CrossMark

ORIGINAL PAPER

Effect of Monomer Structure on Crystallization and Glass Transition of Flexible Copolyesters

Chengqian Pan[1] · Jing Lu[1] · Binshuang Wu[1] · Linbo Wu[1] · Bo-Geng Li[1]

Abstract Amorphous flexible (co)polyesters with low glass transition temperature (T_g) are very desirable in impact modification of biodegradable brittle polymers and synthesis of biodegradable elastomers. However, most flexible polyesters and binary copolyesters made from linear diacid(s) and diol(s) are crystalline polymers. In order to investigate the effect of monomer structure on the crystallization and T_g of such copolyesters, novel ternary or multiple flexible copolyesters containing various structural units were designed and synthesized in this study, and characterized with ^{1}HNMR, GPC, DSC, WAXD, TGA and tensile testing. Introducing aromatic diacid (especially asymmetric one) or short-chain branched diol is favorable to depress copolyester crystallization, and leads to higher T_g at the same time. From easily crystallized to fully amorphous copolyesters with low T_g were successfully synthesized by adopting different combination of structural units. In addition, the existence of aromatic structural unit in copolyesters is helpful to improve their tensile properties.

Graphical Abstract Flexible copolyesters containing various structural units were designed and synthesized. Introducing asymmetric, rigid aromatic or short-chain branched unit is favorable to depress copolyester crystallization, and leads to higher T_g at the same time. Crystalline to fully amorphous copolyesters with low enough T_g have been successfully synthesized by adjusting the structural units.
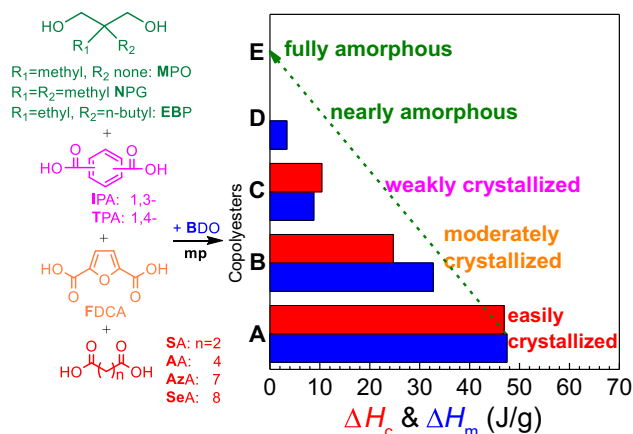
Keywords Biodegradable polymers · Flexible copolyesters · Aliphatic–aromatic copolyesters · Crystallization · Glass transition

Introduction

It is well-known that using biodegradable polymers instead of non-degradable ones is a promising way to avoid the environmental harm resulted from using the latter. To date, some important biodegradable (co)polyesters including

---

✉ Linbo Wu
  wulinbo@zju.edu.cn

[1] State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

✑ Springer

poly(lactic acid) (PLA) [1], poly(butylene succinate) (PBS) [2–5], poly(butylene succinate-co-adipate) (PBSA) [6–8], poly(butylene adipate-co-terephthalate) (PBAT) [9–12] and poly(hydroxyalkanoate)s (PHAs) [13] have been commercialized and applied to a variety of fields in the last decades due to their desirable biodegradability, reasonably good processability and thermo-mechanical properties. Among them, flexible (co)polyesters made from linear diacid(s) and diol(s) like PBS and copolyesters like PBSA and PBAT are often used directly as tough plastics for end uses such as film, bottle and other disposable goods. They are also attempted to be used as impact modifiers of brittle biodegradable polymers like poly(lactic acid) (PLA) [14–19], biodegradable elastomers [20] or components of elastomers [21–25].

For impact modification or elastomer applications, amorphous flexible copolyesters with low glass transition temperature (T_g) are often more desired as they can provide better chain flexibility than crystalline counterparts. For an example, ultratough PLA was successfully developed by synergistical introduction of amorphous ε-caprolactone-based copolyester and silica nanoparticles in Odent et al.'s recent report [26]. However, most of linear aliphatic polyesters like PBS [27] and PBA [28] and binary copolyesters like PBSA [6], poly(butylene succinate-co-azelate) (PBSAz) [29], poly(butylene-co-ethylene succinate) (PBES) [30], poly(hexamethylene sebacate-co-suberate) (PHSeSu) [31], poly(hexamethylene suberate-co-adipate) (PHSuA) [31], poly(butylene-co-propylene succinate) (PBPS) [32] and poly(ethylene-trimethylene succinate) (PETS) [33] have excellent to good crystallizability in whole composition range. Aliphatic–aromatic binary copolyesters like PBAT [10], poly(butylene succinate-co-terephthalate) (PBST) [34], poly(butylene succinate-co-furandicarboxylate) (PBSF) [35] and poly(butylene adipate-co-furandicarboxylate) (PBAF) [36] have less crystallizability than the aliphatic counterparts, but still kept certain crystallizability, even at the least crystallizable composition. For an example, typical PBAT (Ecoflex®) has a melting enthalpy over 10 J/g [10]. Few ternary or multiple copolyesters were reported in literature. As an example, poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) is also a crystallizable copolyester [37]. But poly(2-methyl-1,3-propylene succinate), a polyester containing side methyl groups [38] was reported to be an amorphous polyester. Recently, some sugar-derived bicyclic diol or diacid compounds were used as comonomers to synthesize novel biobased copolyesters [39–42]. These copolyesters are characterized by high T_g and are amorphous at certain composition rage. This implies that monomer structure is another important factor besides composition to affect crystallization and glass transition of flexible (co)polyesters, but relative research is lacked in literature.

In this study, we aim to make clear the effect of monomer structure on crystallization and glass transition of flexible copolyesters and to synthesize from crystalline to amorphous flexible copolyesters with low T_g. To this end, ternary and multiple linear copolyesters were designed and synthesized from 1,4-butanediol and 3–4 symmetric and asymmetric linear diacids. Diols with various side groups were further incorporated to synthesize multiple copolyesters with side groups. The copolyesters were characterized with ^{1}HNMR, GPC, DSC, TGA and tensile testing. The effects of structural factors including chain length of aliphatic diacids, symmetry and rigidity of aromatic diacids and short-chain side groups of diols on crystallizability and T_g of the copolyesters were discussed. From easily crystallized to fully amorphous copolyesters with low T_g were successfully synthesized by adopting different monomer combinations.

Experimental

Materials

Succinic acid (SA or S, Sanxin Chem. Co), adipic acid (AA or A, Aladdin), azelaic acid (AzA or Az, Sinoreagent), sebacic acid (SeA or Se, Sinoreagent), terephthalic acid (TPA or T, Sinoreagent), isophthalic acid (IPA or I, Sinoreagent), 2,5-furandicarboxylic acid (FDCA or F, Ruiyuan Chem. Co), 1,4-butanediol (BDO or B, Wulian Chem. Co), 2-methyl-1,3-propanediol (MPO or M, Aladdin), Neopentyl glycol (NPG or N, Aladdin), 2-ethyl-2-butyl-1,3-propanediol (EBP or E, TCI), tetrabutoxyl titanium (TBT, Aladdin) were all used as received. All other reagents were analytical reagent grade and used as received.

Synthesis of Copolyesters

Copolyesters were synthesized in a 250 mL flask via esterification followed by melt polycondensation. At least three diacids (0.5 mol in total) and BDO (or BDO and a branched diol, 1:1 molar ratio, 1 mol in total) was added in the flask. The diol/diacid molar ratio was fixed at 2:1. More detailed feed ratios of the monomers are shown in Table 1. TBT (0.1 mol% based on diacids) was added as catalyst under stirring and N_2 protection. For Runs 1–2, esterification was conducted under atmospheric pressure at 190, 200 and 210 °C for 1, 2 and 1 h respectively. Then, the temperature was raised to 230 °C and the pressure was reduced to 200–400 Pa in about 45 min. Finally, melt polycondensation was carried out at 230 °C for 4 h. For Runs 3–17, the reaction temperatures were 10 °C higher. The resulting product was collected and

Table 1 Synthetic conditions[a] and chain structure parameters of the flexible copolyesters

Run	Copolyester	Feed ratio	Copolyester composition	R^f	M_n*10^{-3} [g]	M_w*10^{-3} [g]	Đ[h]
1	PBSeAS334	0.3:0.3:0.4[b]	0.311:0.291:0.398[d]	0.98	39.4	74.6	1.89
2	PBAzAS334	0.3:0.3:0.4[b]	0.317:0.301:0.382[d]	1.02	42.1	82.5	1.96
3	PBSeAT334	0.3:0.3:0.4[b]	0.335:0.266:0.399[d]	1.00	35.4	66.7	1.88
4	PBAzAT334	0.3:0.3:0.4[b]	0.304:0.270:0.426[d]	0.98	46.5	82.7	1.78
5	PBSeAzT334	0.3:0.3:0.4[b]	0.299:0.282:0.419[d]	0.99	75.1	146	1.95
6	PBSeTI622	0.6:0.2:0.2[b]	0.601:0.199:0.200[d]	1.00	41.4	69.4	1.68
7	PBSeST334	0.3:0.3:0.4[b]	0.300:0.285:0.415[d]	0.97	37.4	65.3	1.75
8	PBSeSI334	0.3:0.3:0.4[b]	0.309:0.287:0.404[d]	0.98	42.5	73.1	1.72
9	PBSeSF334	0.3:0.3:0.4[b]	0.309:0.298:0.393[d]	0.97	40.3	72.8	1.81
10	PBSeAzST2224	0.2:0.2:0.2:0.4[b]	0.193:0.198:0.187:0.422[d]	1.02	50.0	84.4	1.68
11	PBSeAzAT2224	0.2:0.2:0.2:0.4[b]	0.190:0.200:0.200:0.410[d]	0.99	42.0	73.4	1.74
12	PBSeSTI3322	0.3:0.3:0.2:0.2[b]	0.305:0.286:0.205:0.204[d]	1.01	36.1	60.1	1.66
13	PBSeATI3322	0.3:0.3:0.2:0.2[b]	0.313:0.283:0.202:0.202[d]	1.00	42.3	76.3	1.81
14	PBSeSTF3322	0.3:0.3:0.2:0.2[b]	0.301:0.292:0.207:0.200[d]	1.00	48.0	86.0	1.79
15	PBMSeST334	1:1[c]&0.3:0.3:0.4[b]	0.499:0.501[e]&0.310:0.288:0.400[d]	1.05	51.8	103	1.99
16	PBNSeST334	1:1[c]&0.3:0.3:0.4[b]	0.518:0.482[e]&0.300:0.293:0.407[d]	1.05	47.2	89.9	1.90
17	PBESeST334	1:1[c]&0.3:0.3:0.4[b]	0.429:0.571[e]&0.303:0.291:0.406[d]	1.01	54.8	110	2.00

Run 1–2: aliphatic ternary; Run 3–9: aliphatic–aromatic ternary; Run 10–14: aliphatic–aromatic quaternary copolyesters; Run 15–17: short-chain branched

[a] Tetrabutoxyl titanium (TBT, 0.1 mol% based on diacid) was used as catalyst. The diol/diacid molar ratio was 2/1; [b,d] Molar ratio of diacids in feed and of corresponding structure units in copolyesters, respectively. The order of the numbers is the same as the order of the initials of monomers appeared in the name of copolyesters in the second column. For an example, B:M:Se:S:T molar ratio is 1:1:0.3:0.3:0.4 in Run 15; [c,e] Molar ratio of diols in feed and of corresponding structure units in copolyesters, respectively; [f] Randomness degree; [g] g/mol in unit; [h] Polydispersity

stored in a dessicator under vacuum before characterization. The copolyesters were named with the acronyms of the monomers used. For an example, PBSeAzST2224 is a copolyester made from sebacic acid (Se), azelaic acid (Az), succinic acid (S) and terephthalic acid (T) in a diacid molar feed ratio of 2:2:2:4.

Characterization

Molecular weight and its distribution of the copolyesters were measured with a Waters 1525/2414 gel permeation chromatography (GPC) at 30 °C. Tetrahydrofuran was used as eluent and polystyrene as standard. The sample concentration was about 4 mg/mL, and the eluent flow rate was 1.0 mL/min.

^{1}H NMR spectra of the copolyesters were recorded with a 400 M BRUKER AC-80 spectroscopy. Deuterated chloroform was used as solvent and tetramethylsilane as internal reference. X-ray diffraction measurements of the samples were performed using a Pert X-ray diffraction system (PANalytical Company) with CuKa radiation (0.154 nm) working at 40 kV and 40 mA. The samples

were scanned from $2\theta = 5°$ to $2\theta = 60°$ with a step size of 0.026° and an acquisition time of 30 s per step.

Thermal transition behaviors of the copolyesters were recorded with a TA DSC Q200. A standard heat-cool-heat program was performed between −80 and 200 °C for all samples. The heating and cooling rates were of 10 °C/min. The temperature was hold at 200 °C and −80 °C for 3 min respectively before cooling and second heating. Thermal stability of the copolyesters was assessed with a TA Q500 thermal gravimetric analyzer under nitrogen atmosphere. The samples were measured from 50 to 800 °C at 20 °C/min.

Tensile properties of some copolyesters were measured using dumbbell-shaped specimens (2 mm in thickness and 4 mm in width) with a Zwick/Roell Z020 testing machine at 25 °C according to ASTM D638. The specimens were prepared with different processing methods, namely, injection molding and hot pressing, according to their different thermal transition properties. The details are interpreted in the Mechanical Properties section. All the specimens were conditioned at 25 °C and 50 % relative humidity for over 48 h prior to testing. The crosshead speed was 20 mm/min. For each sample, at least five specimens were tested.

Results and Discussion

Synthesis and Characterization of Chain Structure

The chemical structure of monomers used is illustrated in Scheme 1. The copolyesters were designed using SA, AA and BDO as main monomers. As binary aliphatic copolyester PBSA is crystalline in the whole composition range [6], aliphatic ternary copolyesters (Runs 1–2) were first designed in this study. Long chain diacids, namely, azelaic acid (Az) and sebacic acid (Se) were copolycondensed with succinic acid (S) and adipic acid (A) as their long aliphatic chains can provide better chain mobility [25] and low T_g. In addition, they are both biobased monomers. Furthermore, aliphatic–aromatic ternary (Runs 3–9) or quaternary (Runs 10–14) copolyesters were also designed to further depress crystallization. Besides TPA, IPA and biobased FDCA were also introduced considering that their asymmetric structure may favor to further depress crystallization. Besides, short side groups were introduced into copolyesters (Runs 15–17) by using 2- or 2,2-substituted 1,3-propanediol as a diol comonomer in order to study its effect on crystallization and T_g.

There are lots of possible combinations with these monomers. As the main purpose of this study is to investigate the effect of structural unit on the thermal transition of flexible copolyesters, the effect of copolymer composition was not considered. Copolyesters were designed with some fixed compositions. It is known that binary flexible copolyesters are usually least crystallizable when the content of short chain or aromatic diacid unit is of 20–40 mol% [6, 10, 34, 36]. For binary aliphatic–aromatic copolyesters, 40–50 mol% aromatic diacid unit can assure good balance between thermo-mechanical properties and biodegradability [10, 12]. Therefore, in syntheses of aliphatic copolyesters (Runs 1–2), the molar fraction of SA in total diacids was fixed at 40 mol% and that of other two took the average (30 %). In the syntheses of aliphatic–aromatic copolyesters, the molar ratio of aromatic diacid(s) in total diacids were also fixed at 40 mol%. On the premise of this rule, diacid feed ratios took the averages of aliphatic or aromatic acids. For the synthesis of short-chain branched copolyesters, the molar ratio of substituted 1,3-propanediol to BDO was arbitrarily fixed at 1:1. The detailed feed ratio of monomers are listed in Table 1.

Molecular weight of copolyesters usually affects their glass transition temperature (T_g), mechanical properties and end uses. Low molecular weight of thousands gram per mol is suitable for soft segments in multi-block copolymers used for elastomers, however, high molecular weight around 10^5 g/mol is often required for tough plastics, impact modifiers and elastomers to ensure sufficient thermo-mechanical properties. In this study, we aimed to design and screen flexible amorphous (or nearly amorphous) copolyesters with low T_g and acceptable mechanical properties. Therefore, high molecular weight copolyesters were synthesized so that the molecular weight dependence of T_g can be avoided and mechanical properties can be assessed.

Most copolyesters are colorless/white or pale yellow. But there is clear discoloration for adipate-containing copolyesters. The GPC results listed in Table 1 indicate that high molecular weight copolyesters were successfully synthesized. The number- and weight-average molecular weights (M_n and M_w) range in 36,000–75,000 g/mol and 60,000–146,000 g/mol, respectively. And the polydispersity index ($Đ$) ranges in 1.7–2.0.

Chemical structure of the copolyesters was characterized by ^{1}H-NMR. The spectra and attribution of chemical shifts are shown in Fig. 1 and Scheme 2. The characteristic chemical shifts of succinate, adipate, azelate, sebacate, terephthalate, isophthalate, furandicarboxylate, BDO, MPO, NPG and EBP locate at 2.63 ppm (**s**), 2.33 ppm (**a**), 1.32 ppm (**z**), 1.30 ppm (**l**), 8.10 ppm (**t**), 8.22 ppm (**i**), 7.21 ppm (**f**), 4.44–4.09 ppm (**b**), 1.21–0.98 ppm (**m**), 1.18–0.96 ppm (**n**) and 0.97–0.80 ppm (**v**), respectively. For the aliphatic–aromatic copolyesters, the chemical shifts of CH$_2$ in diol unit split into four peaks (b$_{4-1}$, c$_{4-1}$, o$_{4-1}$, q$_{4-1}$, r$_{4-1}$), corresponding to different sequence structures as shown in Scheme 2. The attributions of other chemical
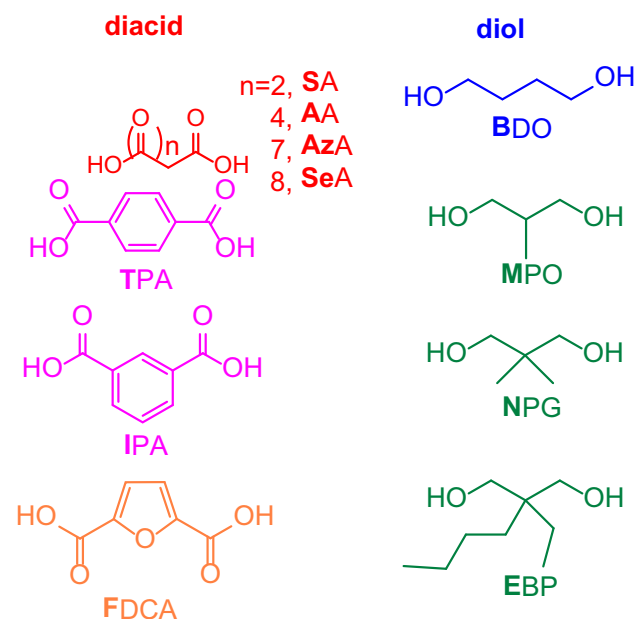

Scheme 1 Diacids and diols used for synthesis of the flexible copolyesters. **SA**, succinic acid; **AA**, adipic acid; **AzA**, azelaic acid; **SeA**, sebacic acid; **TPA**, terephthalic acid; **IPA**, isophthalic acid; **FDCA**, 2,5-furandicarboxylic acid; **BDO**, 1,4-butanediol; **MPO**, 2-methyl-1,3-propanediol; **NPG**, neopentyl glycol or 2,2-dimethyl-1,3-propanediol; **EBP**, 2-ethyl-2-butyl-1,3-propanediol
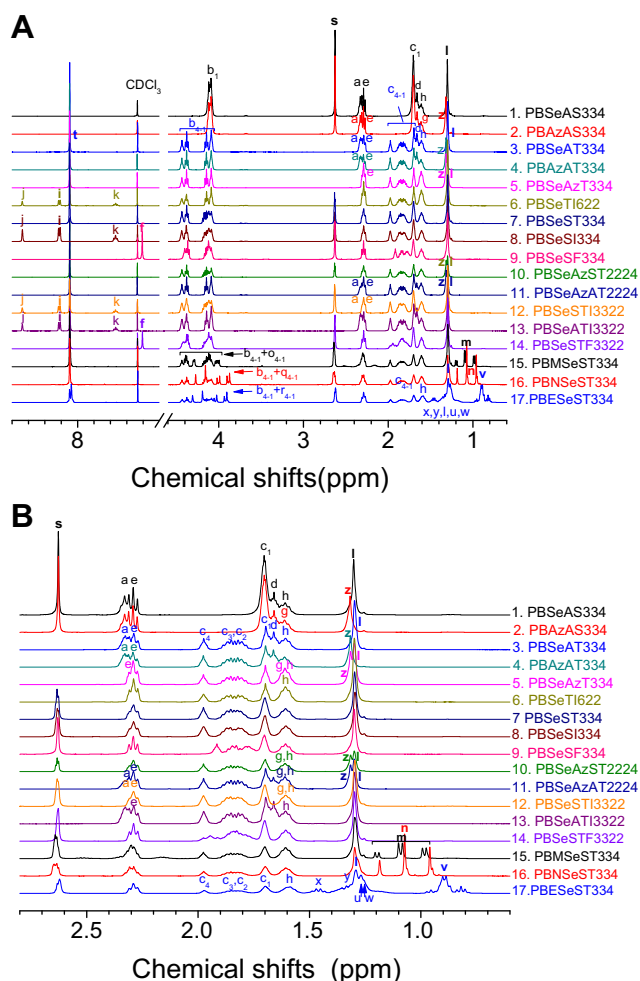
Fig. 1 ^{1}H NMR spectra of the flexible copolyesters in CDCl$_3$ at 400 MHz. **a** The full spectra, **b** partially enlarged spectra

shifts are also shown in this scheme. From the peak area of characteristic chemical shifts, the copolyester composition and randomness degree were calculated and the results are listed in Table 1. It can be seen that the composition is
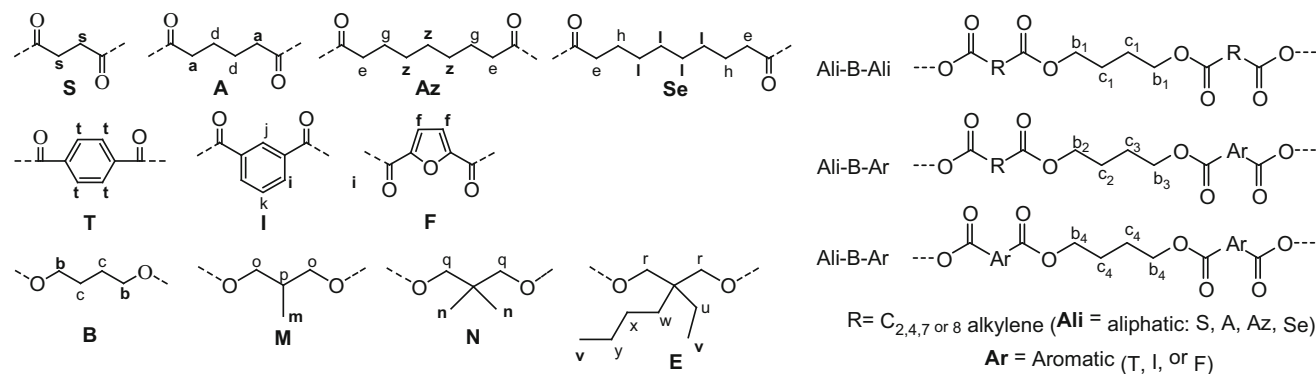
close to the monomer feed ratio and the randomness degree is close to one. These qualitative and quantitative results indicate that random copolyesters with expected structure and composition were successfully synthesized.
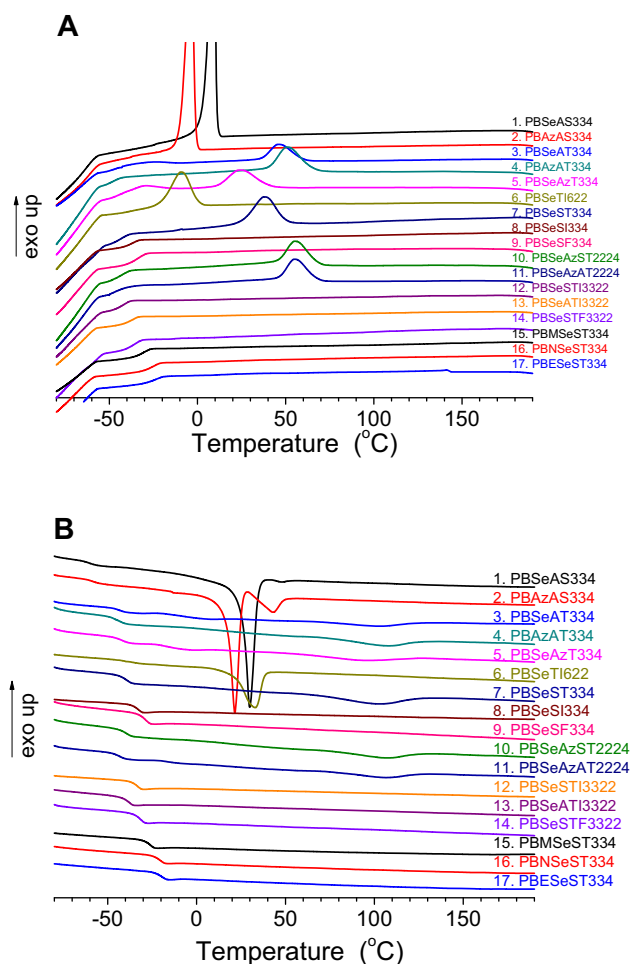
Thermal Transition Behaviors

The thermal transition behaviors of the copolyesters were recorded with DSC using a standard heat/cool/heat procedure. The cooling and second heating DSC curves are shown in Fig. 2. The transition temperatures and enthalpies are listed in Table 2.

In the two aliphatic ternary copolyesters PBSeAS334 and PBAzAS334 (Runs 1–2) the long chain diacids, namely sebacic and azelaic acid, were introduced in order to lower down T_g. Both copolyesters have only one T_g, suggesting random sequence structure. And the T_gs (−60, −58 °C) are lower than PBSA46 (−53 °C) [6]. However, both copolyesters exhibit rapid melt crystallization with high crystallization (49.5, 44.3 J/g) and melting enthalpies (50.5, 45.5 J/g). The melting enthalpies are even higher than that of PBSA46 (23.7 J/g [6]), possibly due to the favorable contribution of the long Se or Az alkylene chain to crystallization. The results indicate that the introduction of the third aliphatic long chain diacid monomer does not help to depress the crystallization of the resultant copolyesters.

In the next study, aromatic acid(s) was(were) introduced to synthesize aliphatic–aromatic ternary or quarternary copolyesters. When TPA is used instead of SA, the resultant random copolyesters PBSeAT334 and PBAzAT334 (Runs 3–4) have higher T_g, T_c and T_m, but much slower crystallization and enthalpies (10.4–10.7 vs. 44.3–49.5 J/g). When the adipate is replaced with azelate or sebacate (Run 5 vs. Run 3 or 4), both T_c and T_m decreased and the crystallization and melting enthalpies kept nearly unchanged. In comparison with PBSeAT334 and PBAzAT334

Scheme 2 Chemical structure of various structural units in the flexible copolyesters (The bold capitals denote the abbreviation of the diacid structure units; the structural formulas on right side denote the BDO diol units in different chemical environments: Ali–B–Ali, Ali–B–Ar, Ar–B–Ar)

Fig. 2 DSC thermograms of the flexible copolyesters. **a** Cooling scan at 10 °C/min, **b** 2nd heating scan at 10 °C/min

(Runs 3 and 4), the ternary copolyester (PBSeTI622, Run 6) has slightly higher T_g, much lower T_c and T_m, and higher crystallization and melting enthalpies.

Effect of the structure of aromatic diacid on copolyester crystallization can be seen by comparing the DSC results of PBSeST334, PBSeSI334 and PBSeSF334 (Runs 7–9). Clearly, PBSeST334 has crystallizability nearly equivalent to PBSeAT334, PBAzAT334 and PBSeAzT334 (Runs 3–5). However, PBSeSI334 and PBSeSF334 containing asymmetric isophthalate and furandicarboxylate unit respectively neither crystallize from melt nor from glass state at 10 °C/min. These results indicate that introducing asymmetric structural unit can effectively destroy the structural regularity and therefore depress the crystallization.

In comparison with the ternary copolyesters PBSeAT334, PBAzAT334 (Runs 3–4), the quarternary copolyesters PBSeAzST2224 and PBSeAzAT2224 (Runs 10–11) have comparable T_c and T_m and crystallization enthalpy. However, when two aromatic units are

introduced, amorphous PBSeSTI3322, PBSeATI3322 and PBSeSTF3322 (Runs 12–14) are obtained. Neither melt nor glass crystallization was observed in the DSC thermograms.

In addition to number, chain length, symmetricity of diacid monomers, the effect of short-chain branching on crystallization and T_g of copolyesters was further studied. Using BDO, an equimolar short-chain branched 1,3-propanediol (MPO or NPG or BEP) and three diacids (Se, S, T), PBMSeST334, PBNSeST334, PBESeST334 (Runs 15–17), were synthesized. In comparison with the ternary linear counterpart PBSeST334 (Run 7), these copolyesters are all amorphous. This indicates that introducing short-chain branching is also an effective way to depress crystallization of copolyesters. However, it can be seen that they have T_g (−25.9 to −19.6 °C) higher than PBSeST334 (−39.2 °C) and the T_g increases with the substituted number (1–2) and side group size. This is possibly because the steric hindrance of the substituent group(s) hinders the segment motion, especially for the 2,2-substituted copolyesters.
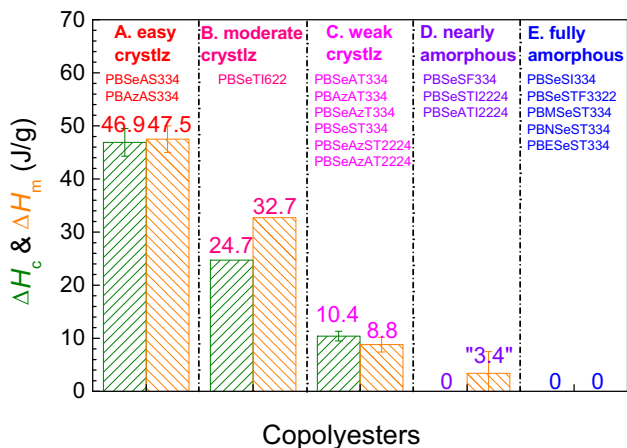
According to the crystallization and melting enthalpies (ΔH_c and ΔH_m), all the copolyesters are classified into five classes, as shown in Fig. 3. The aliphatic ternary copolyesters, PBSeAS334 and PBAzAS334 (Runs 1–2) are classified to class A. They can crystallize easily with high ΔH_c and ΔH_m (ca. 47 J/g) which are equivalent to those of poly(butylene adipate) (ca. 50 J/g) [43]. The aliphatic–aromatic ternary copolyester PBSeTI622 (Run 6) is classified to class B. It crystallizes with moderate ΔH_c and ΔH_m of about 25 J/g which is equivalent to those reported for PBSA46 (ca. 24 J/g) [6]. This suggests the big contribution of the sebacate unit to crystallizability. Class C includes six aliphatic–aromatic copolyesters, four ternary (Runs 3–5, 7) and two quarternary (Runs 10–11). They weakly crystallize and have ΔH_c and ΔH_m (ca. 10 J/g) close to those of commercial Ecoflex®. The others neither showed any phase transition in the cooling scan nor in subsequent melting scan both at 10 °C/min. But some of them, namely PBSeSF334, PBSeSTI2224 and PBSeATI2224 did show some melting peak in the first heating scan, especially for PBSeSF334 (Run 9). This phenomenon means that these copolyesters still have certain crystallizability. So, they are classified to "nearly amorphous". Finally, PBSeSI334, PBSeSTF3322 and the three short chain branched copolyesters are fully amorphous. There is no melting peak observed even in the first heating scan for them. Such order of crystallizability of these copolyesters was also confirmed by WAXD patterns of six representative copolyester samples shown in Fig. 4. Clearly, the intensity of the characteristic peaks decreases from strong (Run 1) and moderate (Run 6) to weak (Run 7), faint (Run 9) and none (Runs 8 and 15). In addition, it can

Table 2 Thermal transition properties of the seventeen flexible copolyesters

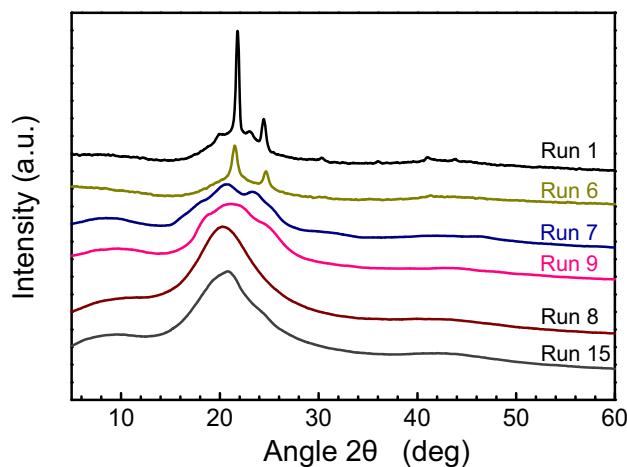| Run	copolyester	First heating scan			Cooling scan		Second heating scan			App.[a]
		T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	
1	PBSeAS334	−58.3	25.6,46.3	40.8	9.2	49.5	−60.4	29.9	50.5	O
2	PBAzAS334	−60.0	10.0,33.5,45.0	36.9	−3.8	44.3	−58.0	21.5/42.8	45.5/9.7	O
3	PBSeAT334	−44.6	66.1105	12.2	49.3	10.4	−47.4	101.2	8.71	O
4	PBAzAT334	−45.9	67.9102	13.9	51.0	10.7	−46.5	107	8.32	O
5	PBSeAzT334	−42.8	73.8	11.2	23.9	10.8	−41.9	94.2	10.4	O
6	PBSeTI622	−40.1	32.4	29.9	−9.4	24.7	−40.3	32.8	32.7	O
7	PBSeST334	−39.4	77.9108	16.5	37.7	11.7	−39.2	102	10.5	O
8	PBSeSI334	−35.2	–	0	–	0	−33.3	–	0	T
9	PBSeSF334	−33.8	72.0	8.1	–	0	−28.6	–	0	TL
10	PBSeAzST2224	−41.2	69.5109	14.7	55.8	9.1	−39.0	106	7.39	O
11	PBSeAzAT2224	−44.1	69.2104	12.3	55.3	9.7	−42.9	106	7.3	O
12	PBSeSTI3322	−36.1	46.6	0.6	–	0	−33.2	–	0	T
13	PBSeATI3322	−40.7	46.3	1.4	–	0	−38.0	–	0	TL
14	PBSeSTF3322	−32.2	–	0	–	0	−31.5	–	0	T
15	PBMSeST334	–	–	0	–	0	−25.9	–	0	T
16	PBNSeST334	−21.5	–	0	–	0	−20.1	–	0	T
17	PBESeST334	–	–	0	–	0	−19.6	–	0	T

O opaque, *TL* translucent, *T* transparent

[a] Appearance of copolyesters

Fig. 3 Classification of the flexible copolyesters according to their average crystallization and melting enthalpies (ΔH_c and ΔH_m, in cooling and 2nd heating scanning at 10 °C/min). **a** Easily crystallized, **b** moderately crystallized, **c** weakly crystallized, **d** nearly amorphous and **e** fully amorphous. *Note* Both ΔH_c and ΔH_m are zero for class D, so the "ΔH_m" obtained from the 1st heating scan is shown as a reference

Fig. 4 WAXD patterns of six representative copolyester samples (Run 7 annealed at 30 °C for 48 h, others at −5 °C for 48 h)

be seen from Table 2 that the crystallizability of the copolyesters was also reflected by their appearance, from opaque, translucent to transparent. From detailed comparison of above results, it can be concluded that the monomer structure contributes to the crystallization of multiple

copolyesters in such orders: Se > Az > A > S > T > F > I, B ≫ M ≈ N ≈ E.

All the copolyesters only exhibit one T_g, suggesting that they are all random copolymers. To analyze the effect of structural unit on T_g, all the copolyesters are ranked according to T_g, as shown in Fig. 5. Clearly, introduction of aliphatic diacid(s) with longer alkylene chain (Az, Se) reduces T_g of the copolyesters, but introduction of aromatic
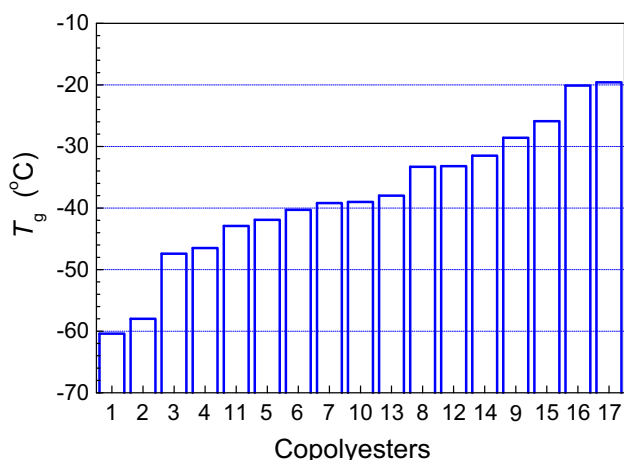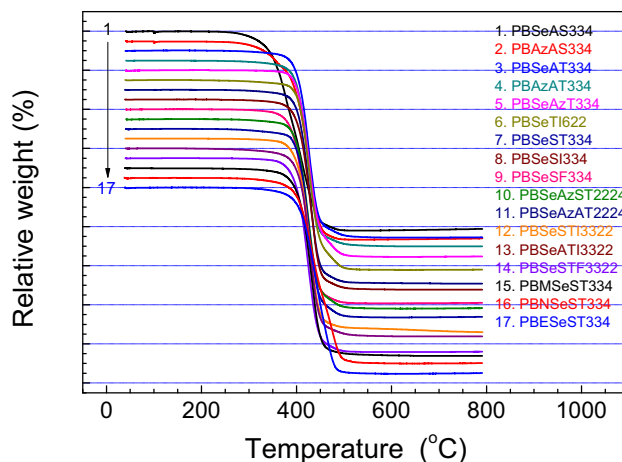
Fig. 5 Ranking of the copolyesters according to their T_g. The tick lables in the horizontal ordinate are the Run numbers of copolyesters indicated in Table 1

Fig. 6 TGA curves of the flexible copolyesters (20 °C/min, in N_2 atmosphere)

diacid(s) or substituted 1,3-propanediol raises T_g of the copolyesters. For the three aromatic diacids, the asymmetry and/or rigidity of the aromatic ring also contribute(s) to higher T_g. It was reported that FDCA has higher rigidity than TPA and lead to less chain mobility [44]. So, the following order of T_g is observed: PBSeST334 (−39.2 °C) < PBSeSI334 (−33.3 °C) ≈ PBSeSTI3322 (−33.2 °C) < PBSeSTF3322 (−31.5 °C) < PBSeSF334 (−28.6 °C). From detailed comparison of T_g data, the monomer structure contributes to T_g in such orders: Se ≈ Az < A < S < T < I < F, B < N ≈ E < M.

In summary, copolycondensation with shorter chain aliphatic diacid, asymmetric aromatic diacid or short-chain branched diol is helpful to depress copolyester crystallization. On the other hand, these factors lead to higher T_g. By compromising these factors, easily crystallized to fully amorphous copolyesters with low enough T_g can be synthesized as required. These copolyesters are reasoned to be biodegradable. And the biodegradability of some of them will be reported later.

Thermal Stability

Thermal stability of the copolyesters was further assessed. The TGA curves are shown in Fig. 6, and the characteristic decomposition temperatures, namely $T_{d,5}$, $T_{d,c}$, $T_{d,max}$, are listed in Table 3. Clearly, all the copolyesters present good to excellent thermal stability. Clearly, in comparison with the aliphatic copolyesters, the aliphatic–aromatic copolyesters exhibit better thermal stability, especially in terms of $T_{d,5}$. Terephthalate- and/or isophthalate-containing aliphatic–aromatic copolyesters have slightly better thermal stability than furandicarboxylate-containing ones. And introduction of short side group(s) does not result in clear

change in thermal stability. So, the existence of benzene ring is favorable to improve the thermal stability of the copolyesters. And the thermal stability of the thirteen copolyesters containing only benzene ring as aromatic unit shows little composition and structure dependence ($T_{d,5}$ 387 ± 4 °C, $T_{d,c}$ 401 ± 2 °C, $T_{d,max}$ 429 ± 4 °C).

Mechanical Properties

Finally, the tensile properties of some copolyesters were measured at room temperature. Specimens of Runs 3–5, 7 and 10–11 were prepared with injection molding and those of Runs 1–2, 6 and 9 were prepared with hot pressing. Different processing methods were used because of their different thermal transition properties. The DSC results show that Runs 3–5, 7 and 10–11 can crystallize at 24–56 °C and have high T_m (∼100 °C), so they crystallized to certain extent during injection molding and could be demolded. The T_m of Runs 1–2 and 6 is around room temperature (21–33 °C) and they can only crystallize at lower temperature. Run 9 is a "nearly amorphous" copolyester. Therefore, it is difficult for them to crystallize and demold in injection molding. But with hot pressing followed by long time cooling with water, specimen preparation still succeeded. Other copolyesters are much less crystallizable or fully amorphous. Their soft or even flowable nature at room temperature prevented them from specimen preparation and mechanical testing.

The Young' modulus, tensile strength and elongation at break are listed in Table 3. Although the two aliphatic copolyesters PBSeAS334 and PBAzAS334 (Runs 1–2) have best crystallizability, their T_ms are low and close to testing temperature, so they have lowest tensile modulus

Table 3 Thermal stability and tensile properties of the flexible copolyesters

Run	Polyester	Decomposition temperature			Tensile property			
		$T_{d,5}$ (°C)	$T_{d,c}$ (°C)	$T_{d,m}$ (°C)	E (MPa)	σ_y (MPa)	σ_b (MPa)	ε_b (%)
1	PBSeAS334	320	340	412	36.5 ± 4.6	2.2 ± 0.2	2.4 ± 0.1	233 ± 53
2	PBAzAS334	331	383	428	26.4 ± 1.9	1.9 ± 0.1	2.7 ± 0.4	560 ± 102
3	PBSeAT334	389	401	427	36.7 ± 1.7	4.4 ± 0.1	7.6 ± 0.3	786 ± 68
4	PBAzAT334	384	399	426	42.5 ± 1.3	5.4 ± 0.2	8.8 ± 0.3	444 ± 52
5	PBSeAzT334	393	402	426	40.6 ± 1.2	6.1 ± 0.2	10.3 ± 0.2	121 ± 14
6	PBSeTI622	393	402	427	56.9 ± 1.9	3.1 ± 0.3	6.3 ± 0.6	1050 ± 163
7	PBSeST334	389	402	427	43.7 ± 4.4	4.5 ± 0.1	7.1 ± 0.2	671 ± 80
8	PBSeSI334	386	401	432	–	–	–	–
9	PBSeSF334	376	389	420	19.3 ± 1.9	2.9 ± 0.1	8.3 ± 0.4	928 ± 81
10	PBSeAzST2224	386	398	426	38.8 ± 1.7	4.7 ± 0.1	7.8 ± 0.2	555.5 ± 28
11	PBSeAzAT2224	389	401	426	41.6 ± 3.2	4.5 ± 0.1	6.7 ± 0.1	490 ± 45
12	PBSeSTI3322	387	402	430	–	–	–	–
13	PBSeATI3322	383	404	427	–	–	–	–
14	PBSeSTF3322	380	397	425	–	–	–	–
15	PBMSeST334	381	404	432	–	–	–	–
16	PBNSeST334	384	399	434	–	–	–	–
17	PBESeST334	388	403	441	–	–	–	–

(E, 26–36 MPa) and strength (σ_b, ca. 2.4–2.7 MPa). In comparison, PBAzAS334 has lower modulus (26 vs. 36 MPa) and higher elongation at break (ε_b, 560 vs. 230 %) than PBSeAS334 due to lower T_m. In comparison with the aliphatic copolyesters, the six weakly crystallizable aliphatic–aromatic copolyesters (Runs 3–5, 7, 10–11) with higher T_m (ca. 100 °C) exhibit higher E (40.7 ± 2.6 MPa), higher σ_b (7.0 ± 0.8 MPa) and even higher ε_b (590 ± 140 %, except for PBSeAzT334). In comparison with these six copolyesters, PBSeTI622 and PBSeSF334 (Runs 6 and 9) have roughly equivalent σ_b and much higher ε_b (930–1050 %) because of low T_m (32 °C) of Run 6 and nearly amorphous nature of Run 9. The above results suggest that introduction of terephthalate into copolyesters can improve the tensile properties possibly due to higher intermolecular interaction among aromatic units, and introduction of isophthalate or furandicarboxylate can further improve the elongation at break because of less crystallizability.

$T_{d,5}$ and $T_{d,m}$ are the characteristic decomposition temperatures at 5 % and maximum weight loss respectively, and $T_{d,c}$ is the characteristic decomposition temperature corresponding to the intersection point of the horizontal line of zero decomposition and the tangent line of maximum decomposition. E, σ_y, σ_b and ε_b are tensile modulus, yielding stress, breaking stress and elongation respectively. For tensile testing, specimens were prepared by injection molding for Runs 3–5, 7, 10–11 and hot pressing for Runs 1, 2, 6, 9.

Conclusions

In this study, novel ternary or multiple random copolyesters containing various structural units were designed, synthesized and characterized, and the effects of chain length, aromaticity, symmetry, rigidity and short-chain branching of the structural units on the crystallization, glass transition temperature and tensile properties of the resultant copolyesters were investigated. Copolyester crystallization can be depressed and glass transition temperature can be raised by incorporating aromatic diacid (especially asymmetric one) or short-chain branched diol. The monomer structure contributes to copolyester crystallization in such an order: Se > Az > A > S > T > F > I, B ≫ M ≈ N ≈ E, but contributes to T_g in an almost reverse order: Se ≈ Az < A < S < T< I < F, B < N ≈ E < M. Through adopting suitable monomer combinations, copolyesters with different aggregating structures, from easily crystallized to fully amorphous, can be synthesized. In addition, the existence of aromatic structural units in copolyesters is helpful to improve their tensile properties. These results will be helpful to design and synthesize biodegradable copolyesters with desired properties for use in impact modifiers and elastomeric materials. Further studies are under way and will be reported soon.

References

1. Drumright RE, Gruber PR, Henton DE (2000) Polylactic acid technology. Adv Mater 12:1841–1846
2. Xu J, Guo BH (2010) Poly(butylene succinate) and its copolymers: research, development and industrialization. Biotechnol J 5:1149–1163
3. Fujimaki T (1998) Processability and properties of aliphatic polyesters, 'BIONOLLE', synthesized by polycondensation reaction. Polym Degrad Stab 59:209–214
4. Yang J, Zhang SP, Liu XY, Cao AM (2003) A study on biodegradable aliphatic poly(tetramethylene succinate): the catalyst dependences of polyester syntheses and their thermal stabilities. Polym Degrad Stab 81:1–7
5. Lim S-K, Jang S-G, Lee S-I, Lee K-H, Chin I-J (2008) Preparation and characterization of biodegradable poly(butylene succinate) (PBS) foams. Macromol Res 16:218–223
6. Tserki V, Matzinos P, Pavlidou E, Vachliotis D, Panayiotouet C (2006) Biodegradable aliphatic polyesters. Part I. Properties and biodegradation of poly(butylene succinate-co-butylene adipate). Polym Degrad Stab 91(2):367–376
7. Tserki V, Matzinos P, Pavlidou E, Panayiotouet C (2006) Biodegradable aliphatic polyesters. Part II. Synthesis and characterization of chain extended poly(butylene succinate-co-butylene adipate). Polym Degrad Stab 91:377–384
8. Nikolic MS, Djonlagic J (2001) Synthesis and characterization of biodegradable poly(butylene succinate-co-butylene adipate)s. Polym Degrad Stab 74:263–270
9. Yamamoto M, Witt U, Skupin G, Beimborn D, Müller R-J. Biodegradable aliphatic–aromatic polyesters: "Ecoflex®". Published Online: 15 Jan 2005. http://onlinelibrary.wiley.com/doi/10.1002/3527600035.bpol4011/full
10. Gan Z, Kuwabara K, Yamamoto M, Abea H, Doiaet Y (2004) Solid-state structures and thermal properties of aliphatic–aromatic poly(butylene adipate-co-butylene terephthalate) copolyesters. Polym Degrad Stab 83(2):289–300
11. Kuwabara K, Gan Z, Nakamura T et al (2002) Crystalline/amorphous phase structure and molecular mobility of biodegradable poly(butylene adipate-co-butylene terephthalate) and related polyesters. Biomacromolecules 3(2):390–396
12. Müller R-J, Kleeberg I, Deckwer W-D (2001) Biodegradation of polyesters containing aromatic constituents. J Biotechnol 86:87–95
13. Chen GQ (2009) A microbial polyhydroxyalkanoates (PHA) based bio-and materials industry. Chem Soc Rev 38:2434–2446
14. Liu HZ, Zhang JW (2011) Research progress in toughening modification of poly(lactic acid). J Polym Sci, Part B: Polym Phys 49:1051–1083
15. Harada M, Ohya T, Iida K, Hayashi H, Hirano K, Fukuda H (2007) Increased impact strength of biodegradable poly(lactic acid)/poly(butylene succinate) blend composites by using isocyanate as a reactive processing agent. J Appl Polym Sci 106:1813–1820
16. Lee S, Wook J (2005) Characterization and processing of Biodegradable polymer blends of poly(lactic acid) with poly(butylene succinate adipate). Korea Aust Rheol J 17:71–77
17. Jiang L, Wolcott MP, Zhang JW (2006) Study of biodegradable polylactide/poly(butylene adipate-co-terephthalate) blends. Biomacromolecules 7:199–207
18. Zhang NW, Zeng C, Wang L, Ren J (2013) Preparation and properties of biodegradable poly(lactic acid)/poly(butylene adipate-co-terephthalate) blend with epoxy-functional styrene acrylic copolymer as reactive agent. J Polym Environ 21:286–292
19. Dong WF, Zou BS, Ma PM, Liu WC, Zhou X, Si DJ, Ni ZB, Chen MQ (2013) Influence of phthalic anhydride and bioxazoline on the mechanical and morphological properties of biodegradable poly(lactic acid)/poly[(butylene adipate)-co-terephthalate] blends. Polym Int 62:1783–1790
20. Park H-S, Seo J-A, Lee H-Y, Kim H-W, Wall IB, Gong M-S, Knowles JC (2012) Synthesis of elastic biodegradable polyesters of ethylene glycol and butylene glycol from sebacic acid. Acta Biomater 8(8):2911–2918
21. Zeng XQ, Wu BS, Wu LB, Hu JJ, Bu ZY, Li B-G (2014) Poly(L-lactic acid)-block-poly(butylene succinate-co-butylene adipate) multiblock copolymers: from synthesis to thermo-mechanical properties. Ind Eng Chem Res 53:3550–3558
22. Ba C, Yang J, Hao Q, Liu X, Cao AM (2003) Syntheses and physical characterization of new aliphatic triblock poly(L-lactide-b-butylene succinate-b-L-lactide)s bearing soft and hard biodegradable building blocks. Biomacromolecules 4:1827–1834
23. Xu C-L, Zeng J-B, Zhu QY, Wang Y-Z (2013) Poly(ethylene succinate)-b-poly(butylene succinate) multiblock copolyesters: the effects of block length and composition on physical properties. Ind Eng Chem Res 52:13669–13676
24. Li S-L, Zeng J-B, Wu F, Yang Y, Wang Y-Z (2014) Succinic acid based biodegradable thermoplastic poly(ester urethane) elastomers: effects of segment ratios and lengths on physical properties. Ind Eng Chem Res 53:1404–1414
25. Li WD, Zeng JB, Li YD, Wang XL, Wang YZ (2009) Synthesis of high-molecular-weight aliphatic-aromatic copolyesters from poly(ethylene-co-1,6-hexene terephthalate) and poly(L-lactic acid) by chain-extension. J Polym Sci, Part A: Polym Chem 47:5898–5907
26. Odeng J, Habibi Y, Raquez J-M, Dubois P (2013) Ultra-tough polylactide-based materials synergistically designed in the presence of rubbery ε-caprolactone-based copolyester and silica nanoparticles. Comp Sci Technol 84:86–91
27. Qiu ZB, Fujinam S, Komura M, Nkajima K, Ikehara T, Nishi T (2004) Nonisothermal crystallization kinetics of poly(butylene succinate) and poly(ethylene succinate). Polym J 36:642–646
28. Kai WH, Zhu B, He Y, Inoue Y (2005) Crystallization of poly(butylene adipate) in the presence of nucleating agents. J Polym Sci, Part B: Polym Phys 43:2340–2351
29. Mincheva R, Delangre A, Raquez JM, Narayan R, Dubois P (2013) Biobased polyesters with composition-dependent thermomechanical properties: synthesis and characterization of poly(butylene succinate-co-butylene azelate). Biomacromolecules 14:890–899
30. Cao AM, Okamura T, Nakayama K, Inoue Y, Masuda T (2002) Studies on syntheses and physical properties of biodegradable aliphatic poly(butylene succinate-co-ethylene succinate)s and poly(butylene succinate-co-diethylene glycol succinate)s. Polym Degrad Stab 78:107–117
31. Liang ZC, Pan PJ, Zhu B, Inoue Y (2011) Isomorphic crystallization of aliphatic copolyesters derived from 1, 6-hexanediol: effect of the chemical structure of comonomer units on the extent of cocrystallization. Polymer 52:2667–2676
32. Papageorgiou GZ, Bikiaris DN (2007) Synthesis, cocrystallization, and enzymatic degradation of novel poly(butylene-co-propylene succinate) copolymers. Biomacromolecules 8:2437–2449
33. Tsai C-J, Chang W-C, Chen C-H, Lu H-Y, Chen M (2008) Synthesis and characterization of polyesters derived from succinic acid, ethylene glycol and 1,3-propanediol. European Polym J 44:2339–2347

34. Nagata M, Goto H, Sakai W, Tsutsumi N (2000) Synthesis and enzymatic degradation of poly(tetramethylene succinate) copolymers with terephthalic acid. Polymer 41:4373–4376

35. Wu L, Mincheva R, Xu Y, Raquez J-M, Dubois P (2012) High molecular weight poly(butylene succinate-co-butylene furandicarboxylate) copolyesters: from catalyzed polycondensation reaction to thermomechanical properties. Biomacromolecules 13(9):2973–2981

36. Wu B, Xu Y, Bu Z et al (2014) Biobased poly(butylene 2,5-furandicarboxylate) and poly(butylene adipate-co-butylene 2,5-furandicarboxylate)s: from synthesis using highly purified 2,5-furandicarboxylic acid to thermo-mechanical properties. Polymer 55(16):3648–3655

37. Deng L-M, Wang Y-Z, Yang K-K, Wang X-L, Zhou Q, Ding S-D (2004) A new biodegradable copolyester poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate). Acta Mater 52(20):5871–5878

38. Chen C-H, Yang C-S, Chen M, Shih Y-C, Hsu H-S, Lu S-F (2011) Synthesis and characterization of novel poly(butylene succinate-co-2-methyl-1,3-propylene succinate)s. Express Polym Lett 5:284–294

39. Japu C, de Ilarduya AM, Alla A, García-Martín MG, Galbis JA, Muñoz-Guerra S (2014) Bio-based PBT copolyesters derived from D-glucose: influence of composition on properties. Polym Chem 5(9):3190–3202

40. Japu C, de Ilarduya AM, Alla A, García-Martín MG, Galbis JA, Muñoz-Guerra S (2013) D-Glucose-derived PET copolyesters with enhanced T g. Polym Chem 4(12):3524–3536

41. Japu C, Martínez de Ilarduya A, Alla A, Jiang Y, Loos K, Muñoz-Guerra S (2015) Copolyesters made from 1, 4-butanediol, sebacic acid, and D-glucose by melt and enzymatic polycondensation. Biomacromolecules 16(3):868–879

42. Japu C, de Ilarduya AM, Alla A, Muñoz-Guerra S (2013) Bio-based poly(hexamethylene terephthalate) copolyesters containing cyclic acetalized tartrate units. Polymer 54(6):1573–1582

43. Woo EM, Wu MC (2005) Thermal and X-ray analysis of polymorphic crystals, melting, and crystalline transformation in poly(butylene adipate). J Polym Sci, Part B: Polym Phys 43:1662–1672

44. Burgess SK, Leisen JE, Kraftschik BE, Mubarak CR, Kriegel RM, Koros WJ (2014) Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate). Macromolecules 47:1383–1391