

SYNTHESIS AND CHARACTERIZATION OF BIODEGRADABLE POLYESTERAMIDES CONSTRUCTED MAINLY BY ALTERNATING DIESTERDIAMIDE UNITS FROM *N,N'*-BIS(2-HYDROXYETHYL)-ADIPAMIDE AND DIACIDS*

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Abstract Two kinds of aliphatic alternating polyesteramide prepolymers were prepared through melt polycondensation from *N,N'*-bis(2-hydroxyethyl)-adipamide and adipic acid or sebacic acid. Chain extension of them was conducted with 2,2'-(1,4-phenylene)-bis(2-oxazoline) and adipoyl biscaprolactamate as combined chain extenders. The chain extended polyesteramides (ExtPEAs) were characterized by IR, ¹H-NMR, differential scanning calorimetry, thermogravimetric analysis, wide angle X-ray scattering, tensile test and enzymatic degradation. The results showed that the ExtPEA(4,*m*)s were mainly constituted with the diester adipamide alternating units. ExtPEA(4,4) and ExtPEA(4,8) had *T_m* of 83.8°C and 85.8°C and initial decomposition temperature above 310.0°C. They crystallized similarly as Nylon-66 did and were flexible thermoplastic materials with tensile strength up to 25.64 MPa and strain at break up to 737%.

Keywords: Alternating polyesteramides; Polycondensation; Chain extension; Diamidediol; Properties.

INTRODUCTION

With the increasing concern for white pollution, more and more researchers have focused their attention on the synthesis, properties and biodegradation of the biodegradable polymers^[1, 2]. At present, aliphatic polyesters such as poly(butylene succinate) (PBS), poly(l(3-hydroxybutyrate)-*co*-3-hydroxyvalerate) (PHBV) and polylactic acid (PLA), are the most important kinds of the synthetic biodegradable polymers and are gradually used as domestic plastics^[3]. Meanwhile, aliphatic polyesteramides are also an important kind of biodegradable polymeric materials. They are constituted with many ester groups and amide groups. The ester groups in the main chains ensure them susceptible to enzymes and microbes. The amide groups increase the intermolecular force and benefit the improvement of their thermal and mechanical properties. Polyesteramides become a promising kind of biodegradable polymers because they have good processing and end-use properties. Polyesteramides are usually classified into three kinds: random, alternating and segmented or block polyesteramides. The random and block polyesteramides are commonly synthesized through ring-opening polymerization and polycondensation directly from simple commercial monomers. Roda and Deshayes synthesized random or block polyesteramides from ring-opening copolymerization of ϵ -caprolactam with ϵ -caprolactone or its polymer^[4–6]. Bayer Company^[7, 8] patented random polyesteramides synthesized from adipic acid, butanediol and hexanediamine or

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caprolactam, and commercialized them in the BAK series. Diamidediols were also used as starting materials to synthesize aliphatic polyesteramides. Dijkstra^[9–11] synthesized random polyesteramides from dimethyl adipate, butanediol and diamidediols which were prepared through the reaction of butanediamine or ethanediamine with caprolactone.

Alternating polyesteramides usually show intermediate properties between polyesters and polyamides. Serrano *et al.*^[12–14] synthesized a series of semiaromatic alternating polyesteramides through melt and solid polycondensation from 1,4-butylene terephthalamide dimethyl with glycols. Luston *et al.*^[15] synthesized some semiaromatic alternating polyesteramides through polyaddition from aromatic bis(2-oxazoline)s with aliphatic dicarboxylic acids. Up to now, aliphatic alternating polyesteramides are still seldom reported in the literatures. Shalaby *et al.*^[16] had synthesized the random and alternating aliphatic polyesteramides from the reaction of diamidediols with dicarboxylic acid diesters at the presence or absence of 1,6-hexanediol. The diamidediols they used were *N,N'*-bis(ω -hydroxyalkylene)-oxamides, which were prepared by reacting diethyl oxalate with amino-alcohols such as 3-amino-1-propanol, 5-amino-1-pentanol and 6-amino-1-hexanol. Alternating polyesteramides with high molecular weight were difficult to be prepared. To increase the molecular weight, some 1,6-hexanediol needed to be added. But the alternating structure of the polyesteramides was destroyed.

In the literatures, polyesteramides having diesterdiamide units were commonly prepared through transesterification from dicarboxylic acid diesters with diamidediols and glycol in high vacuum system. Dicarboxylic acids were seldom used directly to react with diamidediols in their synthesis, maybe because high extent of the side reaction might be caused by the dicarboxylic acids. However, dicarboxylic acids had obviously higher reactivity than their diesters. In this article, we studied the polycondensation of a diamidediol directly with the dicarboxylic acids, and synthesized two kinds of biodegradable polyesteramides constructed mainly by alternating diesterdiamide units. The diamidediol, *N,N'*-bis(2-hydroxyethyl)-adipamide (HEHA), synthesized from the reaction of diethyl adipate with 2-aminoalcohol was used as starting material. Two alternating polyesteramide prepolymers (PrePEAs) with both HO— and HOOC— terminal groups were synthesized by reacting HEHA with adipic acid (AA) or sebacic acid (SA) at moderate reaction conditions. The PrePEAs were chain-extended with 2,2'-(1,4-phenylene)-bis(2-oxazoline) (PBOX) and adipoyl biscaprolactamate (ABC) as combined chain extenders to increase the molecular weight. The chain extended polyesteramides (ExtPEAs) were characterized by IR and ¹H-NMR spectra, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide angle X-ray scattering (WAXS), tensile test and enzymatic degradation.

EXPERIMENTAL

Materials

Adipic acid was purchased from Beijing Chemical Factory, China. Sebacic acid was purchased from Tianjin Fuchen Chemical Reagent Plant, China. AA and SA were purified by crystallization in de-ionized water before use. SnCl₂·2H₂O was purchased from Beijing Shuanghuan Weiyi Reagent Co. Ltd. Lipase (from porcine pancreas) was purchased from Tokyo Chemical Industry Co. Ltd. Other materials such as ether, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were all obtained as reagent grade and used directly. HEHA (m.p.: 136°C) was prepared through condensation of diethyl adipate with ethanolamine, purified by crystallization in absolute methanol^[17]. The chain extender PBOX (m.p.: 249°C) was prepared according to the procedure described by Néry^[18]. ABC (m.p.: 73°C) was prepared according to the procedure by Wilfong^[19].

Synthesis of PrePEAs

In a 250 mL 3-necked flask equipped with mechanical stirrer, the polycondensation of HEHA with AA or SA was carried out at 160°C under N₂ atmosphere for 3 h with SnCl₂·2H₂O as a catalyst. Water was removed by distillation from the reaction mixture. Afterwards, the temperature was increased by about 10 K and the vacuum in the reaction system was slowly decreased to 666.5 Pa over a period of 2 h and kept 2 h. PrePEAs with different acid values (*A_v*) and hydroxyl numbers (*Q_v*) were obtained.

Chain Extension of the PrePEAs

In a 100 mL 3-necked flask equipped with mechanical stirrer, 6.0 g PrePEAs was stirred and heated under N₂ to 200°C. Chain extenders PBOX and ABC were added at molar ratios of (1/2)PBOX/—COOH = 1.0 and (1/2)ABC/—OH = 1.0, and the reaction mixture was homogeneously mixed. The chain extension was conducted at normal pressure for 1 h and at reduced pressure of 666.5 Pa for 3 h. The chain extended polyesteramides were poured out and cooled at room temperature.

Characterization

The acid value and the hydroxyl number of PrePEAs were detected according to the procedure described in the literature^[20]. 1.0 g PrePEA was dissolved in 15 mL DMF and titrated with 0.05 mol/L NaOH ethanol solution to detect the acid values. As the PrePEAs and the ExtPEAs were insoluble in THF, their intrinsic viscosity was determined at 30°C with a Ubbelohde viscometer using 1:1 (V/V) DMF/DMSO as mixture solvents.

The polyesteramide prepolymers and the chain extended polyesteramides used for the IR and NMR detections were purified three times through dissolving-precipitation cycles using 20 mL DMSO as solvent and 200 mL ether as nonsolvent. FTIR spectra were recorded on a NICOLET 60SXB FTIR spectrometer. The ¹H-NMR spectra were recorded on a Bruker AC-600 spectrometer using DMSO-d₆ as the solvent and tetramethylsilane as the labeling compound.

The DSC analyses of the polymers were performed on a Q200 V24.2 Build 107 DSC analyzer under nitrogen atmosphere by heating the samples from −100°C to 250°C at a heating rate of 10 K/min. The thermogravimetric analysis (TGA) was carried out by employing a TA TGAQ50 analyzer in the temperature range of 20–500°C at a heating rate of 10 K/min under nitrogen atmosphere. The wide angle X-ray scattering measurements of the polymer samples were detected using a Bruker D8 Advance diffractometer with Cu Kα radiation. The samples were continuously scanned over the 2θ range from 5° to 50°.

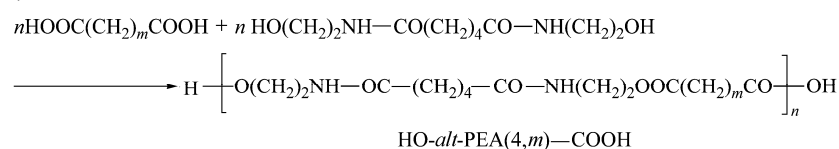
The sample plates (50 mm × 50 mm × 1 mm) were hot pressed with a 70911-24B powder press machine (Tianjin New Technical Instrument Co.). The polymer samples were heated at 120°C for 5 min under 15 MPa and cooled to room temperature under same pressure, and then cut into dumbbell-shaped bars (50 mm × 4 mm × 1 mm). Mechanical properties were determined on an Instron 1185 tensile testing machine with crosshead speed at 50 mm/min. Five measurements were performed for each sample, and the results were averaged to obtain a mean value.

The enzymatic degradation was conducted at 37°C using lipase from porcine pancreas. Flat-bottomed flasks containing a 10 mm × 10 mm × 0.1 mm film, 10 mL sodium phosphate buffer with pH 7.4 and 1 mg lipase were placed on a mechanical shaker with a speed of 100 r/min. After every 12 h, the ExtPEA films were taken out, washed three times with distilled water and dried overnight at 50°C. Enzyme and buffer solution were renewed for further degradation. All the dried ExtPEA films were weighed to determine the degradation rate.

RESULTS AND DISCUSSION

Chain Extension of the PrePEA(4,*m*)s

Two kinds of alternating aliphatic polyesteramides were synthesized by a melt polycondensation and a chain extending reaction with PBOX and ABC as combined chain extenders. The alternating polyesteramide prepolymers PrePEA(4,*m*)s with both HO— and HOOC— terminal groups were prepared through polycondensation of *N,N'*-bis(2-hydroxyethyl)-adipamide with adipic acid or sebacic acid. The synthesis reaction of the PrePEA(4,*m*)s was described in Scheme 1.



Scheme 1 The synthesis reaction of the PrePEA(4,*m*)s

Table 1 shows the properties of the PrePEA(4,*m*)s and their chain extension. PrePEA(4,*m*)s were synthesized at AA/HEHA or SA/HEHA molar ratios of 1.2 or 1.3. Higher AA/HEHA or SA/HEHA molar ratios, more than 1.0, made the PrePEA(4,*m*)s mainly terminated with the HOOC— terminal groups, and the HO— terminal groups were in less amount. The A_v of the PrePEA(4,*m*)s was in the range of 62.2–71.4 mgKOH/g, and the hydroxyl number was in the range of 0.0–3.5 mgKOH/g. The molecular weight calculated from the A_v and Q_v values was also shown in Table 1. SnCl₂ was used as a catalyst. But higher amount of SnCl₂, more than 0.10 wt%, often resulted in amorphous PrePEA(4,*m*)s which hardly crystallized when they were cooled. Reaction temperature and reaction time were other important influencing factors to synthesize crystallizable PrePEA(4,*m*)s. If the reaction temperature was above 180°C and the reaction time was too long, amorphous PrePEA(4,*m*)s were often obtained. The reason might be that during the polycondensation of AA or SA with HEHA, the HOOC— reacting groups had acid characteristics. They had higher reactivity than the ester groups in the starting materials like the dicarboxylic acid diesters, and benefited the condensation with the HO— groups in the HEHA. But it was likely that the HOOC— groups also catalyzed the ester-amide interchanging side reaction, and led to the amorphous PrePEA(4,*m*)s. So, lower reaction temperature and shorter reaction time were adopted to reduce the ester-amide interchanging reaction and to obtain the crystallizable PrePEA(4,*m*)s. As the crystallizable PrePEA(4,*m*)s were insoluble in THF, their intrinsic viscosity was determined at 30°C with a Ubbelohde viscometer using 1:1 (V/V) DMF/DMSO as mixture solvents. Their intrinsic viscosity was in the range of 0.095–0.22 dL/g.

Table 1. Chain extension of PrePEA(4,*m*)s with different A_v/Q_v values

PrePEA(4, <i>m</i>)	PrePEA(4, <i>m</i>) ^a					ExtPEA(4, <i>m</i>) ^b		
	AA (or SA):HEHA (molar ratio)	SnCl ₂ (%)	A_v/Q_v (mgKOH/g)	M^c	M^d	$[\eta]$ (dL/g)	SnCl ₂ (wt%)	$[\eta]$ (dL/g)
PrePEA(4,4)-1	1.2	0.10	66.41/3.47	1605	2408	0.12	0.3	Cross-linked
							—	0.51
PrePEA(4,4)-2	1.2	0.0	62.17/0	1804	4533	0.22	0.1	0.59
							—	0.31
PrePEA(4,8)	1.3	0.05	71.38/0	1571	3252	0.095	0.1	0.44
							0.05	0.48

^a The synthesis conditions for PrePEA(4,4)-1 and PrePEA(4,8) were as follows: 160°C, 1.01×10^5 Pa, 3 h; 170°C, 666.5 Pa (gradually reduced), 2 h; 170°C, 666.5 Pa 2 h. The synthesis conditions for PrePEA(4,4)-2 were the same as those for PrePEA(4,4)-1 and PrePEA(4,8) except the final vacuum was 226.6 Pa;

^b The chain extension conditions were as follows: (1/2)PBOX/—COOH = 1.0 (molar ratio), (1/2)ABC/—OH = 1.0 (molar ratio); Reaction temperature: 200°C; Reaction time: 1.01×10^5 Pa, 1 h; 666.5 Pa, 3 h;

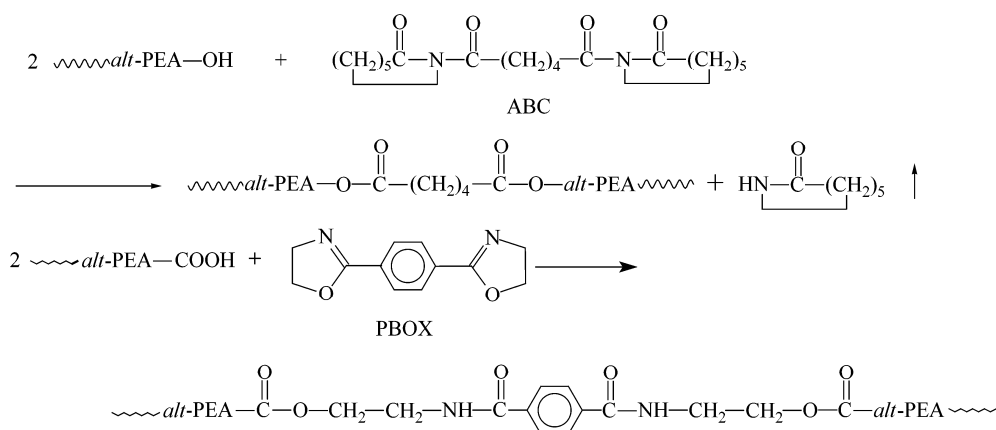
^c The molecular weight calculated from the A_v and Q_v ;

^d The molecular weight detected by ¹H-NMR spectra

PBOX and ABC were effective chain extenders in the chain extension of the HOOC— or HO— terminated polymers such as polyesters and polyamides to increase the molecular weight at short time^[18, 21–24]. PBOX and ABC were also used as combined chain extenders effectively in the chain extension of the aliphatic polyesters and random polyesteramides having both the HOOC— and the HO— terminal groups^[25, 26]. For the PrePEA(4,*m*)s terminated by both HO— and HOOC— groups, PBOX and ABC were chosen as combined chain extenders. As for the PrePEA(4,*m*)s terminated only by the HOOC— groups, just PBOX was used as chain extender. The chain extension was shown as Scheme 2.

Table 1 shows the chain extension of the PrePEA(4,*m*)s with PBOX and ABC as combined chain extenders. From Table 1, it was found that SnCl₂ also acted as a catalyst in the chain extension. The total amount of SnCl₂ including that used in the preparation of the PrePEA(4,*m*)s and that added in the chain extension up to 0.1 wt% showed the best chain extension efficiency. ExtPEA(4,4) with $[\eta]$ up to 0.59 dL/g and ExtPEA(4,8) with $[\eta]$ up to 0.48 dL/g were prepared. Higher amount of SnCl₂, more than 0.15 wt%, resulted in a little portion of cross-

linked polymers, and the $[\eta]$ decreased slightly. When the total amount of SnCl_2 up to 0.40 wt% was used, complete cross-linking happened. PrePEA(4,*m*)s were mainly terminated by $\text{HOOC}-$ groups. SnCl_2 catalyzed the reaction between the $\text{HOOC}-$ groups of the PrePEA(4,*m*)s and the oxazoline groups in PBOX, and promoted the chain extension. But high amount of SnCl_2 plus the $\text{HOOC}-$ groups of the PrePEA(4,*m*)s might also catalyze the cationic polymerization of the terminal oxazoline groups, because monomers having oxazoline groups can be initiated by cationic initiators and polymerize through cationic mechanism^[27]. Chain extension at 200°C for 4 h did not influence the crystallization of the ExtPEA(4,*m*)s obviously. Crystallizable ExtPEA(4,*m*)s were obtained at the chain extension conditions above mentioned.



Scheme 2 The chain extension of the PrePEA(4,*m*)s with PBOX and ABC

¹H-NMR and FT-IR Characterization of the PrePEA(4,4) and ExtPEA(4,4)

The structure of the PrePEA(4,*m*)s and the chain extended polyesteramides was characterized by FT-IR and ¹H-NMR spectra. Figure 1 shows the ¹H-NMR spectrum of PrePEA(4,4)-2. In Fig. 1, the peaks at $\delta = 4.01$, 3.28, 2.06 and 1.47 corresponded to 1-, 2-, 4- and 5-CH₂ hydrogens in the alternating adipamide adipate units (I). The peak at $\delta = 7.93$ corresponded to the 3-NH hydrogens in the same alternating adipamide adipate units (I). Peaks at $\delta = 2.30$ and 1.52 corresponded to the 6- and 7-CH₂ hydrogens in the adipate linkages. These peaks verified the major alternating and crystallizable poly(adipamide adipate) structure. And, a broad and very weak peak was shown at $\delta = 12.00$, which corresponded to 8 hydrogens in the terminal $\text{HOOC}-$ groups of the PrePEA(4,4)-2. Meanwhile, some ester-amide interchanging side reaction was observed in Fig. 1. The peak at $\delta = 2.22$ corresponded to the 6'-CH₂ hydrogens in the esteramide units (II) formed because of the ester-amide interchanging side reaction. By comparison of the area ratio with that of the 6-CH₂ hydrogens in the normal alternating adipamide adipate units (I), the amount of the ester-amide interchanging reaction was about 15.3%. The molecular weight of the PrePEA(4,*m*)s detected by ¹H-NMR spectra was also shown in Table 1. In the ¹H-NMR spectra, the terminal $\text{HOOC}-$ groups just showed a very weak peak, and the terminal $\text{HO}-$ groups could not show any detectable peaks due to its low amount. As their resonance was sensitive to the solvents and environments, their resonance areas were often lower than those they should be. The molecular weight detected by ¹H-NMR spectra was in the range of 2408–4533, and was much higher than that calculated from A_v and Q_v . The molecular weight obtained from A_v and Q_v was more accurate than that detected by ¹H-NMR spectra, because the A_v and Q_v can be accurately detected by the titration methods.

Figure 2 shows the ¹H-NMR spectrum of the ExtPEA(4,4)-2 with the $[\eta]$ of 0.59 dL/g. In Fig. 2, the peaks corresponding to the 1- to 7-CH₂ hydrogens in the alternating adipamide adipate units (I) and the 6'-CH₂ hydrogens in the esteramide units (II) formed by the ester-amide interchanging side reaction were still present. The PrePEA(4,4)-2 was just terminated by $\text{HOOC}-$ terminal groups. In Fig. 2, the peaks corresponding to the terephthalamide diesters units (III) were also observed. Peaks at $\delta = 4.17$ and 3.52 corresponded to 1''-CH₂ and 2''-CH₂ hydrogens in the terephthalamide diesters units (III). The peak at $\delta = 8.70$ corresponded to the 9-C₆H₄

benzene hydrogens. It verified that the chain extension took place between the $\text{HOOC}-$ terminal groups of the PrePEA(4,4)s and the chain extender PBOX. Meanwhile, after chain extension, the amount of the ester-amide interchanging reaction increased to 18.0%. The results showed that the ester-amide interchanging reaction mainly occurred in the melt polycondensation and the preparation of the PrePEA(4,*m*)s. Adipic acid and sebacic acid reacted with the $\text{HO}-$ groups of the HEHA and formed the alternating adipamide adipate units (I) or adipamide sebacate units in the melt polycondensation. But AA and SA had acid characteristics, a lot of the $\text{HOOC}-$ terminal groups remained in the earlier period also catalyzed the ester-amide interchanging reaction of the PrePEA(4,*m*)s and resulted in the esteramide units like (II). So the ester-amide interchanging reaction mainly occurred in the melt polycondensation of HEHA with AA or SA. In the chain extension, as the PrePEA(4,*m*)s had relatively higher molecular weight and lower amount of the $\text{HOOC}-$ terminal groups, the ester-amide interchanging reaction just happened in a little amount. So the amount of the ester-amide interchanging reaction increased to a little extent in the chain extension, although the reaction temperature was higher than that in the melt polycondensation of HEHA with AA or SA. The crystallizable ExtPEA(4,*m*)s were obtained through this chain extension.

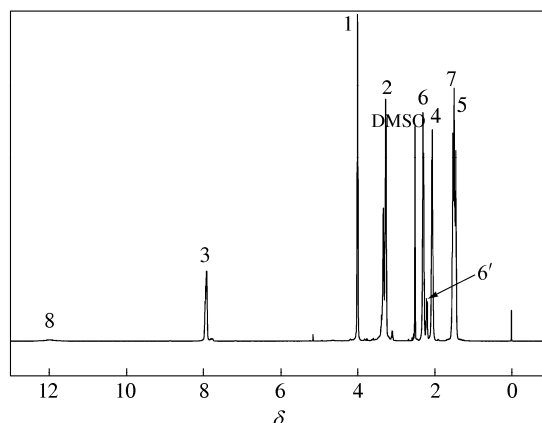
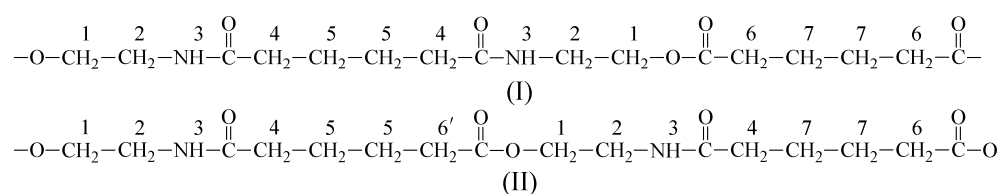


Fig. 1 The ^1H -NMR spectrum of the PrePEA(4,4)-2

Figure 3 shows the FTIR spectrum of the ExtPEA(4,4)-2. In Fig. 3, the strong absorption peak at 3297.5 cm^{-1} was assigned to the $\text{N}-\text{H}$ stretching vibration of the alternating adipamide adipate units (I), or the esteramide units (II) formed by the ester-amide interchanging reaction and the amide groups in the terephthalamide diesters units (III) formed in the chain extension between the $\text{HOOC}-$ terminal groups of the PrePEA(4,4) and the chain extender PBOX. The weak peak at 3079.8 cm^{-1} corresponded to the $\text{H}-\text{C}$ stretching vibration of the aromatic $-\text{C}_6\text{H}_4-$ units in the terephthalamide diesters units (III). The peak at 2945.6 cm^{-1} corresponded to the $\text{H}-\text{C}$ stretching vibration in the $-\text{CH}_2-$ groups. There were two characteristic peaks corresponded to the amide groups: one at 1650.1 cm^{-1} was assigned to the $\text{C}=\text{O}$ stretching vibration of the amide groups, and the other at 1548.3 cm^{-1} was assigned to the $\text{N}-\text{H}$ bending vibration in the secondary amide groups (amide II band). Meanwhile, the characteristic peak at 1733.7 cm^{-1} corresponded to the stretching vibration of the ester $\text{C}=\text{O}$ groups in the adipamide adipate units (I) in the main chains and those in the terephthalamide diesters units (III) formed during the chain extension of PBOX.

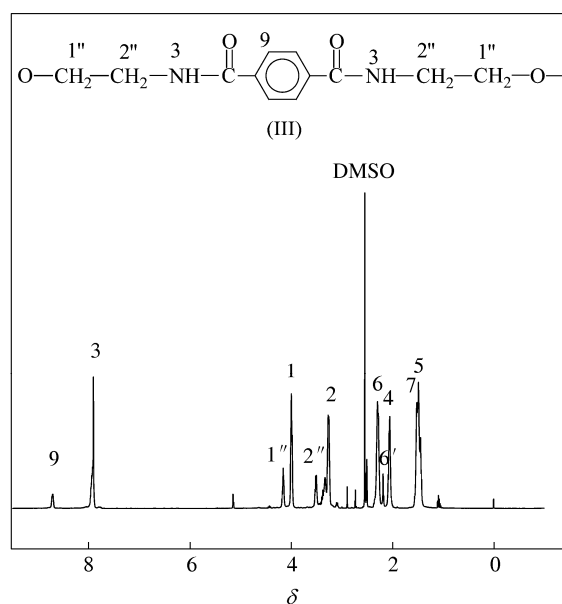


Fig. 2 The ^1H -NMR spectrum of the ExtPEA(4,4)-2 ($[\eta] = 0.59 \text{ dL/g}$)

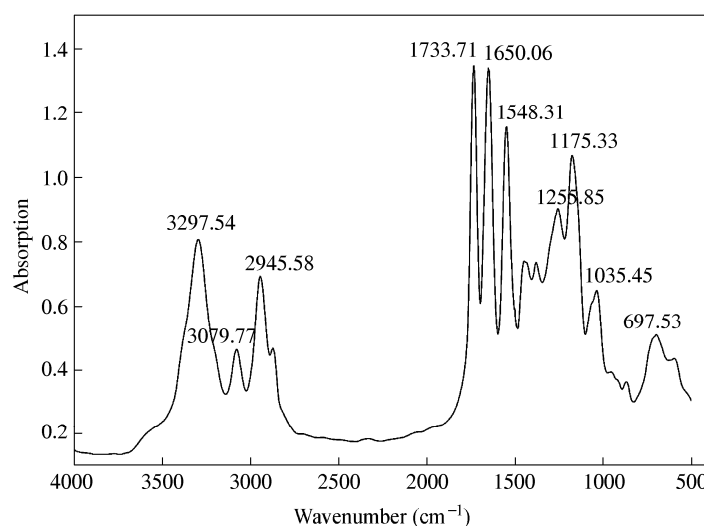


Fig. 3 FTIR spectra of the ExtPEA(4,4)-2 ($[\eta] = 0.59 \text{ dL/g}$)

DSC and TGA Characterization

The thermal behavior of the PrePEA(4,*m*)s and the ExtPEA(4,*m*)s was characterized by DSC measurements. Figure 4 shows the heating DSC curves of the PrePEA(4,4)-2, PrePEA(4,8), ExtPEA(4,4)-2 and the ExtPEA(4,8). The glass transition temperature (T_g), melting point (T_m), and enthalpy of melting (ΔH_m) of them are compiled in Table 2. From Fig. 4 and Table 2, it was found that the prepolyesteramides PrePEA(4,4)-2, PrePEA(4,8) and the chain extended polyesteramides ExtPEA(4,4)-2, ExtPEA(4,8) were all the crystallized polymers. They all had two T_m , a predominant exothermic peak and a small additional peak. These multiple fusion peaks showed similar characteristics to the polyamides^[28] and were usually associated with different populations of lamellar crystals. The higher T_m of the PrePEA(4,4)-2 and PrePEA(4,8) was 101.65°C and 98.03°C, but that of the ExtPEA(4,4)-2, ExtPEA(4,8) was 83.79°C and 85.77°C. After the chain extension, the T_m decreased. As the PrePEA(4,4)-2 and PrePEA(4,8) were all mainly terminated by $\text{HOOC}-$ terminal groups,

chain extending reaction between the HOOC— terminal groups and the chain extender PBOX was the major chain extension. The terephthalamide diesters units (III) formed through chain extension between the HOOC— terminal groups of the PrePEA(4,*m*)s and PBOX were different from the major alternating adipamide adipate units (I) or adipamide sebacate units in the prepolyesteramides, making the regularity of the ExtPEA(4,4)-2 and ExtPEA(4,8) lowered. So the crystallization became difficult to some extent and the T_m decreased. Meanwhile, the T_g of the ExtPEA(4,4)-2 and ExtPEA(4,8) was higher than that of the PrePEA(4,4)-2 and PrePEA(4,8), because the terephthalamide diester units (III) introduced through the chain extension were rigid units.

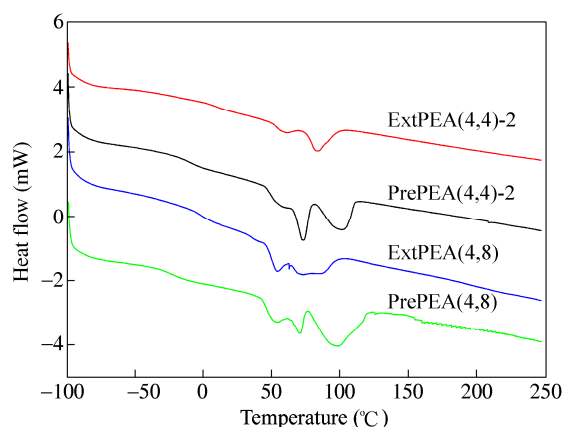


Fig. 4 The heating DSC curves of the PrePEA(4,4)-2, PrePEA(4,8), ExtPEA(4,4)-2 and the ExtPEA(4,8) Heating rate: 10 K/min

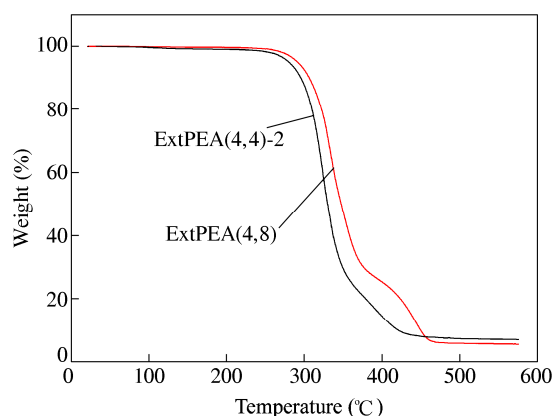


Fig. 5 TGA curves of the ExtPEA(4,4)-2 and the ExtPEA(4,8) (heating rate: 10 K/min, in N_2)

Table 2. The heating DSC data of PrePEA(4,4)-2, PrePEA(4,8), ExtPEA(4,4)-2 and ExtPEA(4,8) (heating rate: 10 K/min)

PEA(4, <i>m</i>)	T_g (°C)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)
PrePEA(4,4)-2	-10.60	72.18	21.89	101.65	18.31
PrePEA(4,8)	-20.11	70.20	18.48	98.03	33.04
ExtPEA(4,4)-2 ^a	11.79	59.24	2.93	83.79	11.73
ExtPEA(4,8) ^b	2.86	53.48	5.23	85.77	11.57

^a ExtPEA(4,4)-2 ($[\eta]$ = 0.59 dL/g); ^b ExtPEA(4,8) ($[\eta]$ = 0.48 dL/g)

Figure 5 shows the TGA curves of the ExtPEA(4,4)-2 and the ExtPEA(4,8). Table 3 shows the initial decomposition temperature (T_i) of them. From Fig. 5 and Table 3, it was found that the T_i of the ExtPEA(4,4)-2 and the ExtPEA(4,8) was 310.0°C and 316.1°C, respectively. They had similar thermal stability, which were high enough for them to be processed with normal thermally processing machines.

Table 3. The mechanical properties and the TGA data of ExtPEA(4,4)-2 and ExtPEA(4,8)

ExtPEA(4, <i>m</i>)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	T_i (°C)
ExtPEA(4,4)-2 ^a	25.64	737	178.0	310.0
ExtPEA(4,8) ^b	14.75	683	53.7	316.1

^a ExtPEA(4,4)-2 ($[\eta]$ = 0.59 dL/g); ^b ExtPEA(4,8) ($[\eta]$ = 0.48 dL/g)

WAXS Analysis

The crystalline structure of the PrePEA(4,*m*)s and the ExtPEA(4,*m*)s was also determined by WAXS measurements. Figure 6 shows WAXD curves of the PrePEA(4,4)-2, PrePEA(4,8), ExtPEA(4,4)-2 and the ExtPEA(4,8). The peaks corresponding to the PrePEA(4,4)-2 and ExtPEA(4,4)-2 occurred at 2θ of 21.20° and 22.27°, and those corresponding to the PrePEA(4,8) and ExtPEA(4,8) occurred at 2θ of 21.51° and 22.34° respectively. The crystallites of PrePEA(4,*m*)s and ExtPEA(4,*m*)s are similar to those of the nylon-66^[29, 30]. After chain extension, the crystallization of the ExtPEA(4,*m*)s decreased. The terephthalamide diester units (III) formed through the chain extension lowered the regularity of the ExtPEA(4,*m*)s, so the crystallization decreased.

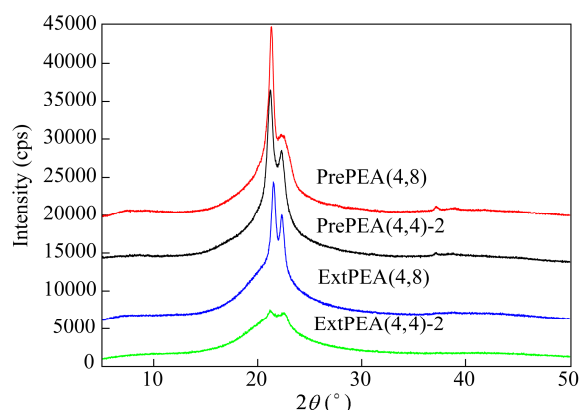


Fig. 6 WAXD curves of PrePEA(4,4)-2, PrePEA(4,8), ExtPEA(4,4)-2 and ExtPEA(4,8)

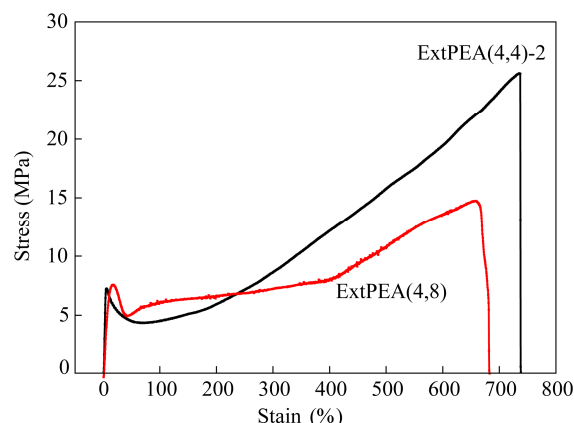


Fig. 7 The strain-stress diagrams of ExtPEA(4,4)-2 and ExtPEA(4,8)

Tensile Testing

The mechanical properties of the ExtPEA(4,4)-2 and ExtPEA(4,8) were measured and shown in Fig. 7 and Table 3. The tensile strength of the ExtPEA(4,4)-2 and ExtPEA(4,8) was 25.64 and 14.75 MPa, and the strain at break of them was 737% and 683%, respectively. Meanwhile, the tensile modulus of the ExtPEA(4,4)-2 was much higher than that of the ExtPEA(4,8). The characterization of the mechanical properties showed that they were all flexible materials with moderate tensile strength.

Enzymatic Degradation

The enzymatic degradation of the ExtPEA(4,4)-2 and the ExtPEA(4,8) was conducted at 37°C using lipase from porcine pancreas. Figure 8 shows the degradation diagrams of them. It was found that the enzymatic degradation for 112 h in the presence of 0.1 mg/mL lipase brought about 8.5% weight loss of the ExtPEA(4,4)-2, and that for 126 h just resulted in 4.2% weight loss of the ExtPEA(4,8). The ExtPEA(4,4)-2 showed higher degradation rate than the ExtPEA(4,8). ExtPEA(4,4) and ExtPEA(4,8) were synthesized from HEHA with adipic acid and sebacic acid, respectively. AA had short alkylene chain than the SA. So the ExtPEA(4,4) had higher polarity and hydrophilicity than the ExtPEA(4,8), and the ExtPEA(4,4)-2 had higher degradation rate than the ExtPEA(4,8). Lipase catalyzed the hydrolytic breakage of the ester linkages in the ExtPEA(4,4) and ExtPEA(4,8), and led to the enzymatic degradation of them.

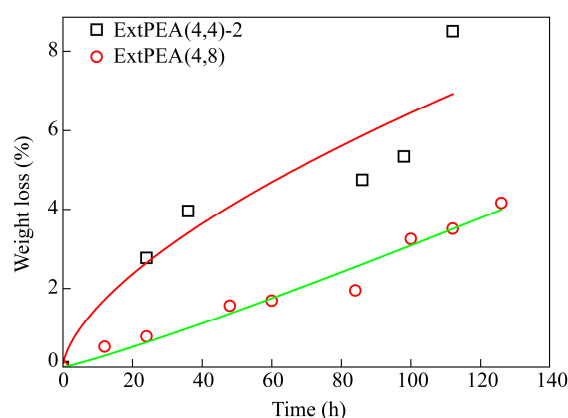


Fig. 8 Enzymatic degradation of the ExtPEA(4,4)-2 and the ExtPEA(4,8) with lipase from porcine pancreas (10 mL phosphate buffer, 0.1 mg/mL lipase, pH 7.4, 37°C)

CONCLUSIONS

Two alternating polyesteramide prepolymers PrePEA(4,*m*)s were prepared through the polycondensation of *N,N'*-bis(2-hydroxyethyl)-adipamide with adipic acid or sebacic acid. Under the catalysis of SnCl₂ at reaction temperatures not higher than 180°C and reaction time no longer than 7 h, crystallizable PrePEA(4,*m*)s were prepared through polycondensation from HEHA and AA or SA, with rare occurrence of ester-amide interchanging side reaction. Through chain extension of the PrePEA(4,*m*)s with PBOX and ABC as combined chain extenders, the ExtPEA(4,*m*)s with $[\eta]$ up to 0.59 dL/g were obtained. FT-IR and ¹H-NMR characterization showed that the ExtPEA(4,*m*)s were mainly constituted with the alternating diester adipamide units like (I). The ExtPEA(4,4)-2 and ExtPEA(4,8) had *T_m* of 83.8°C and 85.8°C respectively and initial decomposition temperature above 310.0°C. They form crystallites similar to those of Nylon-66. They were flexible materials with moderate tensile strength and biodegradability. This method provided a promising way to synthesize biodegradable polyesteramides mainly constructed by alternating diesterdiamide units through polycondensation and chain extension directly from diamidediols and diacids as starting materials.

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