Degradable Polyesters based on Oxygenated Fatty Acid Monomer

CHENG Zhengzai[1,2*], LI Yi[1], Lesly Dasilva Wandji Djouonkep[1,3], ZENG Sheng[1], WANG Huan[1], WANG Linfeng[1], CAI Shuanpu[1], LIU Panpan[1], HU Hai[1], YANG Yingao[1], LI Jiaqi[1], QIN Jisong[1], Mario Gauthier[1,4]

(1. Research Institute of Fine Organic Chemicals & Organic Materials at School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, China; 2. Coal Conversion and New Carbon Materials Hubei Key Laboratory, Wuhan University of Science and Technology, Wuhan 430081, China; 3. Department of Petroleum Engineering, Applied Chemistry in Oil and Gas Fields, Yangtze University, Wuhan 43010, China; 4. Department of Chemistry, University of Waterloo, 200 University Avenue West, Waterloo, Ontario N2L 3G1, Canada)

Abstract: A series of degradable polyesters was synthesized via melt polymerization of 3,6-dioxaoctane-1,8-dioic acid and five different diols, catalyzed by antimony trioxide (Sb_2O_3). The polymers were characterized by FT-IR and ^{1}H NMR spectroscopy, gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) analysis. The polydispersity index (PDI = M_w/M_n) of the polyesters ranged from 1.55 to 1.99, the weight-average molecular weight (M_w) from 1.8×10^4 to 3.2×10^4 Da, the melting point from 63 to 123 ℃, and the highest decomposition temperature observed was 363 ℃. The influence of the structure of the polymer chain on hydrolytic degradability was investigated with tests performed at three different values of pH. The findings obtained provide useful insight for the molecular design and the synthesis of degradable polyesters.

Key words: degradable polyesters; melt polymerization; thermal properties; aliphatic-aromatic polyester

1 Introduction

Aromatic polyesters such as poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET) are widely used in our daily lives, especially in food and beverage packaging, owing to their excellent mechanical and thermal properties[1-5]. Unfortunately, serious environmental problems arise from these polyesters, due to poor degradability when they are discarded in the environment. For example, PET degrades very slowly under natural conditions. One way to solve these problems is using degradable aliphatic polyester such as poly(butylene succinate) (PBS), poly(hydroxy fatty acid esters) (PHA), poly(caprolactone) (PCL), poly(lactic acid) (PLA), and their derivatives[6-11]. Based upon aliphatic diols and dicarboxylic acids as raw ma-

terials, these aliphatic polyesters are considered to be the most economically competitive degradable polymers. Interestingly, their use may delay the increase in atmospheric carbon dioxide content, even after their incineration. For instance, PBS decomposes chemically or biologically with weight losses reaching 30% in aqueous media over 25 weeks[12,13]. Shortcomings of PBS include low tensile strength and elongation at break, seriously impeding its widespread applications in the industry.
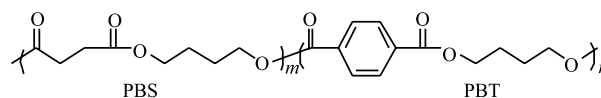

Fig.1 *m*-PBST copolyesters

Over the last few years, many studies concerned degradable polyesters with satisfying mechanical properties, which is synthesized from biobased aliphatic and aromatic monomers. Based on succinic acid and 2,5-furandicarboxylic acid (FDCA) as raw materials, degradable poly(butylene succinate-*co*-butylene furanoate) (PBSF) copolyesters synthesized by Jacquel *et al*[14,15] were thus shown to have elongation at break values of up to 1400%. PBSF containing 15% FDCA units displayed 90% biodegradability in less than 180 days,
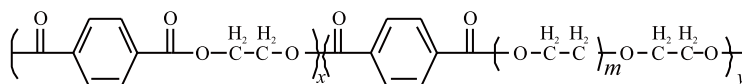
Fig.2　PEGET copolyesters

satisfying the European degradation standard EN13432. Another investigation by Yoshiharu and coworkers[16] addressed the synthesis of a multi-block *m*-PBST copolyesters (Fig.1) via melt/solid interfacial co-polycondensation of a melt-blend of PBS and PBT. This polyester had good mechanical and thermal properties. Moreover, it was found to undergo degradation by lipases under the enzymatic action of Pseudomonas cepacia.

Recently, we successfully synthesized thiophene-aromatic polyesters with high processing temperatures, high molecular weights, and mechanical properties comparable to commercial PET. These polyesters also displayed good biodegradability[17]. As shown above, polyesters with lower aromatic component contents display enhanced degradability, but their physical properties also degrade correspondingly. Taking into account both physical properties and degradability, the incorporation of polar bonds into the molecular chain of polyesters is considered an effective strategy to obtain novel degradable polyesters. Liu[18] thus synthesized the copolyester PEGET (Fig.2) via transesterification of PET and poly(ethylene glycol) (PEG). The results indicated that the incorporation of PEG into the polyester effectively improved the degradability of the copolymers, due to their increased aliphatic content. For instance, using succinic acid, 1,4-butanediol and PEG as raw materials the copolyester poly(butylene succinate-*co*-ethylene glycol succinate) PBSEG, containing many ether bonds within the main chain, was synthesized by Zhou[19]. The degradation of PBSEG reached 23% after only 8 days, which is much higher than the degradation of PBS.
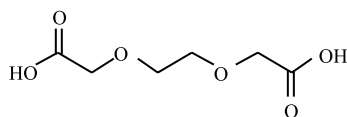

Fig.3　3,6-dioxaoctane-1,8-dioic acid

In an attempt to improve the degradability of polyesters while maintaining good physical properties, we synthesized polyesters containing additional ether bonds within the monomer, namely 3,6-dioxaoctane-1,8-dioic acid (Fig.3). Using Sb_2O_3 as catalyst, a series of degradable polyesters was synthesized by melt polymerization with a series of five different diols and 3,6-dioxaoctane-1,8-dioic acid. These polyesters were characterized by FT-IR, ^{1}H NMR, DSC, TG, and GPC. The thermal properties and degradability of these materials were strongly influenced by the structure of the main chain. The findings obtained provide useful insight for the molecular design and the synthesis of degradable polyesters.

2　Experimental

2.1　Materials and measurements

3,6-Dioxaoctane-1,8-dioic acid (99%) and Sb_2O_3 (97%) were supplied by Aladdin (Shanghai, China). 1,3-Bis(2-hydroxyethoxy)benzene (98%), 1,2-bis(2-hydroxyethoxy)benzene (98%), 1,8-octanediol (99%), 1,9-nonanediol (99%), 1,10-decanediol (99%), methanol (99%) and dichloromethane ($CDCl_3$) (97%) were purchased from the China National Pharmaceutical Group Corporation (Beijing, China).

FT-IR spectra were obtained using a Bruker VERTEX 70 spectrometer with KBr pellets in a range from 4 000 to 400 cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker Advance DMX600 (600 MHz) instrument, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Thermogravimetry (TG) was performed on a NETZSCH 301 F2 instrument at a heating rate of 10 ℃/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was carried out from 40 to 300 ℃ on a NETZSCH STA 449 F3 Jupiter analyzer under nitrogen, at a heating rate of 10 ℃/min, with about 5 mg samples. Gel permeation chromatography (GPC) was performed on a Waters-Breeze instrument with N,N-dimethylformamide (DMF) or tetrahydrofuran (THF) as solvents; the instrument was calibrated with monodisperse polystyrene standards.

2.2　Synthesis of polyesters

A mixture of 3,6-dioxaoctane-1,8-dioic acid, dihydric alcohol and Sb_2O_3 was added to a single-necked flask at a molar ratio of about 1:1:0.01, and the flask was purged with nitrogen using a Shlenk double-tube system. To begin, the reaction was stirred and rapidly heated to 150-180 ℃ at atmospheric pressure for 4 h. To complete the polycondensation reaction, the reaction was then heated to 210-240 ℃ for 3 h longer under vacuum (< 50 Pa). Heating was stopped when the mixture displayed the climbing-rod phenomenon, at which
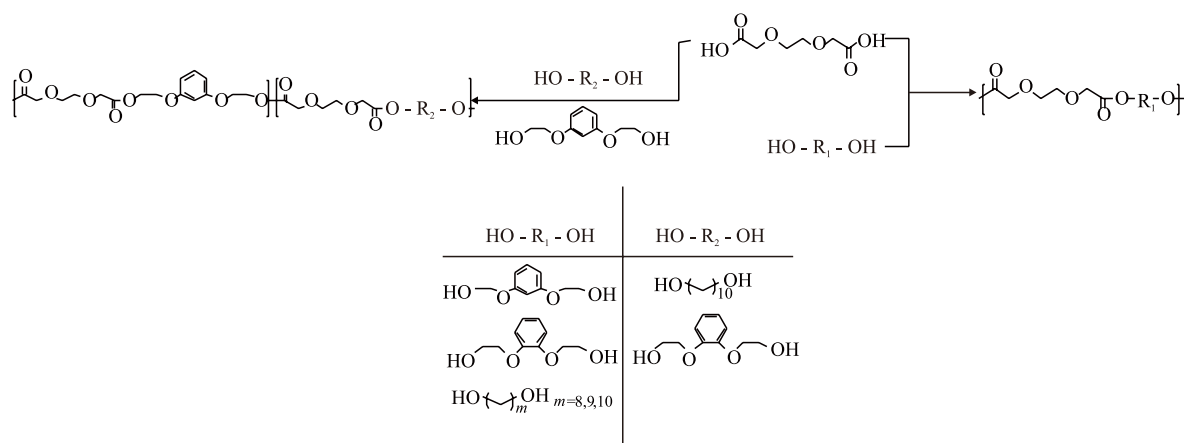
Fig.4 Synthesis of polyesters from different monomers

point the system was cooled to room temperature under nitrogen atmosphere to obtain the crude polyester. The product was dissolved in an appropriate amount of chloroform and isolated by precipitation in methanol. The purified polymer was obtained by drying at 50 ℃ for 6 h under vacuum. The synthetic route for the polyesters is outlined in Fig.4.

The amounts of each reagent used under the conditions described above, and basic characterization results for the polymers obtained are summarized below for each of the polyesters **a-g**, with structure shown in Fig.5.

Poly(3,6-dioxaoctane-1,8-dioic acid 1,8-octanediol) (**PDO**) (**a**) was synthesized from 3,6-dioxaoctane-1,8-dioic acid (15 mmol, 2.672 g) and 1,8-octanediol (15 mmol, 2.193 g). ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 4.12-4.15 (m, 8H, OOCC**H**$_2$OCH$_2$CH$_2$OC**H**$_2$CO-OC**H**$_2$(CH$_2$)$_6$C**H**$_2$O), 3.77 (s, 4H, OC**H**$_2$C**H**$_2$O), 1.62 (d, *J* = 13.5, 6.7 Hz, 4H, COOCH$_2$C**H**$_2$-(CH$_2$)$_4$C**H**$_2$CH$_2$OOC), 1.31 (s, 8H, COOCH$_2$CH$_2$(C**H**$_2$)$_4$CH$_2$CH$_2$OOC); IR (KBr) *v*: 2916, 2857, 1740, 1566, 1450, 1205, 1124, 971, 751, and 612 cm^{-1}.

Poly(3,6-dioxaoctane-1,8-dioic acid 1,9-nonanediol) (**PDN**) (**b**) was synthesized from 3,6-dioxaoctane-1,8-dioic acid (20 mmol, 3.562 g) and 1,9-nonanediol (20 mmol, 3.205 g). ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 4.23-4.06 (m, 8H, OOC-C**H**$_2$OCH$_2$CH$_2$OC**H**$_2$COOC**H**$_2$(CH$_2$)$_7$C**H**$_2$O), 3.78 (d, *J*=12.1 Hz, 4H, OC**H**$_2$C**H**$_2$O), 1.71-1.60 (m, 4H, COOCH$_2$C**H**$_2$-(CH$_2$)$_5$C**H**$_2$CH$_2$OOC), 1.30 (s, 10H, COOCH$_2$CH$_2$(C**H**$_2$)$_5$CH$_2$CH$_2$OOC). IR (KBr) *v*: 2928, 2846, 1718, 1357, 1240, 1159, 1043, and 775 cm^{-1}.

Poly(3,6-dioxaoctane-1,8-dioic acid 1,10-decanediol) (**PDD**) (**c**) was synthesized from 3,6-dioxaoctane-1,8-dioic acid (20 mmol, 3.562 g) and

1,10-decanediol (20 mmol, 3.486 g). ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 4.17-4.11 (m, 8H, OOC-C**H**$_2$OCH$_2$CH$_2$OC**H**$_2$CO-OC**H**$_2$(CH$_2$)$_8$C**H**$_2$O), 3.77 (s, 4H, OC**H**$_2$C**H**$_2$O), 1.67-1.59 (m, 4H, COOCH$_2$C**H**$_2$(CH$_2$)$_6$-C**H**$_2$CH$_2$OOC), 1.29 (d, *J* = 13.6 Hz, 12H, COOCH$_2$CH$_2$(C**H**$_2$)$_6$CH$_2$CH$_2$OOC). IR (KBr) *v*: 2939, 2857, 1741, 1589, 1217, 1135, 972, 844, 751, and 601 cm^{-1}.

Poly(3,6-dioxaoctane-1,8-dioic acid 1,3-bis(2-hydroxyethoxy)benzene) (**PDB$_1$**) (**d**) was synthesized from 3,6-dioxaoctane-1,8-dioic acid (22 mmol, 3.919 g) and 1,3-bis(2-hydroxyethoxy)benzene (20 mmol, 3.964 g). ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 7.17 (t, *J* = 8.1 Hz, 1H, ArH), 6.51 (d, *J* = 8.5 Hz, 2H, ArH), 6.46 (s, 1H, ArH), 4.48 (d, *J* = 4.0 Hz, 4H, OC**H**$_2$CH$_2$OArO-CH$_2$C**H**$_2$O), 4.20 (s, 4H, OCH$_2$C**H**$_2$OArOCH$_2$CH$_2$O), 4.15 (d, *J* = 4.6 Hz, 4H, OOCC**H**$_2$OCH$_2$CH$_2$OC**H**$_2$COO), 3.77 (s, 4H, OC**H**$_2$C**H**$_2$O). IR (KBr) *v*: 2921, 1717, 1594, 1240, 1136, 1053, 762, 679, and 606 cm^{-1}.

Poly(3,6-dioxaoctane-1,8-dioic acid 1,2-bis(2-hydroxyethoxy)benzene) (**PDB$_2$**) (**e**) was synthesized from 3,6-dioxaoctane-1,8-dioic acid (15 mmol, 2.672 g) and 1,2-bis(2-hydroxyethoxy)benzene (15 mmol, 2.973 g). ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 6.87 (s, 4H, ArH), 4.46-4.39 (m, 4H, OC**H**$_2$CH$_2$OArOCH$_2$C**H**$_2$O), 4.18-4.14 (m, 4H, OCH$_2$C**H**$_2$OArOC**H**$_2$CH$_2$O), 4.13 (s, 4H, OOCC**H**$_2$OCH$_2$CH$_2$OC**H**$_2$COO), 3.69 (d, *J* = 12.4 Hz, 4H, OC**H**$_2$C**H**$_2$O). IR (KBr) *v*: 2931, 2851, 1718, 1357, 1241, 1159, 1055, 961, and 786 cm^{-1}.

Poly(1,10-decanediol 3,6-dioxaoctane-1,8-dioic acid 1,2-bis(2-hydroxyethoxy)benzene) (**PDDB**) (**f**) was synthesized from 1,10-decanediol (10 mmol, 1.982 g), 3,6-dioxaoctane-1,8-dioic acid (20 mmol, 3.562 g) and 1,2-bis(2-hydroxyethoxy)benzene (10 mmol, 1.982 g). ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 7.17 (d, *J* =
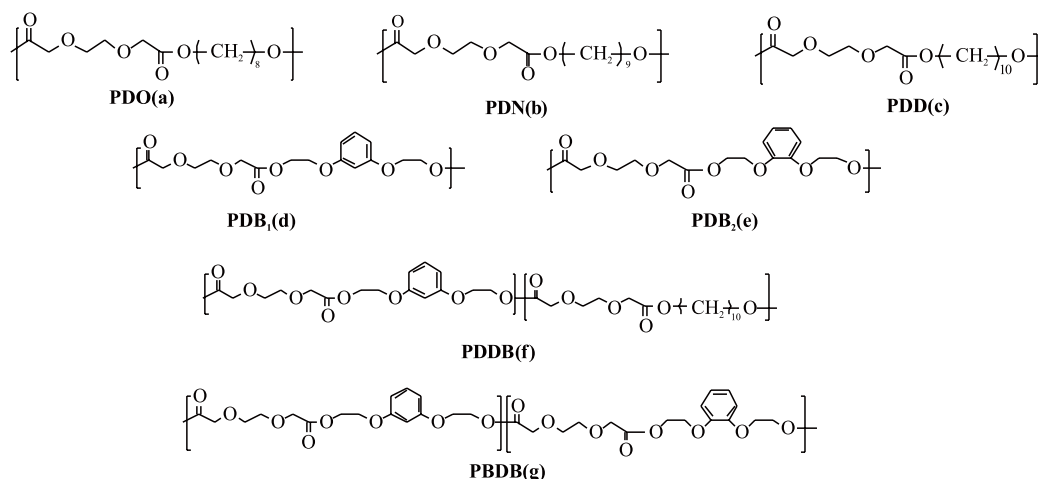
Fig.5 Structure of polyesters **a-g**

6.9 Hz, 1H, ArH), 6.51 (d, J = 8.0 Hz, 2H, ArH), 6.46 (s, 1H, ArH), 4.49 (s, 4H, OC$\underline{H}_2$CH$_2$OArOCH$_2$C$\underline{H}_2$O), 4.21-4.15 (m, 16H, OC$\underline{H}_2$OOCCH$_2$C$\underline{H}_2$OArOC$\underline{H}_2$CH$_2$OOC$\underline{H}_2$O), 3.77 (s, 8H, OC$\underline{H}_2$C$\underline{H}_2$O), 1.63 (s, 4H, COOCH$_2$C$\underline{H}_2$(CH$_2$)$_6$C$\underline{H}_2$CH$_2$OOC), 1.29 (d, J = 11.0 Hz, 12H, COOCH$_2$CH$_2$(C$\underline{H}_2$)$_6$CH$_2$ -CH$_2$OOC). IR (KBr) v: 2940, 1740, 1589, 1485, 1321, 1148, 763, and 670 cm^{-1}.

Poly(1,2-bis(2-hydroxyethoxy)benzene 3,6-dioxaoctane-1,8-dioic acid 1,3-bis(2-hydroxyethoxy)benzene) (**PBDB**) **(g)** was synthesized from 1,2-bis(2-hydroxyethoxy)benzene (5 mmol, 0.991 g), 3,6-dioxaoctane-1,8-dioic acid (10 mmol, 1.781 g) and 1,3-bis(2-hydroxyethoxy)benzene (5 mmol, 0.991 g). ^{1}H NMR (600 MHz, CDCl$_3$), δ (ppm): 7.16 (t, J = 8.2 Hz, 1H, ArH), 6.92 (d, J = 2.2 Hz, 4H, ArH), 6.50 (d, J = 8.2, 1.8 Hz, 2H, ArH), 6.45 (s, 1H, ArH), 4.48 (s, 8H, OC$\underline{H}_2$CH$_2$OArOCH$_2$C$\underline{H}_2$O), 4.20 (d, J = 7.9 Hz, 8H, OCH$_2$C$\underline{H}_2$OArOC$\underline{H}_2$CH$_2$O), 4.16 (d, J = 17.1 Hz, 8H, OOCC$\underline{H}_2$OCH$_2$CH$_2$OC$\underline{H}_2$COO), 3.78-3.73 (m, 8H, CH$_2$OC$\underline{H}_2$C$\underline{H}_2$OCH$_2$). IR (KBr) v: 2 928, 1 740, 1 659, 1 589, 1 484, 1 321, 1 170, 786, and 670 cm^{-1}.

2.3 Hydrolytic degradation tests of polyesters

Distilled water (50 mL) was added to a series of 15 glass ampoules. The pH was adjusted to either 5, 7 or 9 with NaOH and HCl using a pH meter. Polyester (**a-e**) balls with a diameter of about 3 mm and an initial mass m_0 were added to the ampoules at the different pH values, which were sealed and placed in a biological shaker at 20 ℃. The samples were taken out carefully every 15 days, mildly rinsed with distilled water (to stop the reaction and avoid large mass losses), dried at 50 ℃ until constant mass, and then weighed (m_1). The mass loss was calculated as: mass loss% = ($m_1 - m_0$) / $m_0 \times 100\%$.

3 Results and discussion

3.1 GPC, DSC, and TG analysis of polyesters a-g

Table 1 GPC, DSC, and TG characterization results for polymers a-g

Entry	Yield/%	M_w/Da[a]	M_n/Da[a]	PDI/%[a]	T_m/℃[b]	$T_{5\%}$/℃[c]
1	87	19900	12800	1.55	77	349
2	86	31900	19700	1.62	71	357
3	90	20900	11100	1.88	63	336
4	89	19800	11100	1.78	123	363
5	84	18600	10300	1.81	86	331
6	81	21200	10600	1.99	82	320
7	83	22100	11600	1.90	90	326

[a] GPC in THF or DMF at 40℃; [b] Determined by DSC analysis; [c] Temperature at which a 5% mass loss was observed under nitrogen

The yield, molecular weight, and thermal analysis data for the polyesters are summarized in Table 1. This includes the yield of the reactions, the number-average molecular weight (M_n), the weight-average molecular weight (M_w), the PDI, the melting temperature (T_m) and the temperature of 5% mass loss ($T_{5\%}$) of polyesters **a-g**. The seven polyesters were obtained in high yield (81%-90%), with appreciable molecular-weights. M_n, M_w, and PDI values for polyesters **a-g** were found to vary from 10600-19700 Da, 19800-31900 Da, and 1.55-1.99, respectively, depending on the composition. T_m and $T_{5\%}$ values for the polyesters ranged from 63-123 ℃ and 320-363 ℃, respectively. Recently, poly(terephthalic acid 2,5-furandicarboxylic acid-1,8-octanediol) copolyesters derived from the same diol monomer (1,8-octanediol) were reported to display decomposition temperatures in the 332-356 ℃ range, with maximum

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decomposition rates at 390-410 ℃[20].

3.2 Structure analysis of polyesters

The molecular structure of the polyesters was investigated by ^{1}H NMR spectroscopy and FT-IR analysis. The infrared spectrum obtained for **PDB$_1$ (d)** is provided in Fig.6 as an example. The peaks around 2 921 cm^{-1} belong to the C-H stretching vibrations of alkanes, and the absorption peak at 1 717 cm^{-1} is attributed to C=O stretching vibrations. In addition, the absorption peaks at 1 240 and 1 136 cm^{-1} belong to sp^2 C-O and sp^3 C-O stretching vibrations, respectively. The absorption peaks in the 600-900 cm^{-1} region are mainly attributed to the C-H bending of aromatic rings. It can be noticed that O-H vibrations (3 200-3 650 cm^{-1}, depending on the extent of hydrogen bonding) are absent, while a sp^2 C-O vibration absorption peak is present. Based upon the information obtained from the infrared spectrum and from ^{1}H NMR analysis (*vide infra*), it can be concluded that the polyester was successfully synthesized. Similar FT-IR analysis results were obtained for the other polyesters.
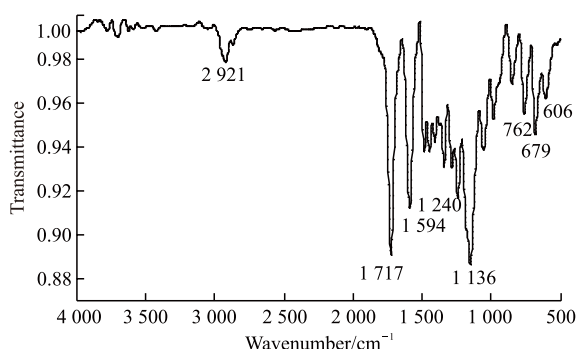

Fig.6 FT-IR spectrum for **PDB$_1$ (d)**
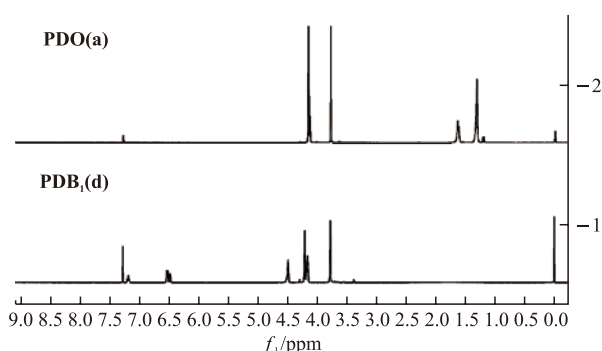

Fig.7 ^{1}H NMR spectra for **PDO (a)** and **PDB$_1$ (d)**

The ^{1}H NMR spectra obtained for aliphatic-aromatic polyester PDB$_1$ (**d**) are shown in Fig.7. Signals corresponding to OC**H**$_2$CH$_2$OArOCH$_2$C**H**$_2$O, OCH$_2$C**H**$_2$OArOC**H**$_2$CH$_2$O, OOCC**H**$_2$OCH$_2$ -CH$_2$OC**H**$_2$COO and OC**H**$_2$C**H**$_2$O were observed at δ 4.48, 4.20, 4.15, and 3.77 ppm, respectively, while the peaks centered at δ 7.17, 6.46, and 6.51 ppm were assigned to the pro-

tons on the benzene rings. Furthermore, no absorptions corresponding to COO**H** and O**H** on the monomers occurred in the ^{1}H NMR spectrum of **PDB$_1$ (d)**, which confirms that the product obtained is a polyester rather than a mixture of monomers. The ratio of integrations for the peaks at δ 6.51-7.17 and 3.77-4.48 ppm was 1 : 4, which matches the structure of the expected product. The structure of **PDB$_2$ (e)** was confirmed by similar analysis.

The ^{1}H NMR spectrum for aliphatic polyester **PDO (a)** is also shown in Fig.7 for comparison. Signals corresponding to OOCC**H**$_2$OCH$_2$CH$_2$OC**H**$_2$ COOC**H**$_2$(CH$_2$)$_6$C**H**$_2$O and OC**H**$_2$C**H**$_2$O were observed at δ 4.12-4.15 and 3.77 ppm, respectively, while the peaks centered at δ 1.31 and 1.62 ppm were assigned to COOCH$_2$C**H**$_2$(CH$_2$)$_4$C**H**$_2$CH$_2$OOC and COOCH$_2$ CH$_2$(C**H**$_2$)$_4$CH$_2$CH$_2$OOC. Again, no signals corresponding to COO**H** and O**H** in the monomers occurred in the spectrum of **PDO (a)**, which confirms that the product obtained is a polyester. The ratio of integrations for the peaks at δ 3.77-4.15 and 1.31-1.62 ppm is 1 : 1, which matches the molecular structure of the expected product. The structure of **PDN (b)** and **PDD (c)** was confirmed by similar analysis, while the structure of **PBDB (g)** and **PDDB (f)** was confirmed by comparison with **PDO (a)** and **PDB$_1$ (d)**.

3.3 Thermal properties

The thermal properties of polyesters (**a-g**) were characterized by DSC and TG analyses. The data presented in Table 1 shows that the melting point of the aliphatic polyesters (**a-c**) shifted to lower temperatures, from 77 to 63 ℃, as the number of methylene units in the diol spacer increased. The melting point of the aliphatic-aromatic polyesters (**d** and **e**) was 123 and 86 ℃, respectively, higher than for the aliphatic polyesters (**a-c**). Moreover, the melting point of PDDB (**f**) was lower than for PBDB (**g**), with a higher aromatic component content.

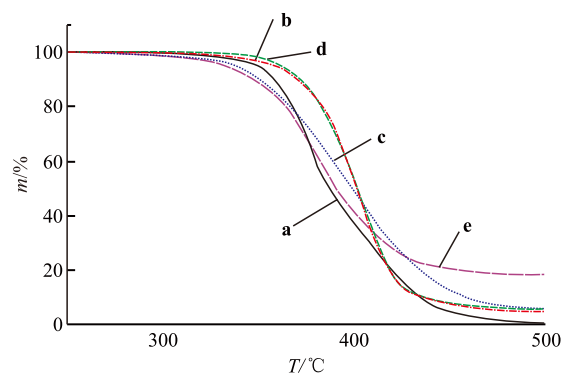Fig.8. TG curves for polyesters **a-e**

As can be seen in Fig.8-9, and summarized in Table 1, the initial decomposition temperature of polyesters (**a-g**) varied from 320 to 363 ℃, which demonstrates that these polyesters have good thermal stability. Comparing the TG curves obtained for **PBDB (g)** and **PDDB (f)** in Fig.9, it can be seen that both polyesters have similar decomposition behaviors, but the residual mass for **PBDB (f)** is greater than for **PDDB (g)**. The reason for this is that the structure of **PDDB (g)** contains more ether bonds, which leads to a lower thermal stability as compared with a backbone containing more C-C bonds.
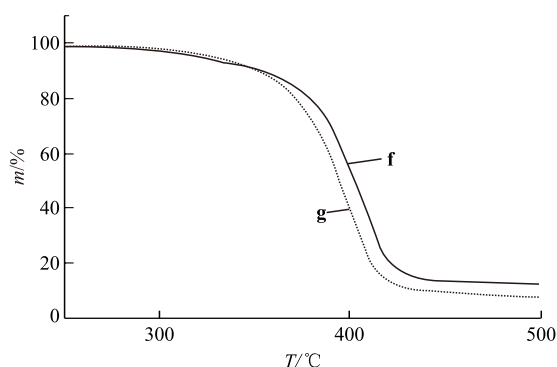

Fig.9　TG curves for polyesters **f** and **g**

3.4 Degradation behavior

To study the degradation of the polyesters, hydrolysis tests were conducted at 20 ℃ in distilled water at different pH values ranging from 5-9. The hydrolysis of polyesters is affected by many factors such as the environmental conditions and the structure of the polyester. As can be seen in Figs.10-12, all the polyesters **a-g** can be degraded. The extent of degradation ranged from 23%-38% at pH 5, 19%-33% at pH 7, and 27%-47% at pH 9 after five months. The degradation rate of the polyesters was therefore faster under alkaline conditions as compared with acidic and neutral environments, as expected for the hydrolysis of esters. The extent of degradation of aliphatic polyesters **a-c** reached 41%, 44%, and 47% at pH 9, respectively, which shows that the degradability of the polyesters improved with the number of methylene units in the aliphatic diol spacer. Additionally, the degradation rate of the aliphatic polyesters (**a-c**) was higher than for the aliphatic-aromatic polyesters (**d** and **e**), containing rigid ring structures. In contrast with PBT and PET, both considered to have low biodegradability, the degradation rate of **PDB$_2$ (e)** reached 19% in water at pH 7 after 5 months of incubation, in spite of containing benzene ring structures, which indicates that polyesters containing more ether (C-O-C) bonds display better degradability.

Similarly, C-S-C bonds in thiophene-containing polyesters were shown make these compounds sensitive to hydrolysis by relatively abundant sulfur-loving bacteria and other microorganisms in the soil, allowing them to decompose in the environment after their life cycle is completed[17].
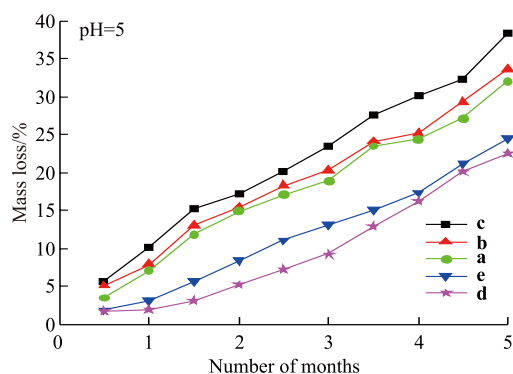

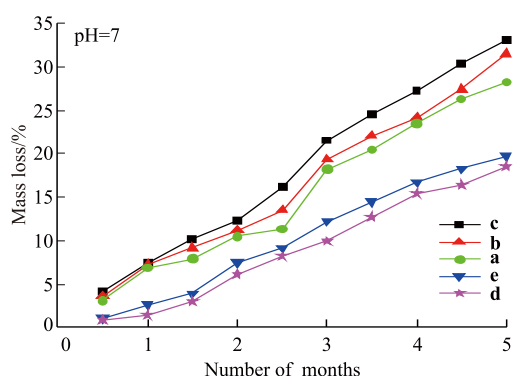Fig.10　Degradation of polyesters in water at pH 5

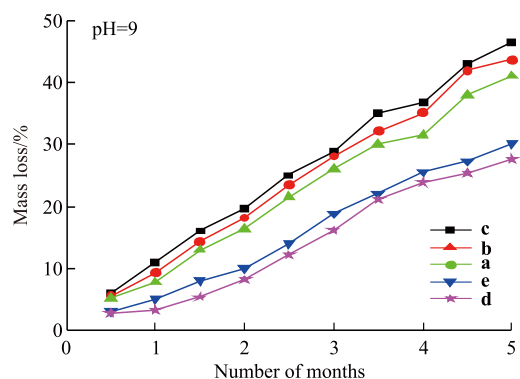Fig.11　Degradation of polyesters in water at pH 7

Fig.12　Degradation of polyesters in water at pH 9

Plastics, while enhancing the quality of human life, represent a serious ecological threat for the planet via "white pollution" due to their long life span. This is mainly because the stable, long-chain hydrocarbon molecules present in traditional plastics degrade very slowly in nature, due to difficult photolytic, thermal or bacterial decomposition of these crystalline materials. In the absence of an immediate, concerted and vigorous

intervention, it is estimated that by 2040, the amount of plastic waste entering the aquatic and terrestrial ecosystems will reach 23-37 million tons each year. Among these, polyesters accounts for about 10% of the global plastics market. One of the solutions put forward by the scientific community to tackle this problem is to develop degradable and environmentally friendly "greener" polymeric materials. From an environmental protection viewpoint, such materials should exhibit rapid degradation (chemical or biological), releasing non-toxic products into the environment, thereby contributing to environmental protection and sustainable development. The development of greener synthetic routes, and the application of biodegradable polymeric materials of the type reported in the current investigation can greatly reduce pollution caused by the existing non-degradable polyesters. The development of degradable polymeric materials with energy savings and reduced emissions will thus contribute to the development of a low-carbon economy.

4   Conclusions

A series of degradable polyesters was synthesized via melt polymerization of 3,6-dioxaoctane-1,8-dioic acid with five aliphatic and aromatic diols, catalyzed by Sb_2O_3. The PDI of the polyesters ranged from 1.55 to 1.99, and the M_W from 1.1×10^4 to 3.2×10^4 Da. The melting point of the materials varied from 63 to 123 ℃, being lower for the aliphatic polyesters than for the aliphatic-aromatic polyesters containing rigid ring structures. Among the aliphatic sample series, the melting point of the polyesters decreased as the number of methylene units in the diol spacer increased. The highest decomposition temperature observed reached 363 ℃

The influence of variations in pH under controlled conditions, and the relation between chain structure and degradability were also investigated. The degradation test results indicate that alkaline environments are more conducive to the hydrolysis of polyesters than acidic and neutral environments. The degradability of the aliphatic polyesters increased with the number of methylene units in the diol spacers. In addition, it was concluded that the degradability of aliphatic polyesters is higher than that of aliphatic-aromatic polyesters containing rigid ring structures. As compared with PBT and PET, the degradability of the polyesters synthesized in the current investigation was still much higher, reaching 19% at pH 7 after 5 months even for the aromatic aliphatic-aromatic polyester **PDB₂**, due to the presence of ether bonds within the polymer backbone. This demonstrates that ether bonds in polyesters induce better degradability, which provides useful insight for the molecular design and the synthesis of degradable polyesters.

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