Supporting Information

A facile method to synthesize bio-based and biodegradable copolymers from furandicarboxylic acid and isosorbide with high molecular weight, excellent thermal and mechanical property

Qing Ouyang,[a,b] *Jiajian Liu,**[a] *Chuncheng Li,**[a] *Liuchun Zheng,*[a] *Yaonan Xiao,*[a] *Shaohua Wua and Bo Zhang*[a]

[a]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Joint Laboratory of Polymer Science and Materials, Centre for Molecular Science, Institute of Chemistry Chinese Academy of Sciences (ICCAS), Beijing 100190, P. R. China.

[b]University of the Chinese Academy of Sciences, Beijing 100049, P. R. China.

† Emails: ljj6609891@iccas.ac.cn, lichch@iccas.ac.cn.

Contents:

Total number of pages: 11

Total number of equations: 6

Total number of figures: 6

Total number of tables: 1

S1: Experimental Section

Materials

Dimethyl 2,5-furandicarboxylate (DMFD) was purchased from Hubei Hongxin Ruiyu Fine Chemical Co., Ltd. (China). Isosorbide (Is) was received as a gift from Roquette Chemical Co. (China). Dimethyl carbonate (DMC) was a commercial product from Shandong Shida Shenghua Chemical Co. (China). 1,4-butanediol (BDO) was purchased from Beijing Chemical Reagents Corp. (China). Dimethyl succinate (DMS) was supplied by Shanghai Energy Chemical Co., Ltd. (China). Lithium hydroxide (LiOH, 98%) and tetrabutyl titanate ($Ti(OBu)_4$) were purchased from Alfa Aesar. Triphenyl phosphite (TPPi) was purchased from Shanghai Energy Chemical Co., Ltd. (China). Porcine pancreas lipase (activity of 1.5 units per milligram) was purchased from TCI Shanghai Chemical Co., Ltd. (China). All chemicals were used as received.

Characterization

The intrinsic viscosity of PICBF(S) was measured in a mixed solvent of phenol and 1,1,2,2-tetrachloroethane (1:1) using an Ubbelohde thermostat viscometer at 25 ± 0.1 ^{o}C. Molecular weights were determined by gel permeation chromatography (GPC) equipped with a Waters 1515 HPLC pump and a refractive index detector (Waters 2414) at 35 ^{o}C. Chloroform was used as the eluent (1.0 mL·min-1) and polystyrene standards were used to establish a calibration curve. 1H spectra with deuterated dimethyl sulfoxide (DMSO) as the solvent and ^{13}C spectra with deuterated chloroform ($CDCl_3$) as the solvent were recorded on a Bruker DMX-400 NMR spectrometer. Tetramethylsilane (TMS) was used as an internal standard for chemical shifts.

The thermal behavior of polymers was examined by differential scanning calorimetry (DSC) on a DSC Q2000 apparatus from TA Instruments. The thermograms were obtained from 4-5 mg samples at heating and cooling rates of 10 ^{o}C·min^{-1} under a nitrogen flow of 50 mL·min^{-1}. Thermogravimetric analysis (TGA) of the samples (2.0-3.0 mg) was performed on a Perkin-Elmer TGA 8000 analyzer in a nitrogen atmosphere with a heating rate of 20 ^{o}C·min^{-1} from 50 to 550 ^{o}C.

Dynamic mechanical analysis (DMA) was conducted on a TA Q800 instrument in conjunction with a liquid nitrogen cooling system. All samples were measured in the single cantilever mode from -140 ^{o}C at a heating rate of 3 ^{o}C·min^{-1} and with an oscillating frequency of 1 Hz. Testing samples were inject-molded at 210 ^{o}C under a pressure of 800 bar.

Tensile tests were performed with dumbbell-shaped samples according to ISO 527 (2012) by using an Instron 1122 tensile testing machine with a 500 N load cell at a crosshead speed of 20 mm·min-1. All testing samples with dimensions of 10.0 mm (length) × 4.0 mm (neck width) × 2.0 mm (thickness) were prepared by inject-molding at 210 ^{o}C under a pressure of 800 bar. At least 5 samples were tested to obtain an average value of mechanical properties.

The gas barrier properties were investigated by Labthink VAC-V2 gas permeability tester at 30 ^{o}C with the relative humidity (RH) of 30%. The testing range was 0.05-50000 cm^{3}/m^{2}·24h·0.1MPa. The polymer films were prepared by casting from chloroform solution at a polymer concentration of 0.1 g·mL^{-1}. The round films with the diameter of 58 mm and the permeability surface area of 4.9 cm^{2} were used. All the permeation data was the average of more than three measurements.

Hydrolytic and enzymatic degradation tests were conducted in vials containing 10 mL phosphate buffer solution (pH = 7.4) at 37 ^{o}C. The films were prepared by casting from chloroform solution at a polymer concentration of 0.1 g·mL^{-1}. The films were cut into 20 × 10 mm, 20-30 mg weight rectangles and dried under a vacuum to constant weight. For enzymatic degradation, the concentration of porcine pancreas lipase was 1.0 mg·mL^{-1} and the buffered solution was replaced every 72 h in order to maintain the enzyme activity. In both cases, disks were withdrawn from the incubation medium at scheduled periods of time, washed carefully with distilled water and dried to constant weight under a vacuum.

S2: Synthesis of oligomers

For the OIC oligomer, Is (29.22 g, 0.2 mol), DMC (135 g, 1.5 mol), LiOH (58.4 mg, 0.2 wt% relative to Is) and TPPi (32.8 mg, 0.02 wt% relative to all chemicals) were charged into a 250 mL four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, reflux condenser, thermometer and feeding funnel under a nitrogen atmosphere. Afterwards, the reaction mixture was performed at 100 ^{o}C for 1 h and then the temperature was gradually increased to 180 ^{o}C and maintained for 1 h to completely distill the methanol and unreacted DMC. For the BHFD oligomer, DMFD (22.1 g, 0.12 mol), BDO (23.76 g, 0.264 mol) and $Ti(OBu)_4$ (22.1 mg, 0.1wt% relative to DMF) were added into another 250 mL four-necked round-bottom flask. After that, the chemicals were heated at 160 ^{o}C under a nitrogen atmosphere for 1 h and then at 185 ^{o}C for additional 3 h. Finally, these two mixtures were allowed to cool down and taken out from flasks. The procedure for synthesis of BHSD was the same as BHFD.

S3: Calculation of sequence distribution

six parameters are needed to describe this four-component system:

[(A1 - B1) x - (A2 - B1) y] m- [(A1 - B2) z - (A2-B2) w] n

In this formula, A1 and A2 represent Is and butylene units, respectively, whereas B1 and B2 are the carbonate and furandicarboxylate units; x, y, z and w represent the average length of the various sequences and can be calculated using eqs 1-4. The fraction of dyads PAiBj is defined by eq 5; m and n are the mean lengths of blocks having in common the same B1 or B2 unit. In this paper, copolymers PICBF(S) was allowed to neglect chain ends in calculations due to high enough degrees of polymerization. Thus, the concentration of Ai and Bj are nearly equal, as shown in the Table 2. According to Devaux's approach, the degree of randomness is calculated using eq 6.

$x = 1/([PA1B2])$ (1)

$y = 1/([PA1B1])$ (2)

$z = 1/([PA2B2])$ (3)

$w = 1/([PA2B1])$ (4)

$$PAiBj = ([AiBj])/([Ai]) \quad (5)$$

$$B = 1/x + 1/w \quad (6)$$

S4: Structure analysis of $PI_{80}CBF_{20}$

The existence of Is moiety in the IF structure unit was certificated by cross peaks H2/H1, H4/H3, H5/H3 and H5/H6 in the COSY spectrum, also the existence of that in the IC structure unit was confirmed by cross peaks H2'/H1', H4'/H3', H5'/H3' and H5'/H6'. Correlation signals H2/H3 and H2'/H3' were not presented in the COSY spectrum, which was attributed to the V-shaped structure of Is and its two five-membered rings. While cross peaks H5/H3 and H5'/H3' were observed in the spectrum because they were in the same plane. Additionally, the existence of butylene moiety in BF and BC structure units was verified by the cross peaks H8/H7 and H8'/H7', respectively.

On the basis of the above results, the proton signals were assigned to the corresponding ^{13}C signals in the, as shown in the Figure 3. The peaks assignment in the ^{13}C NMR spectrum of $PI_{80}CBF_{20}$ was confirmed by correlation signals of H1/C1, H2/C2, H3/C3, H4/C4, H5/C5, H6/C6, H7/C7, H8/C8, H9/C9 and H1'/C1', H2'/C2', H3'/C3', H4'/C4', H5'/C5', H6'/C6', H7'/C7', H8'/C8' at δ 4.10/δ 73.30, δ 5.42/δ 79.08, δ 4.97/δ 81.03, δ 4.63/δ 85.91, δ 5.39/δ 74.91, δ 4.01/δ 70.80, δ 4.36/δ 64.92, δ 1.84/δ 25.13, δ 7.23/δ 119.16 and δ 4.04/δ 73.05, δ 5.09/δ 82.45, δ 4.88/δ 80.93, δ 4.52/δ 85.71, δ 5.08/δ 76.97, δ 3.90/δ 70.56, δ 4.18/δ 67.46, δ 1.77/δ 25.12, respectively.

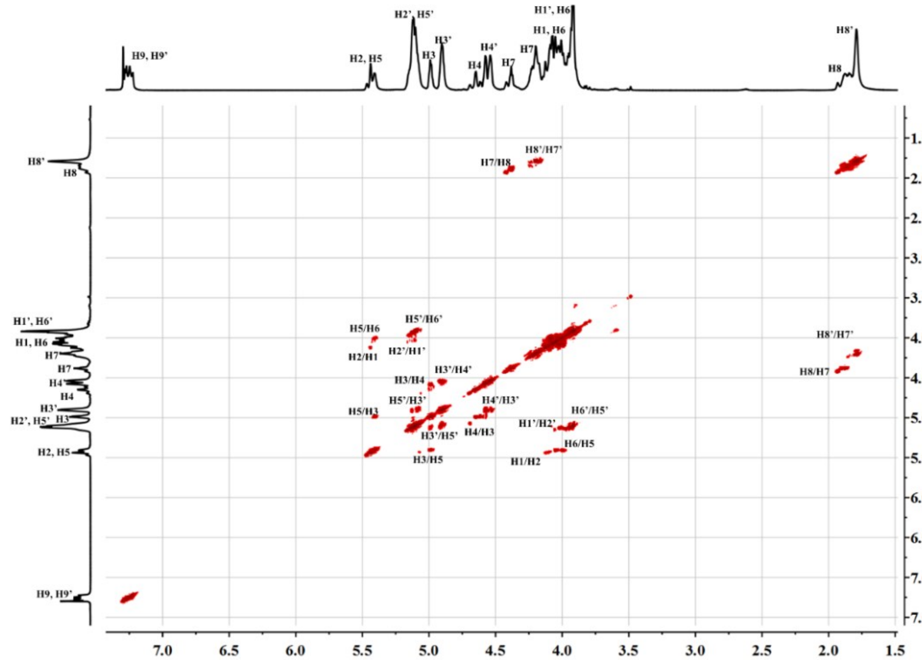

Figure S1. Correlation spectroscopy (COSY) spectrum of $PI_{80}CBF_{20}$.

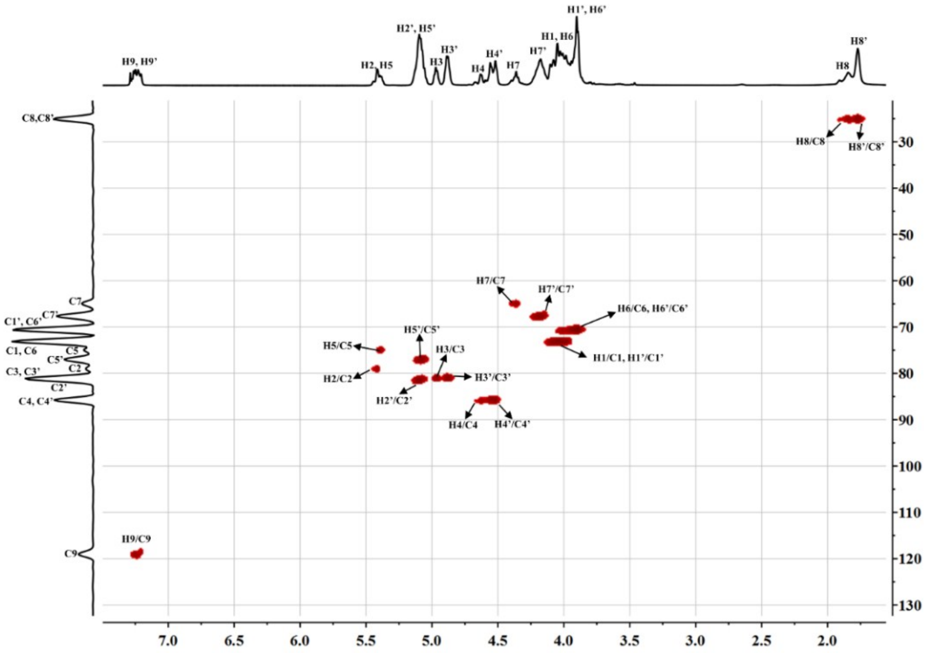

Figure S2. Heteronuclear single-quantum correlation spectrum (HSQC) of $PI_{80}CBF_{20}$

S5: Structure analysis of $PI_{80}CBF_{10}S_{10}$

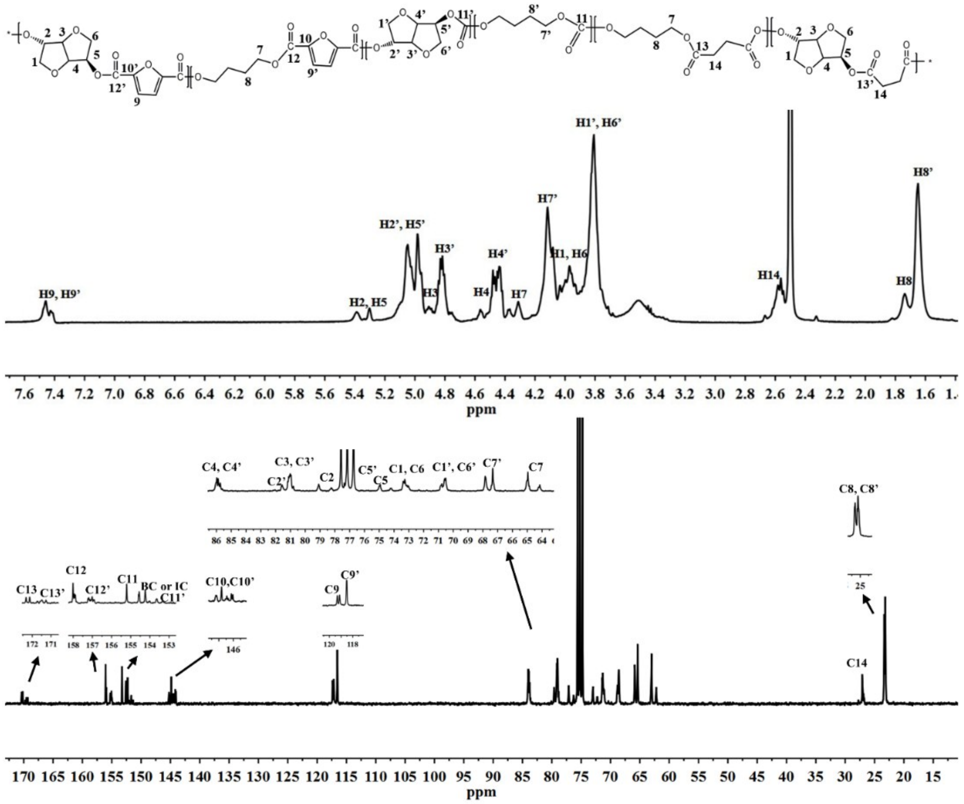

Figure S3. ^{1}H NMR and ^{13}C NMR spectra of PI$_{80}$CBF$_{10}$S$_{10}$.

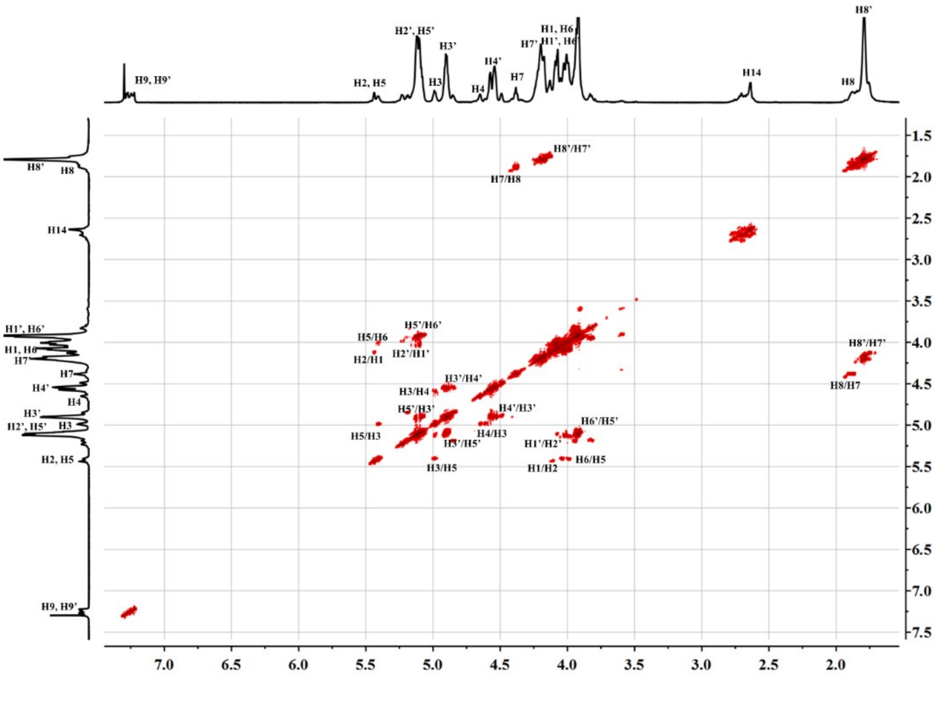

Figure S4. Correlation spectroscopy (COSY) spectrum of $PI_{80}CBF_{10}S_{10}$.

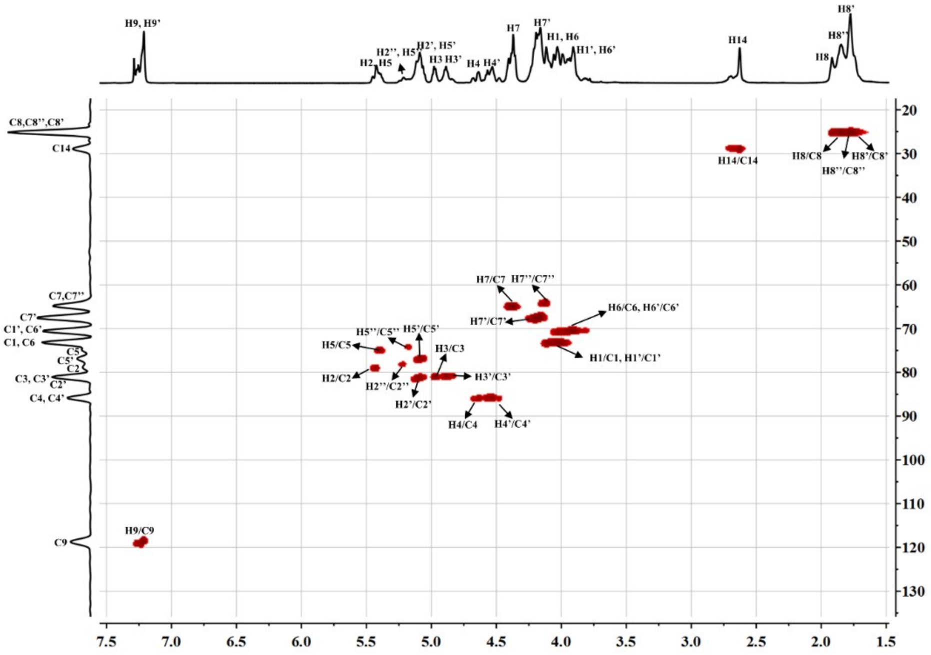

Figure S5. Heteronuclear single-quantum correlation spectrum (HSQC) of $PI_{80}CBF_{10}S_{10}$.

S6: Degradation behavior of synthesized copolymers

Table S1. Microstructure analysis of the PICBF(S) before and after enzymes degradation

Sample code	Type	M_w (g·mol^{-1})	[η] (dL·g^{-1})	M_w/M_n	Composition ratio (Is/F(/S)/B/C)	Dyad fraction			
						F_{IF} (F_{IS})	F_{IC}	F_{BF} (F_{BS})	F_{BC}
$PI_{20}CBF_{80}$	Before	87,300	1.16	1.81	5/42/45/8	8.8	2.2	73.5	15.4
	After	79,500	1.06	2.02	6/42/44/8	9.0	2.3	74.8	13.9
$PI_{40}CBF_{60}$	Before	68,900	1.02	1.74	15/35/35/15	20.6	10.8	49.0	19.6
	After	58,100	0.86	1.85	16/33/36/14	21.3	11.1	50.8	16.8
$PI_{60}CBF_{40}$	Before	46,300	0.58	1.39	27/23/22/28	25.0	31.0	21.8	22.2

	After	36,800	0.44	1.67	30/25/20/25	27.5	33.5	22.5	16.5
$PI_{60}CBF_{30}S_{10}$	Before	67,800	0.89	1.81	23/14(/7)/24/30	11.2 (6.7)	28.3	15.5 (6.3)	32.0
	After	61,300	0.80	2.10	25/15(/7)/25/28	12.5 (7.0)	30.3	17.2 (6.0)	26.0
$PI_{80}CBF_{10}S_{10}$	Before	47,500	0.77	1.60	32/5(/5/)18/40	5.6 (7.3)	50.7	3.1 (3.1)	30.2
	After	44,400	0.71	1.85	34/5(/6/)16/39	5.8 (7.8)	53.6	3.4 (3.0)	26.4

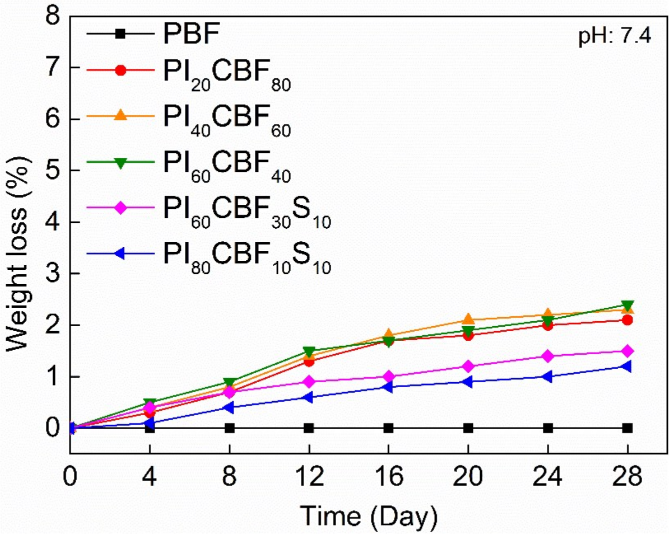

Figure S6. Degradation properties of PICBF(S) in phosphate buffer solution