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Low-crystallinity to highly amorphous copolyesters with high glass transition temperatures based on rigid carbohydrate-derived building blocks

Jingying Chen,^{a,b} Yiming Lin,^a Yong Chen,^{a,c} Cor E Koning,^{b,d} Jing Wu^{c,*} and Huaping Wang^{a,c,*}



Abstract

The current trend of developing novel biobased polymeric materials is focused more on utilizing the unique structural/physical properties of renewable building blocks towards niche market applications. In this work, with the aim of developing low-crystallinity to amorphous polyesters with enhanced thermal properties, a series of copolyesters based on rigid and structurally asymmetric carbohydrate-derived building blocks, namely furan-2,5-dicarboxylic acid and isosorbide, and 1,4-butanediol were successfully synthesized using melt polycondensation. The copolyesters were obtained with varied chemical compositions and rather high molecular weights ($M_n = 24\,000\text{--}31\,000\text{ g mol}^{-1}$) and intrinsic viscosities ($[\eta] = 0.56\text{--}0.72\text{ dL g}^{-1}$). Incorporation of both building blocks significantly enhances the glass transition temperatures ($T_g = 38\text{--}107\text{ }^\circ\text{C}$) of polyesters, and also efficiently inhibits the crystallization of the copolyesters. A low content of isosorbide (ca 10 mol%) leads to complete transition of the homopolyester to nearly fully amorphous materials. Detailed characterizations of the chemical structures and thermal properties of the synthesized copolyesters were conducted using various analytical techniques. In addition, hydrolytic and enzymatic degradations of the copolymers in the presence of porcine pancreatic lipase and cutinase were also investigated.

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

Keywords: amorphous polyesters; biobased monomers; biodegradable polymers; carbohydrates; 2,5-furandicarboxylic acid; isosorbide

INTRODUCTION

Plastics are undoubtedly some of the most important types of materials for modern society, which are typically synthetic polymers of high molecular weight mostly produced from petrochemical feedstock.¹ About a third of plastics are used for packaging, roughly the same proportion for construction applications such as piping, plumbing or vinyl siding and the remainder being used for automobiles (up to 20%), furniture, toys, etc. Worldwide, about 50 kg of plastics are produced annually per person, and this number doubles almost every 10 years.² Polyester takes up about 18% of world plastics production and is the fourth-most-produced polymer after polyethylene, polypropylene and poly(vinyl chloride).¹ Semicrystalline polyesters, such as poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) and poly(butylene terephthalate) (PBT), are currently the major types of polyesters and have been extensively applied for producing fibers, films and engineering plastics. Their good crystallization properties endow them with excellent thermal and mechanical properties, chemical resistance and excellent moldability under various processing conditions.¹

Different from semicrystalline polyesters, polyesters with low crystallinity and even fully amorphous polyesters have also

become more and more important and now constitute a unique type of speciality polyester. The strategy for producing these polyesters is often to copolymerize the known PET or PBT semicrystalline polyesters with one or a few co-monomers, for instance, isophthalic acid,^{3,4} adipic acid,^{5,6} 1,4-cyclohexanedimethanol,⁷ 1,2-propanediol,^{8–10} etc. Incorporation of the co-monomer (s) strongly interferes with the regular crystalline structure of semi-crystalline homopolyesters by increasing entropy or

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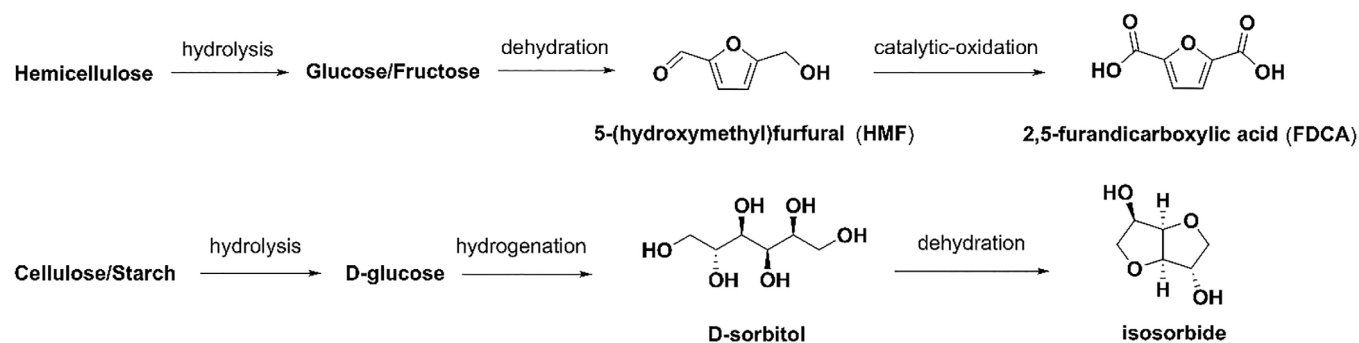
reducing enthalpy, which causes significant decreases of the melting temperatures and the corresponding melting/crystallization enthalpies of polymers. Such an effect is commonly known as a 'melting-depressing effect' during copolymerizations.¹¹ PET-based low-melting polyesters have been used as the sheath component to produce sheath–core composite fibers and have found important applications in nonwoven fabrics. By controlling processing temperatures, only the sheath layer made of low-melting PET melts which smartly glues the entire fiber web together into a nonwoven fabric. This technique is both economically and ecologically favored compared to the traditional nonwoven process where large amounts of adhesives are used to form fiber webs. The nonwoven products have been extensively applied for skin-contact hygiene products in recent years. As crystallinity causes light refraction, amorphous polymers usually provide good transparency when used as films or plastic parts. In the field of engineering plastics, the presence of low-crystallinity or amorphous polyesters in PET/PBT blends brings excellent surface gloss to plastic parts, which significantly increases the added values of products towards high-end applications, for example piano surfaces or automobiles.⁷

Recently, development of novel polymers from renewable resources has become a research focus given the ever-increasing concerns of unrestrained use of fossil feedstock. In 2004, the US Department of Energy released a list of 'top ten biobased chemicals' with high potentials for new generation of synthetic materials, which triggered extensive research into developing novel synthetic polymers based on these molecules.¹² Among them, furan-2,5-dicarboxylic acid (FDCA) is the only aromatic di-functionalized building block suitable for polymer synthesis. It has been widely perceived as a promising renewable alternative to replace terephthalic acid. FDCA can be synthesized from raw biomass in a few steps. A known procedure as depicted in Scheme 1 is: (i) hydrolysis of hemicellulose to glucose; (ii) dehydration of glucose to 5-(hydroxymethyl)furfural; and (iii) catalytic oxidation of 5-(hydroxymethyl)furfural to FDCA. A variety of FDCA-based polyester analogs have been extensively investigated for packaging, textiles, coatings, etc.¹³ In general, FDCA-based polyesters exhibit comparable thermal properties to PET and much improved gas barrier properties (6–11 times higher for oxygen and 13–19 times higher for carbon dioxide, polyethylene furandicarboxylate *versus* PET); and at the same time are featured by significantly lower (*ca* 45%) emission of greenhouse gases from the viewpoint of life cycle assessment.^{14–16}

Besides FDCA, sorbitol is another promising molecule on the same list recommended by the US Department of Energy, which is commonly obtained by depolymerization of polysaccharides

and subsequently hydrogenation of glucose intermediate (Scheme 1). Nevertheless, the presence of multiple primary and secondary hydroxyl groups makes it difficult to be directly used for synthesizing linear step-growth polyesters.¹⁷ As an interesting family of di-functional and cyclic derivatives of sorbitol, 1,4-3,6-dianhydrohexitols (also called isohexides) are obviously more suitable for use in polyester synthesis. Depending on the different stereoconfigurations, there are three isomers of isohexides, namely isosorbide (IS), isomannide and isoidide. The central skeletons of isohexides are uniquely formed by two *cis*-fused tetrahydrofuran rings. This bicyclic structure of isohexides is not entirely planar by showing V-shape openings with dihedral angles of approximately 120°. ¹⁷ Moreover, these aliphatic cyclic building blocks are highly rigid. When incorporated into polymer main chains, they significantly enhance the glass transition temperature (T_g) of the materials. This effect has been clearly demonstrated in several polymer systems, like poly(butylene succinate),^{18–20} poly(ethylene succinate)²¹ and poly(decamethylene 2,5-furandicarboxylate).²² Therefore, it potentially broadens the application window of polymers towards niche markets where enhanced thermal properties are desired. Moreover, the presence of IS moieties in polymers also markedly enhances the wettability of polymer surfaces, which strongly promotes the hydrolytic/enzymatic degradation property of polymers. We recently have systematically investigated such a synergistic effect by incorporating IS units progressively into PBT or poly(butylene succinate).^{23, 24} Crystallinity is known to be a key factor determining the biodegradability of plastics. A high crystallinity of polymers, meaning a dense and ordered packing of macromolecules, tends to prevent fast diffusion of water into the inner part of the plastics. Therefore, the first stage of hydrolysis is strongly inhibited, hence lowering the degradation rate of the materials. Incorporation of asymmetric IS comonomers into polymers, on the one hand, reduces polymer crystallinity through incorporation into the amorphous domain and, on the other hand, evokes faster hydrolyses of esters. As shown for the IS-modified poly(butylene succinate) copolyester, isosorbide succinate units degrade substantially faster than butylene succinate units.²⁴ Given these notable properties of such carbohydrate-derived compounds, isohexides, in particular IS that is commercially available on a metric ton scale, have been extensively explored as (co)monomers for developing novel polycondensates in the last three to four decades, including polyesters, polyamides, polycarbonates and so on.^{25, 26}

In the work reported here, we aimed to develop low-crystallinity to highly amorphous polyesters with enhanced material performance by utilizing two highly promising carbohydrate-derived building blocks, namely FDCA and IS. Given that both molecules



Scheme 1. Production routes of FDCA and IS from biomass raw material.

have asymmetric structures, high rigidity and high hydrophilicity, it was therefore expected that copolyesters based on them can afford novel low-crystallinity to highly amorphous polyesters with high T_g and improved biodegradation properties. Copolyesters based on FDCA, IS and 1,4-butanediol (BDO), namely poly[(butylene furan-2,5-dicarboxylate)-co-(isosorbide furan-2,5-dicarboxylate)]s (PBIFs), with varied chemical compositions were synthesized to systematically elucidate the thermal, crystallization and degradation properties imposed by the two unique oxy-heterocyclic biobased building blocks.

MATERIALS AND METHODS

Materials

Dimethyl 2,5-furandicarboxylate (DMF; >98%) was purchased from Nanjing Para Biotechnology Co. Ltd. BDO (99%) was purchased from TCI. Irganox 1010 antioxidant was received as a gift from BASF. Titanium tetrabutoxide (TBT; >97%), IS (>98%, GC), chloroform ($\geq 99.5\%$), trifluoroacetic acid (TFA; 99%), 1,1,2,2-tetrachloroethane (TTCE; $\geq 98\%$) and methanol were purchased from Adamas-beta. All the reagents and solvents were of technical or high-purity grade, and were used as received without further purification. Porcine pancreatic lipase (PP enzyme; activity 30 000 units mg^{-1}) and cutinase (Novozym 51032; activity 15 000 LU g^{-1}) were purchased from Novozymes Biotechnology Co. Ltd. They were used as biodegradation enzymes; one unit is defined as the amount of enzyme that catalyzes the release of fatty acid from triglycerides at the rate of 1 $\mu\text{mol min}^{-1}$.

Polymer synthesis

PBIF copolyesters with various compositions were synthesized from DMF, BDO and IS using a conventional two-step polycondensation procedure. A typical polycondensation reaction is described as follows. The reaction was performed in a customized 250 mL four-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, a temperature probe and a vacuum distillation outlet. The apparatus was purged with nitrogen five times at room temperature to remove air. The first-step transesterification reaction was carried out at 150–160 °C under mild nitrogen flow for 3–4 h until the volume of the collected methanol condensate reached >90% of its theoretical amount. Next, the pressure was gradually reduced to initiate the polycondensation step. The vacuum was ultimately maintained to be lower than 0.5 mbar, while the temperature of the melt was raised stepwise to 200 to 220 °C. After polymerization for 2.5–3.5 h, the melt was cooled to room temperature. The crude product was dissolved in a $\text{CHCl}_3/\text{TTCE}/\text{TFA}$ (8:1:1, v/v/v) mixture, and then the solution was poured into an excess of methanol. The precipitated polymer was recovered by filtration, washed with methanol and dried under vacuum to constant weight.

Because of the high boiling point of IS, and the difficulty of complete removal of excess IS by vacuum distillation, the feed ratios of diols/DMF were varied for PBIF copolyesters of various chemical compositions. Detailed polymerization conditions can be found in Table S1.

General methods

Intrinsic viscosities of the PBIF copolyesters were measured using an Ubbelohde viscometer with a mixture of phenol and TTCE (60:40, w/w) as solvent at 25 ± 0.1 °C and polymer concentrations of 0.25 g dL^{-1} .

The molecular weight and molecular weight distribution of PBIF copolyesters were measured at 40 °C using a system equipped with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector (35 °C), a Waters 2707 auto-sampler and a PSS PFG guard column followed by two PFG-linear-XL (7 μm , 8 \times 300 mm) columns in series. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) with potassium trifluoroacetate (3 g L^{-1}) was used as the mobile phase at a flow rate of 0.8 mL min^{-1} . The molecular weights were calculated against poly(methyl methacrylate) standards (Polymer Laboratories, $M_p = 580$ up to 7.1×10^6).

^1H NMR and ^{13}C NMR spectra of PBIFs were recorded with a Bruker AV400 spectrometer at frequencies of 600.1 and 75.5 MHz, respectively, and were internally referenced with tetramethylsilane. Samples were prepared by dissolving *ca* 10 and 50 mg of polymer, respectively, for ^1H NMR and ^{13}C NMR in 1 mL of a $\text{CDCl}_3/\text{C}_2\text{Cl}_4\text{D}_2/\text{CF}_3\text{COOD}$ (8:1:1 v/v/v) mixture. The number of scans for ^1H NMR was 64, and between 5000 and 15 000 scans were taken for ^{13}C NMR with 32 000 and 64 000 data points and relaxation delays of 1 and 2 s, respectively. The temperature for all experiments was 25 °C. (*PBF homopolyester*: ^1H NMR (600.1 MHz, $\text{CDCl}_3/\text{C}_2\text{Cl}_4\text{D}_2/\text{CF}_3\text{COOD}$; δ , ppm): 7.3, 4.5, 2.0. ^{13}C NMR (75.5 MHz, $\text{CDCl}_3/\text{C}_2\text{Cl}_4\text{D}_2/\text{CF}_3\text{COOD}$; δ , ppm): 159.7, 146.4, 119.6, 66.2, 24.9. *PBIF copolyesters*: ^1H NMR (600.1 MHz, $\text{CDCl}_3/\text{C}_2\text{Cl}_4\text{D}_2/\text{CF}_3\text{COOD}$; δ , ppm): 7.3, 5.6, 5.2, 4.8, 4.5, 4.3, 4.2, 2.0. ^{13}C NMR (75.5 MHz, $\text{CDCl}_3/\text{C}_2\text{Cl}_4\text{D}_2/\text{CF}_3\text{COOD}$; δ , ppm): 159.7, 146.4, 119.6, 85.6, 81.1, 78.7, 75.1, 73.2, 70.6, 66.2, 24.9.)

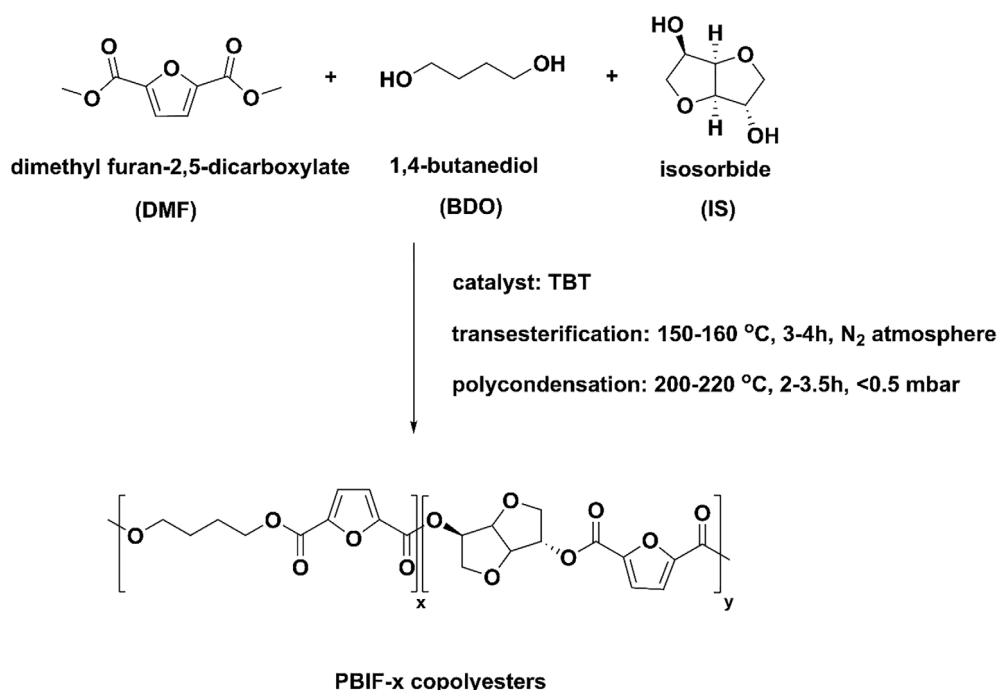
Thermal stability of the polymers was investigated using TGA with TG 209 F1 Iris equipment. Samples (5–10 mg) were heated from 30 to 600 °C under a nitrogen flow of 20 mL min^{-1} . The heating rate was 10 °C min^{-1} .

Thermal behavior of the PBIF polyesters was obtained from 5–10 mg samples using DSC with a TA DSC Q20 apparatus under a nitrogen flow of 20 mL min^{-1} . The heating/cooling rate was 10 °C min^{-1} . Indium and zinc were used as standards for temperature and enthalpy calibration.

Crystalline structure of the polymers was studied using wide-angle XRD (WAXD) measurements in powder form by means of a computer-controlled goniometer coupled to a sealed-tube source of $\text{Cu K}\alpha$ radiation ($\lambda = 0.124$ nm).

SEM images were obtained from Pt/Pd-coated samples using a field-emission 8010 instrument (Hitachi, Japan).

Films of the polymers with a thickness of *ca* 70 μm for hydrolytic and enzymatic degradation studies were prepared by compression molding. The films were cut into rectangular pieces of 15–30 mg in weight and 7 mm \times 15 mm in size and dried under vacuum to constant weight. For hydrolytic degradation, samples were immersed in vials containing 10 mL of citric acid buffer solution (pH 2.4). After incubation at 80 °C for the scheduled period of time, the samples were taken out from the vial, rinsed thoroughly with deionized water and dried to constant weight. Enzymatic degradation was carried out at 37 °C by immersing a piece of PBIF film in 10 mL of sodium phosphate buffer solution (pH 7.2) containing 10 mg of PP enzyme or the same amount of cutinase in each vial. Enzymatic degradation buffer solution was replaced every 72 h to maintain enzyme activity. At the end of the scheduled incubation periods, the films were withdrawn from the vials, washed thoroughly with deionized water, dried to constant weight and analyzed using SEC to characterize the changes of molecular weights and molecular weight distributions.



Scheme 2. Synthetic route to PBIF copolyesters; x denotes the molar percentage of IS units in the copolyesters.

Table 1. Composition, molecular weight, sequence length and degree of randomness of PBIF copolyesters

Copolyester	Yield ^a (%)	Molar ratio (X_B/X_{IS})		Molecular weight			Intrinsic viscosity [η] ^d (dL g ⁻¹)	Sequence length ^e		Randomness ^f (R)
		Feed	Copolyester ^b	M_n^c (g mol ⁻¹)	M_w^c (g mol ⁻¹)	\mathcal{D}^c		$n_{n,BF}$	$n_{n,IF}$	
PBF	95	100/0	100/0	28 900	64 800	2.2	0.68	—	—	—
PBIF-7	90	90/10	93/7	30 600	82 200	2.7	0.72	9.9	1.2	0.93
PBIF-17	92	80/20	83/17	31 000	78 500	2.5	0.72	5.7	1.3	0.94
PBIF-27	88	70/30	73/27	31 000	86 400	2.8	0.72	4.3	1.4	0.95
PBIF-51	82	60/40	49/51	24 400	68 000	2.8	0.56	3.8	1.5	0.93
PBIF-63	70	50/50	37/63	24 000	60 700	2.5	0.56	3.0	1.7	0.99

^a Isolated yield was determined after precipitation from HFIP/methanol.

^b Molar ratios were determined by integration of ¹H NMR spectra.

^c Number- and weight-average molecular weights and \mathcal{D} were measured using SEC in HFIP against poly(methyl methacrylate) standards.

^d Intrinsic viscosity [η] was measured in a mixture of phenol and 1,1,2,2-tetrachloroethane (60:40, w/w) at 25 °C.

^e Sequence lengths of repeat units were determined from Eqns (4) and (5).

^f Randomness values were calculated from Eqn (6) after sequence lengths $n_{n,BF}$ and $n_{n,IF}$ were obtained.

RESULTS AND DISCUSSION

Synthesis and structural characterization of copolyesters

A series of PBIF- x copolyesters were synthesized using a two-stage polycondensation method from DMF, BDO and IS, where x represents the molar percentage of IS relative to the total diol amount in the polyesters (Scheme 2). The well-known TBT was used as transesterification catalyst. Data for chemical composition, molecular weight, polydispersity and microstructure of all synthesized copolyesters are compiled in Table 1.

Because of the high steric hindrance of its secondary hydroxyl groups and also possible engagement of forming intramolecular

hydrogen bonds of *endo*-hydroxyls, the reactivity of IS is considerably lower than those of linear α,ω -alkylene diols, such as ethylene glycol, which often leads to an imbalance of co-monomer ratios before and after polymerizations.^{17, 27–29} As we were investigating the overall properties of PBIF copolyesters, the synthesis of the same type of copolyesters was also reported by Wang *et al.*³⁰ The authors reported the same trend regarding the general lower final fractions of IS incorporated into copolyesters compared to the linear diol BDO in this case. As is evident from Table 1, it seems that thermal loss of IS at higher dosage (>30 mol%) becomes less significant. The reason for this might be due to the much lower

transesterification (150 °C) and polycondensation temperatures (180–200 °C) and the excess amount of diols for high IS feed copolyesters for fast and complete distillation.

The target PBIF copolyesters containing up to 50 mol% IS were obtained with fairly high molecular weights ($M_n = 24\,000\text{--}31\,000\text{ g mol}^{-1}$) and intrinsic viscosities ($[\eta] = 0.56\text{--}0.72\text{ dL g}^{-1}$). Compared with terephthalic acid-based copolyesters with comparable chemical compositions, higher degrees of discoloration were observed for PBIF copolyesters which was due to thermal decomposition side reactions of FDCA and IS. The extent of

gelation side reactions was insignificant given that the synthesized materials with low IS content were fully soluble in HFIP. A certain degree of branching or even gelation occurred, especially when higher contents of IS were used. These samples with high IS content were somehow unable to be completely dissolved in the solvent. Therefore, the final molecular weights obtained using gel permeation chromatography should be the partial sample with a certain degree of branching by showing broadened polydispersity values. Therefore, the molecular weights were generally higher than those expected of fully

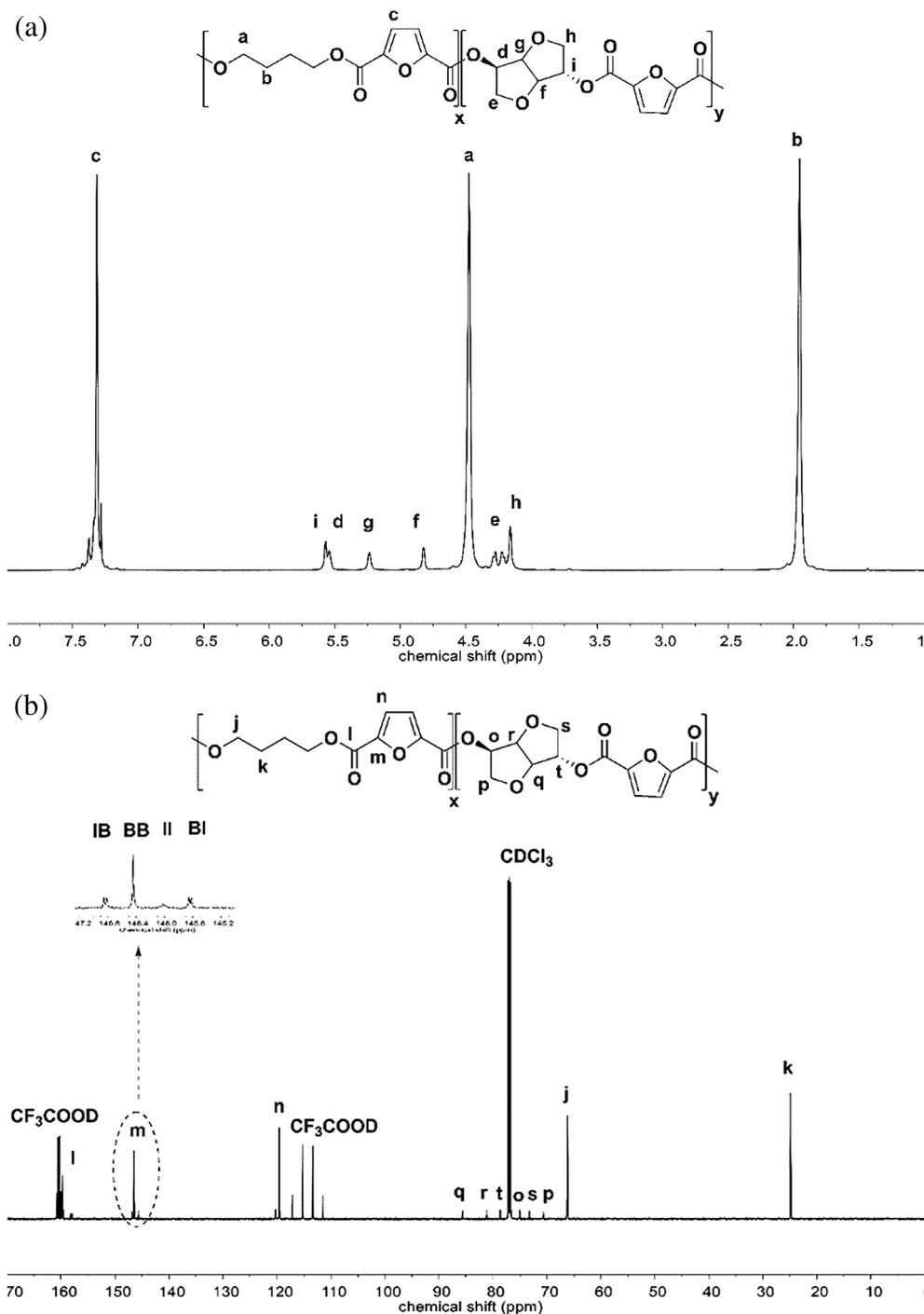


Figure 1. (a) ¹H NMR and (b) ¹³C NMR spectra of PBIF-27 copolyester recorded in a CDCl₃/C₂Cl₄D₂/CF₃COOD (8:1:1 v/v/v) mixture at 600.1 and 75.5 MHz, respectively.

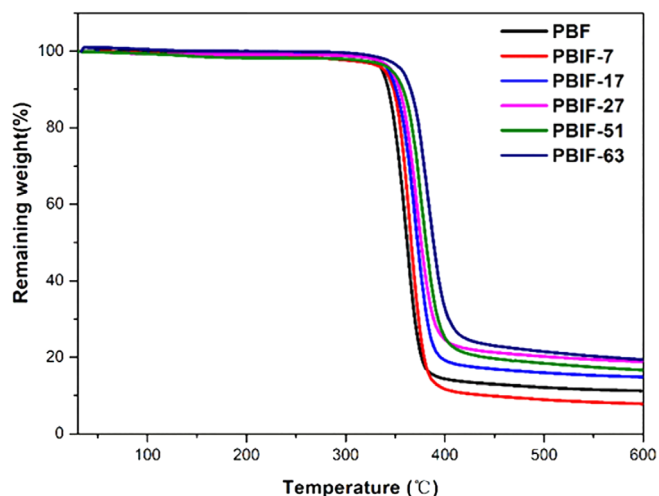


Figure 2. TGA traces of PBIF copolyesters recorded from 30 to 600 °C at 10 °C min⁻¹ under N₂ atmosphere.

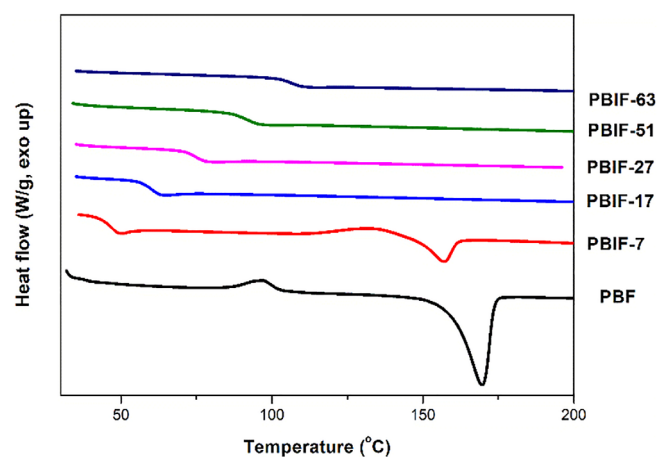


Figure 3. Second heating DSC curves of PBIF copolyesters measured from 20 to 240 °C at 10 °C min⁻¹ heating rate under N₂ atmosphere.

linear products. Although the final products were purified by a dissolution/precipitation step, a slight increase of polydispersity from 2.2 to 2.8 was observed as the content of IS increases. This might be an indication of occurrence of branching side reactions that cause the broadening of the molecular weight distribution.

The constitution of the copolymers was ascertained using ¹H NMR and ¹³C NMR spectroscopy. The NMR spectra of PBIF-27 are representatively shown in Fig. 1. All the ¹H NMR signals of PBIF-27 can be found with correct chemical shifts. The signal patterns are in agreement with results reported in the literature.³⁰ The actual molar ratios of BDO/IS in the products were calculated by integrating the resonance signals appearing at 2.0 and 4.8 ppm assigned as **b** protons of BDO and **f** protons of IS, respectively. Since ¹³C resonances of the nonprotonated aromatic carbons are sensitive to sequence distributions at the level of dyads (BB, BI/IB and II; Fig. 1), the microstructures of PBIF copolyesters were determined by assigning the four well-resolved ¹³C signals appearing in the 145.4–146.9 ppm chemical shift region as shown

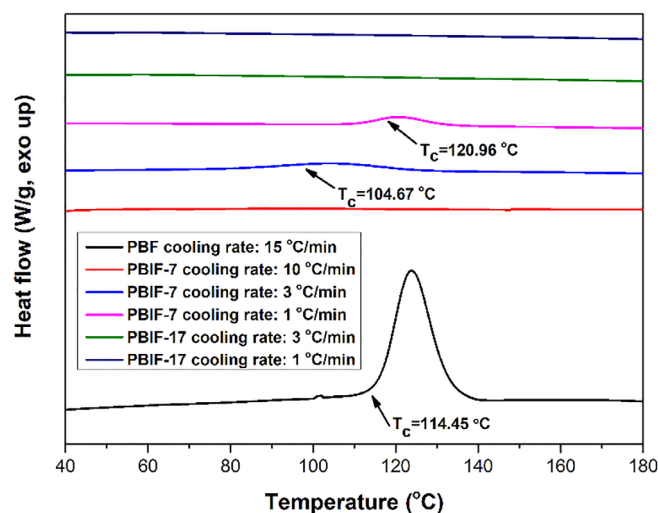


Figure 4. Second cooling DSC scans under non-isothermal crystallization conditions with various cooling rates.

Table 2. Thermal and crystallization properties of PBIF copolyesters measured using TGA, DSC and WAXD

Polyester	TGA			DSC									WAXD Crystallinity ^f (%)
	T _{5%} ^a (°C)	T _{max} ^b (°C)	R _w ^c (%)	First heating			Cooling		Second heating				
				T _g ^d (°C)	T _m ^e (°C)	ΔH _m ^e (J g ⁻¹)	T _c ^e (°C)	ΔH _c ^e (J g ⁻¹)	T _g ^d (°C)	T _m ^e (°C)	ΔH _m ^e (J g ⁻¹)		
PBF	337	362	11.3	38	158	41	104	35	38	160	39	27	
PBIF-7	339	365	7.9	47	149	5	—	—	45	—	—	—	
PBIF-17	343	370	14.8	61	—	—	—	—	54	—	—	—	
PBIF-27	346	371	18.8	76	—	—	—	—	71	—	—	—	
PBIF-51	346	373	16.7	92	—	—	—	—	84	—	—	—	
PBIF-63	357	384	19.4	107	—	—	—	—	105	—	—	—	

^a Temperature at which 5% weight loss was observed in TGA traces recorded at 10 °C min⁻¹.

^b Temperature of maximum degradation rate.

^c Remaining weight at 600 °C.

^d Value of T_g was taken as the inflection point of the heating DSC traces of melt-quenched samples recorded at 10 °C min⁻¹.

^e Melting (T_m) and crystallization (T_c) temperatures and their respective enthalpies (ΔH_m, ΔH_c) measured by DSC at heating/cooling rates of 10 °C min⁻¹.

^f Crystallinities of copolyesters were calculated through peak deconvolution of powder WAXD results using PeakFit v4.12 software.

Table 3. Thermal properties of PBF and PBIF copolyesters during non-isothermal crystallization

Sample	First heating			Second heating			Cooling	
	T_g (°C)	T_m (°C)	ΔH_m (J g ⁻¹)	T_g (°C)	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	ΔH_m (J g ⁻¹)
PBF	63	170	35	—	171	35	115 (15 °C min ⁻¹)	33
PBIF-7	45	158	7	45	158	6	121 (1 °C min ⁻¹)	6
				45	158	3	105 (3 °C min ⁻¹)	3
				42	159	1	— (10 °C min ⁻¹)	—
PBIF-17	58	—	—	58	—	—	— (1 °C min ⁻¹)	—
	62	—	—	59	—	—	— (3 °C min ⁻¹)	—

in Fig. 1. Integration of each quaternary carbon is expressed by I_i , where $i = 1, 2, 3, 4$ indicating the integration of BB, II, BI and IB peaks, respectively (see Fig. 1). The fractions of dyads (N), the number-average sequence lengths of BF and IF repeat units ($n_{n,BF}$ and $n_{n,IF}$) and the degree of randomness (R) were then derived by calculation from Eqns (1)–(6):

$$N_{BB} = I_1 / (I_1 + I_2 + I_3 + I_4) \quad (1)$$

$$N_{BI+IB} = (I_3 + I_4) / (I_1 + I_2 + I_3 + I_4) \quad (2)$$

$$N_{II} = I_2 / (I_1 + I_2 + I_3 + I_4) \quad (3)$$

$$n_{n,BF} = 1 + 2N_{BB} / N_{BI+IB} = (2I_1 + I_3 + I_4) / (I_1 + I_2 + I_3 + I_4) \quad (4)$$

$$n_{n,IF} = 1 + 2N_{II} / N_{BI+IB} = (2I_2 + I_3 + I_4) / (I_1 + I_2 + I_3 + I_4) \quad (5)$$

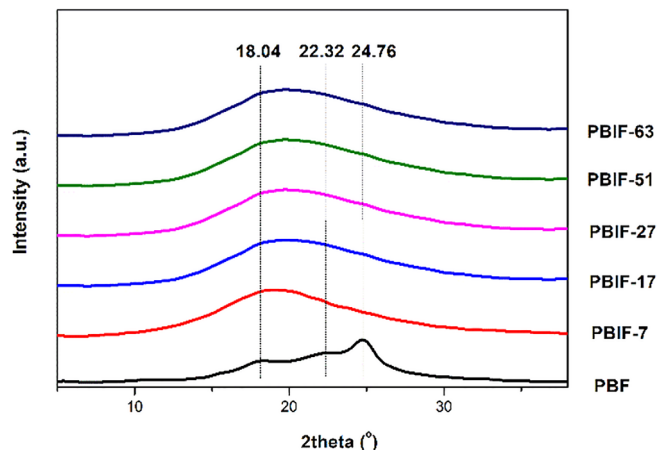
$$R = 1 / n_{n,BF} + 1 / n_{n,IF} \quad (6)$$

Thermal properties of copolyesters

Thermal stability of the synthesized copolyesters was determined using TGA. The TGA traces of the PBIF copolyesters, measured from 30 to 600 °C under N₂ atmosphere, are depicted in Fig. 2. Temperatures at 5% weight loss ($T_{5\%}$) and maximum degradation rates (T_{max}) are listed in Table 2. On the basis of these data, we could see that the PBIF copolyesters were thermally stable up to 350 °C. The degradation profiles of these polyesters basically exhibited one major step with T_{max} values appearing at around 380 °C, leaving approximately 8–20% of degradation residues upon heating to 600 °C.

The thermal transition temperatures including melting, glass transition and crystallization temperatures, as well the respective enthalpies were determined using DSC. Data for these parameters are compiled in Table 2, while the DSC traces are depicted in Fig. 3. The T_g values obtained in our work firmly confirmed the high rigidity of IS that steadily enhanced T_g of the PBIF copolyesters (Fig. 3): PBIF-63 displayed a markedly high T_g of 92 °C, which is slightly higher than that of PET ($T_g = 85$ °C). According to the work of Storbek and Ballauff,³¹ T_g of poly(isosorbide 2,5-furandicarboxylate) homopolymer was estimated to be nearly 196 °C, which obviously puts this polymer in the high-performance category if sufficiently high molecular weight can be achieved.

When comparing with highly symmetric terephthalic acid, although FDCA is an axially symmetric molecule, the two carboxyl groups are actually located with an intersection angle of approximately 129–134°.³² Yet, PBF homopolymer remained a semicrystalline material exhibiting rather good crystallization ability by showing clear crystallization transitions even when the samples were measured under fairly high cooling rate of 10 °C min⁻¹. The melting/crystallization enthalpies are ca 40 J g⁻¹ as evident


Figure 5. WAXD profiles of PBF homopolymer and PBIF copolyesters.

from Table 2. The molecular structure of IS is quite asymmetric not only with a dihedral angle of the two *cis*-fused tetrahydrofuran moieties of approximately 120°,³² but also with opposite stereo-configurations of the two hydroxyls. Incorporation of FDCA and IS molecules into the same polymer main chains strongly interferes with polymer crystallization and usually affords amorphous materials. As observed from DSC analysis, the crystallization exotherms and melting endotherms were only recognizable for PBIF copolyester containing 7 mol% IS (PBIF-7) during DSC scans at heating/cooling rates of 10 °C min⁻¹. PBIF copolymers containing more than 7 mol% IS appeared to be fully amorphous materials.

Further non-isothermal crystallization studies of PBIF-7 and PBIF-17 samples with much lower cooling rates (3 and 1 °C min⁻¹) were performed. According to the DSC curves shown in Fig. 4 and thermal data presented in Table 3, it can be confirmed that PBIF-7 has low crystallinity when treated at a low cooling rate (1 and 3 °C min⁻¹) from the melt, while PBIF-17 was observed to be fully amorphous even at very low cooling rate of 1 °C min⁻¹.

Crystal structures of PBIF copolyesters

WAXD patterns of PBIFs were obtained to further study their crystalline structures. The results are shown in Fig. 5. It was noticed that PBF exhibited strong reflections at 2θ values of 18.04°, 22.32° and 24.76°, which were indexed to the (020), (021) and (110) crystal planes, respectively.^{33, 34} However, for the copolyester samples containing IS, no diffraction peaks were observed, demonstrating the nearly fully amorphous nature of these materials, in agreement with DSC observations on the whole. For

sample PBIF-7, the melting peak can be detected using DSC, but WAXD data do not indicate the existence of its crystalline structure. This is thought to be because the crystalline regions of this

polyester are very small or poorly ordered, which are difficult to detect using WAXD. This is another indication that the crystallization ability of this copolyester is strongly interfered with by the presence of both asymmetric monomers. Based on this analysis, we conclude that a combination of the asymmetric FDCA and IS building blocks is highly efficient for preparing materials with extremely low degrees of crystallinity or even fully amorphous materials. The upper limit of IS content was also very low: a maximum 10 mol% of IS is sufficient to tenable a complete transition from semicrystalline (PBF homopolymer) to completely amorphous materials. The molar fraction of IS in PBT-based copolyesters was known to be at least 40% for efficient inhibition of crystallization.²⁶ With the combined high *T_g* values of PBIF copolyesters, these highly amorphous polyesters might be useful for high-end applications where high surface gloss or high transparency is desired.

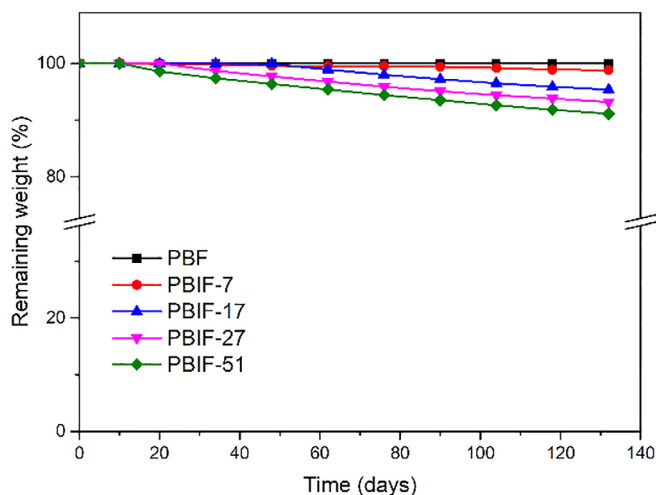


Figure 6. Remaining weight versus degradation time of PBF and PBIF copolyesters incubated in pH 2.4 citric acid buffer solution at 80 °C.

Degradability of copolyesters

It is known that the biodegradability of polymers is comprehensively determined by the condensed-state physicochemical parameters, such as melting and glass transition temperatures, crystallinity, hydrophilicity, etc. Although the oxy-heterocyclic FDCA molecule exhibits a higher hydrophilicity than terephthalic

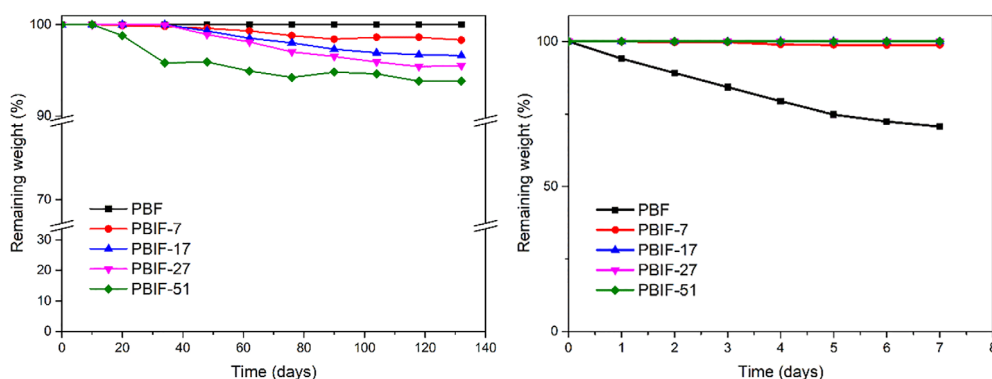


Figure 7. Remaining weight versus degradation time of PBF and PBIF copolyesters in pH 7.2 sodium phosphate buffer solution at 37 °C in the presence of PP enzyme (left) or cutinase (right).

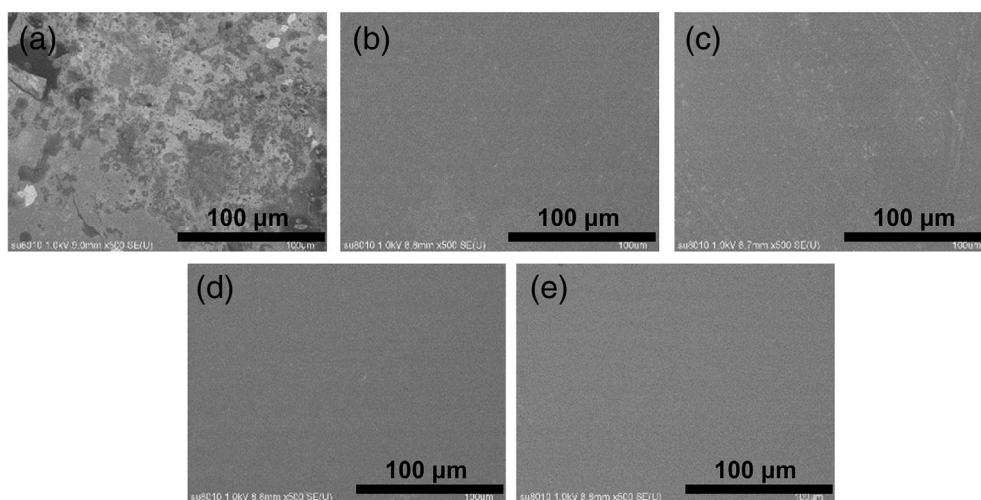


Figure 8. SEM images of PBF (a), PBIF-7 (b), PBIF-17 (c), PBIF-27 (d) and PBIF-51 (e) after incubation in pH 7.2 sodium phosphate buffer solution at 37 °C in the presence of cutinase.

acid, PBF homopolymer remains highly resistant to biodegradation under natural environmental conditions or lipase-catalyzed conditions (37 °C, pH 7.4).³⁵ Our previous study regarding the (bio)degradability of terephthalic acid-based copolyesters showed that the presence of IS moieties enhances the hydrolytic degradation of the polymers to a certain extent, yet insignificantly influences their biodegradation properties.²³ For PBIF copolyesters, the crystallinities are much inhibited which, together with the high hydrophilicity of the materials, might result in degradable polyesters with enhanced thermal properties. To evaluate the degradation performance of the synthesized copolyesters, film samples of PBF homopolymer and PBIF copolyesters containing 7, 17, 27 and 51 mol% of IS were prepared and investigated under neutral hydrolytic, acidic hydrolytic and enzymatic degradation environments. Specific (bio)degradation conditions and testing procedures follow our previous work.²³

Hydrolytic degradation

Hydrolytic degradation of the PBIF copolyesters was performed in aqueous buffer solution at pH 2.4 and 80 °C. The remaining weight (R_w) of PBIF samples determined after certain time intervals is shown in Fig. 6. Compared to the pure PBF, approximately 9% weight loss was observed for PBIF-51 after incubating for 20 weeks. With a higher molar fraction of IS, T_g increased almost linearly which was theoretically unfavorable for promoting higher degradation rate. However, it is clear that the weight loss increased as IS content increased. It was rather evidenced that the content of IS outperformed its influences on T_g and should be the major factor leading to higher hydrolytic degradation rate by enhancing the wettability of the materials.

Enzymatic degradation

Enzymatic degradation of the PBIF copolyesters was further investigated using PP enzyme and cutinase under neutral aqueous conditions at 37 °C. PP enzyme comes from animal pancreas after crystallization and has been frequently employed for biodegradation assay of polyesters.^{23, 36, 37} Recently, a number of studies have shown that cutinase exhibits high efficiency for depolymerizing aliphatic or aromatic polyesters,^{38–40} which significantly reduces the observation duration of enzymatic degradation experiments. The mechanism of both enzymes for degrading polyesters is generally believed to be via ester bond scission by a nucleophilic substitution process.^{23, 41}

The biodegradation results obtained under the catalysis of the two types of enzymes were apparently different. The biodegradation of PBIF in the presence of PP enzyme was closely correlated with IS content. Inserting more IS units seems to be more favorable for degradation by PP enzyme (Fig. 7). Weight loss of PBIF-51 was found to be about 7% which was comparable to that obtained under strong acidic hydrolytic degradation conditions at much higher temperature as demonstrated in the previous subsection. In contrast, no tractable weight loss could be observed for PBF homopolymer showing its excellent resistance under the same conditions. In the case of biodegradation catalyzed by cutinase, a strikingly good biodegradability of PBF homopolymer was observed with a significant 29.3% weight loss after only 7 days of incubation. In contrast, all the PBIF copolyesters were found to be fairly stable under the same conditions without showing appreciable weight loss. Additional evidence regarding the morphology changes further supported these observations (Fig. 8). The specific cutinase species we used in our work, which comes from *Aspergillus* microorganism, is known to be effective

only at 40–45 °C or even lower, while the temperature we chose in this work was 37 °C which was around the T_g of PBF but much lower than those of the PBIF copolyesters, and thus the polymer chains could not move smoothly.⁴² In addition, this fungal cutinase had smaller α/β -hydrolase fold than bacterial cutinase which make it difficult to form covalent intermediates between the carbonyl group of cutinase and ester bonds of IS with large steric hindrance.^{41, 43–45} For the PP enzyme-catalyzed experiments, the crystallinity of these polyesters was the key factor influencing their degradability; too high a crystallinity of PBF homopolymer made it difficult for PP enzyme to combine with ester bonds, and increasing content of IS units gave the polymers increasing hydrophilicity coming from the oxygen atoms in IS molecules which helped the combination of PP enzyme and copolyesters.⁴⁶ These results also indicated that the biodegradation mechanism of cutinase and PP enzymes might be different. In-depth study of the biodegradation of FDCA- and IS-based polymer from the perspectives of various enzymes and full characterization of degradation samples is in progress and will be reported separately.

CONCLUSIONS

A series of biobased polyesters, namely PBIFs, were synthesized by melt polycondensation based on carbohydrate-derived building blocks, namely FDCA and IS. NMR analysis identified the statistically distributed microstructures of these copolyesters. Incorporation of the rigid FDCA and IS units significantly enhances the T_g values of the copolyesters from 38 to 107 °C when IS content varied within the range 0 to 50 mol%, and simultaneously inhibits the crystallization of these copolyesters. A maximum of 10 mol% IS incorporation is sufficient to transform from a highly crystalline PBF homopolymer into nearly fully amorphous copolyester materials. The hydrolytic degradation and enzymatic degradation in the presence of PP enzyme seemed to be effectively promoted by higher IS content. Yet, a different trend was observed for the cutinase-catalyzed biodegradation during which PBF homopolymer was effectively degraded, while the PBIF copolyesters were found to be strikingly stable. Detailed biodegradation study of FDCA and IS copolyesters in terms of various enzymes and full characterization of degradation samples is in progress. The results demonstrated in this work have shown the great potential of FDCA and IS in tuning the crystallization ability of polyesters towards low-crystallinity and even fully amorphous materials. We believe that the results reported in this paper can be valuable for the design of novel biobased and low-crystallinity to amorphous polyesters for engineering plastic, nonwovens or optical film applications. Additional property adjustment to meet the needs of specific industrial applications can be achieved by chemical or physical blending modification techniques.

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SUPPORTING INFORMATION

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

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