxyl groups by a non-aqueous hydroxyl titration method. The titration showed the hydroxyl content for the

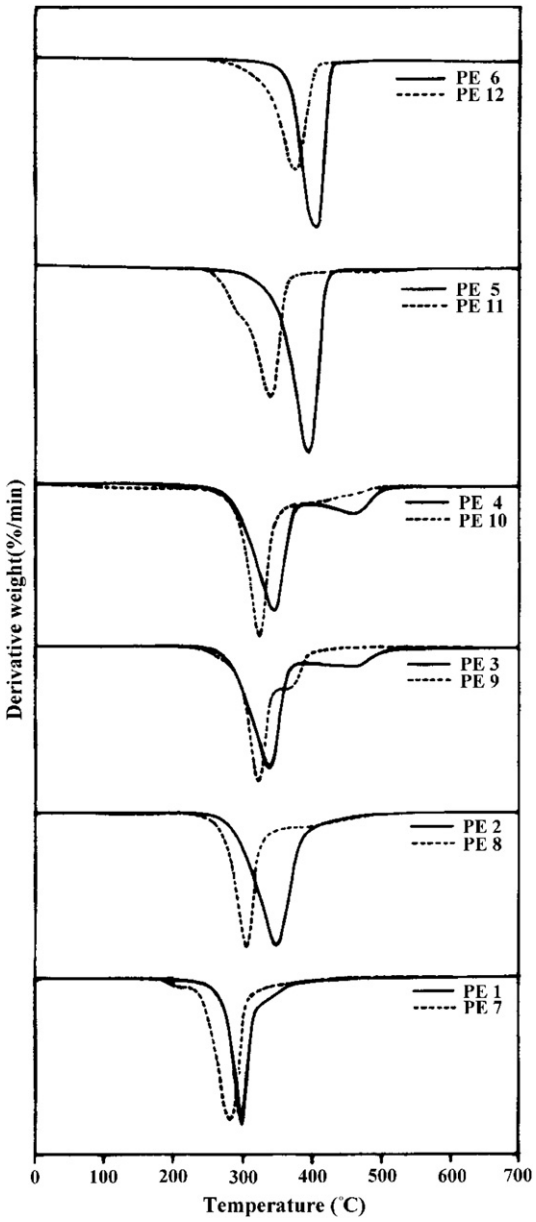


Fig. 9. dTGA traces of polyesters PE1-PE12.

polyesters PE7-PE12 to be in the range of 7.71–10.54 mmol/g. The experimental values are found to be in good agreement with the theoretical values, and the hydroxyl contents for PE7-PE10 were found in the range of 9.62–7.71 mmol/g as compared to the theoretical values which lie 9.80–6.94 mmol/g. The polyesters with long polymethylene chain in the polymer chain show lesser hydroxyl value as expected. The hydroxyl contents for PE11 and PE12 were to be 10.54 and 8.36 mmol/g whereas the theoretical values were 9.80 and 8.62 mmol/g, respectively.

3.3. Solubility in common solvents

The solubility of the polyesters at ambient temperature in common solvents were examined and are summarized in Table 4. Polyesters with lateral isopropylidene groups are highly soluble in non-polar solvents like chloroform and dichloromethane but insoluble in water and methanol. On the other hand, polyesters

with pendant polar hydroxyl groups were soluble in highly polar solvents such as methanol, water, N,N-dimethylformamide (DMF), or dimethysulfoxide (DMSO) and having very low solubility in non-polar solvents.

3.4. Thermal analysis

The thermal properties of the polymers before and after deprotection were examined by DSC and TGA analyses under nitrogen atmosphere. The results from these measurements are summarized in Tables 1 and 3. From DSC measurements (depicted in Figs. 7 and 8), it was found that the polyesters PE1-PE6 having lateral isopropylidene groups and polyesters PE7-PE12 having lateral hydroxyl groups show a glass transition temperature (T_g) in the range of −36.1 to −7.8 °C and −18.0 to 17.9 °C, respectively and did not show well-defined endotherms corresponding to melting transitions.

It is found that the T_g of the polyesters decreases, as expected, when the length of the polymethylene chain is increased in the polymer chain. This can be attributed to the increased segmental mobility with increasing chain length in the polymer. On the other hand, the T_g of polyesters PE7-PE12 with lateral hydroxyl groups have higher T_g as compared to polyesters PE1-PE6 with lateral isopropylidene groups. For example, the T_g of the polyester PE1 having lateral isopropylidene groups was observed at −9.2 °C and after the deprotection of isopropylidene groups, the T_g of the corresponding polyester PE7 with lateral hydroxyl groups was observed at 6.2 °C. The higher T_g might suggest the formation of extended hydrogen bonded network from the lateral hydroxyl functional groups [20,36]. The thermal stability of polyesters was determined by TGA and the derivative weight loss traces (dTGA) are depicted in Fig. 9. It was found that the polyesters PE1-PE6 with lateral isopropylidene groups are having higher thermal stability as compared to polyesters PE7-PE12 with lateral hydroxyl groups.

4. Conclusions

A series of aliphatic polyesters were synthesized starting from protected naturally occurring L-tartaric acid derivatives using bulk and solution polycondensation methods by systematically varying the chain length of either the diol or the diacid. The isopropylidene protecting groups in the polyesters were then selectively hydrolyzed to generate a series of aliphatic polyesters with pendant hydroxyl groups regularly distributed along the polymer backbone. The series of aliphatic polyesters with lateral isopropylidene groups were found to be soluble in less polar solvents and insoluble in water and methanol, whereas the series of aliphatic polyesters with lateral hydroxyl groups were found to be soluble in highly polar solvents like methanol and water and less soluble in non-polar solvents. From the thermal studies it is found that the polyesters with lateral hydroxyl groups show relatively less thermal stability as compared to polyesters with lateral isopropylidene groups. DSC measurements showed that the T_g of polyesters decreases as the length of the polymethylene chain is increased because segmental mobility increases in polymer chains with increasing polymethylene chain length. Furthermore, it was found that the T_g of polyesters with lateral hydroxyl groups have higher T_g as compared to polyesters with lateral isopropylidene groups. The presence of the hydroxyl groups along the polymer chain is expected to enhance the biodegradability and the hydrophilicity of the polymers.

Acknowledgement

S. D. acknowledges a research fellowship from the Council for Scientific and Industrial Research (CSIR), New Delhi, India.

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