## **Electronic Supplementary Information (ESI)**

# High-Performance Chemically Recyclable Multifunctional Polyolefin-Like Biomass-Derived Polyester Materials

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#### **Experimental Section**

#### 1.1 Materials

Succinic acid (SA) (purity ≥99%) and 1,4-butanediol (BDO) (purity 98%) were purchased from Aladdin Reagent (Shanghai) Co., Ltd. China. (1R, 3S) -(+) -Camphoric acid (CA) (purity 99%) was purchased from Adamas-beat (Shanghai) Co., Ltd. China. Titanium (IV) n-butoxide (TBT) (purity 99%) was provided by J&K Chemical. Titanium tetraisopropanolate (TIP) (purity 99%) purchased from Energy Chemical. Sodium hydroxide (NaOH) (purity 98%), Methyl alcohol (MeOH) (purity 99%), Hydrochloric acid (HCl), Ethanol (EtOH) (purity 99%), Acetone (AC) (purity 99%), Dimethyl sulfoxide (DMSO) (purity 99%) and N, N-Dimethylformamide (DMF) (purity 99%) acetonitrile (ACN) (purity 99%), toluene (TOL) (purity>99.5%), acetone (ACE) (purity>99.5%), petroleum ether (PE) and ethyl acetate (EtOAc) (purity 99%) are purchased from Kelong Chemical Factory (Chengdu, China). All the other reagents were used as received without any further purification.

#### **1.2 Synthesis of polyesters**

The PBC<sub>x</sub>S polyesters were synthesized by condensation copolymerization in two steps (**Scheme S1**): esterification and polycondensation. The x represents the molar ratio content of CA in the diacid. Five PBS, PBC<sub>5</sub>S, PBC<sub>10</sub>S, PBC<sub>15</sub>S, and PBC<sub>20</sub>S polyesters with different SA/CA molar ratios (100/0, 95/5, 90/10, 85/15, and 80/20) were synthesized in this work. The synthesis of PBC<sub>20</sub>S is given as an example. SA (23.6 g, 0.2 mol), CA (10.0 g, 0.05 mol), BDO (27.0 g, 0.3 mol), TBT (0.03 g,  $1.3 \times 10^{-4}$  mol, as catalyst), and TIP (0.03 g,  $1.1 \times 10^{-4}$  mol, as catalyst) were added into a 100 mL three-necked flask that was equipped with an agitator, water separator, and N<sub>2</sub> inlet pipe.

The esterification was carried out at 180 °C for 4 hours. After that, the polycondensation was set at 220 °C with a vacuum of 60–80 Pa for 2 hours and 230 °C with a vacuum of 60–80 Pa for about 4 hours. The PBC<sub>x</sub>S copolyesters were prepared as above process.



Scheme S1. Schematic diagram of PBC<sub>x</sub>S a) and b) PBS copolyesters.

#### **1.3 Chemical recycling experiments**

#### 1.3.1 Chemical recycling routes of PBC<sub>x</sub>S

The PBC<sub>10</sub>S was amenable to quantitative chemical recycling under mild conditions without additional organic solvents or expensive catalysts. PBC<sub>10</sub>S (5.0 g), sodium hydroxide (NaOH) (3.9 g), water (30 mL), and BDO (45 mL) mixture were placed into a 150 mL flask with an oil bath at 100 °C for 4 h. Upon cooling of the reaction mixture and vacuum distillation to remove H<sub>2</sub>O, SA sodium salt (r-SA salt) was self-precipitated. The HCl solution was added to adjust the pH of the solvents to 2 (**Figure S1**). Then, the disodium succinate can be transform to obtain recycled SA (r-SA) and separated by filtration.

The chemical recycling of the mixed  $PBC_xS$  and commercial disposable packaging plastics PE and PP was conducted according to similar procedures. The quantitative yield and purification of r-SA and mixture recycle SA (r-SA-MIX) are higher than 92.0% and 98.3%, respectively. Then BDO was obtained by vacuum distillation of the filtrate at 140 °C.

In the <sup>1</sup>H NMR spectrum (**Figure 5c**), the chemical shift at 12.14 ppm is attributed to H<sub>a</sub> in the carboxyl group. The chemical shift at 7.3 ppm is assigned to H<sub>b</sub> in the methylene group. The signals of the carboxyl group and the methylene group ( $C_a$  and  $C_b$ ) in the <sup>13</sup>C NMR spectrum appear at 174.05 and 29.24 ppm, respectively (**Figure S15–19**). The purity of r-SA and r-SA-MIX is higher than the 98.3% detected by LC (**Figure 5d and 5g**).

In the FT-IR spectra (**Figure S20**), as a result of the presence of hydrogen bonding, carboxylic acids in the liquid and solid phases exhibit a broad band at 3315–2455 cm<sup>-1</sup>, due to the O-H stretching vibration. The absorption bands at 1693 cm<sup>-1</sup> and 1310 cm<sup>-1</sup> are attributed to C=O vibration absorption ( $v_{C=O}$ ) and C-O vibration absorption ( $v_{C=O}$ ) of r-SA and r-SA-MIX.

The <sup>1</sup>H NMR, <sup>13</sup>C NMR, and GC data of r-BDO are shown in the following, and their spectra are given in **Figure S21–24.** <sup>1</sup>H NMR (DMSO-d6,  $\delta$ , ppm): the peaks at 4.38 ppm are assigned to the H<sub>a</sub> on the hydroxyl group. The peaks at 3.38 ppm and 1.43 ppm are assigned to the H<sub>b</sub> and H<sub>c</sub> on the methylene group and the methyl group, respectively. <sup>13</sup>C NMR (DMSO-d6,  $\delta$ , ppm): The peak at 61.2 ppm and 29.6 ppm are assigned to the C<sub>a</sub> and C<sub>b</sub> on the methylene group and methyl group, respectively. The GC date showed the purity of r-BDO was 99.6%.

## 1.3.2 Repolymerization of r-PBC<sub>10</sub>S

The r-SA and r-BDO were used to repolymerize the recovered  $PBC_{10}S$  (r-PBC<sub>10</sub>S). The synthesized route of r-PBC<sub>10</sub>S is the same as PBC<sub>10</sub>S.



Figure S1. Schematic diagram of depolymerization and repolymerization of PBC<sub>x</sub>S copolyester.

#### 1.3.3 Characterization

The chemical structures of PBC<sub>x</sub>S, r-SA and r-BDO were characterized by <sup>1</sup>H NMR spectroscopy and <sup>13</sup>C NMR. Deuterated t chloroform-d (CDCl<sub>3</sub>) for the PBC<sub>x</sub>S and (DMSO-d<sub>6</sub>) for the monomer. ATR-FTIR spectra of the polyesters were recorded on a Nicolet 6700 spectrophotometer equipped with a germanium crystal ATR accessory in the wave-number range of 500–4000 cm<sup>-1</sup>.

Intrinsic viscosities of PBC<sub>x</sub>S and PBS were measured with an Ubbelohde viscometer at a concentration of 0.4 g dL<sup>-1</sup> in a mixture solvent (phenol/1,1,2,2-tetrachloroethane, 50:50 V:V) at 30 °C. The [ $\eta$ ] of the polyesters was calculated according to Equation (1).

$$[\eta] = \frac{\sqrt{2 \times (t/t_0 - 1 - \ln(t/t_0))}}{C}$$

(1)

C is the solution concentration, t is the flow time of the solution, and  $t_0$  is the flow time of the solvent. The reported values are the average of three measurements. The molecular weight determinations were performed by GPC. The GPC test was carried out in waters1525 & Agilent PL-GPC220 with 2 mg of the sample dissolved in 2 mL of tetrahydrofuran. With tetrahydrofuran as the mobile phase, the flow rate is 1 mL min<sup>-1</sup>.

The thermal behavior of polyesters was examined by a TA Instrument (DSC-2500). The samples of around 3–5 mg in aluminum pans were first heated to 140 °C (the first heating scan), and then held at 140 °C for 2 min to eliminate the thermal history. After that, it was cooled to -70 °C at a cooling rate of 10 °C min<sup>-1</sup> (the cooling scan), and finally reheated to 140 °C at the same heating rate (the second heating scan).

Thermogravimetric analysis (TGA) was studied with a thermogravimetric analyzer (TGA5500) in a nitrogen atmosphere. The samples were heated from 40 °C up to 700 °C at a 10 °C min<sup>-1</sup> heating rate. Sample weights of about 3–5 mg were used in the experiment.

The crystallinity of polyesters was characterized by wide-angle X-ray scattering (WAXS) in Panalytical X'Pert MPD Pro using Cu Kα radiation. Samples were scanned with a scan rate of 2° min<sup>-1</sup> scanning from 5° to 40°.

The rheological property of polyesters was characterized by a Discovery HR-2 instrument (USA) with a 25 mm diameter parallel-plate geometry at 140 °C. Dynamic oscillatory shear measurements tests were performed from high to low frequency over a 0.01–100 Hz range, at strains of 1%, with a gap size of 1 mm. When the shear rate is zero, the viscosity (zero shear viscosity,  $\eta_0$ ) can not be directly measured in the experiment. Cross modle is applied to fit the relaxation spectra to obtain the  $\eta_0$  of PBC<sub>x</sub>S<sup>2</sup>.

$$\eta^* = \frac{\eta_0}{1 + (\lambda \gamma)^{1-n}}$$

(2)

n is the power law exponent,  $\lambda$  is the relaxation time constant and y is the shear frequency.

Dynamic mechanical thermal analysis (DMA) experiments were carried out in film tension mode. Heating ramps were applied at 3 °C min<sup>-1</sup> from -70 to 50 °C. Rectangular samples with measuring 6 mm ×10 mm were tested at 1 Hz frequency and 10  $\mu$ m amplitude.

The positron annihilation lifetime spectrometer (model PLS-System) tests were carried out with Finder1000 positron annihilation lifetime spectroscopy (PALS). The time resolution of the positron source was 0.23 ns. Two small discs of 25 mm×25 mm×1 mm were placed between the  $^{22}$ Na positron source. The positron lifetime is determined by the time delay between the emission of one of the birth gammas (1.28 MeV) and 0.511 MeV annihilation photons. The voids or pores of polymer materials can be detected by PALS, which utilizes positronium.<sup>1</sup>The average radius (*R*) of the free volume can be calculated by Equation (2).<sup>3</sup>

$$\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{\Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]$$

where  $\Delta R$  is the thickness (empirical value of 0.166 nm) of the electron layer, which is on the surface of the free volume.<sup>4</sup> Equation (3) expresses the average size ( $V_f$ ) of free volume holes of the PBC<sub>x</sub>S and PBS.

$$V_f = \frac{4\pi}{3}R^3$$

(4)

(3)

The relative fractional free volume (FFV,  $f_v$ , %) is defined as Equation (4).<sup>5</sup>

 $f_v = V_f I_3$ (5) where *I*<sub>3</sub> is o-Ps intensity (%)

Molecular Dynamics (MD) simulations of PBC<sub>20</sub>S and PBS systems were performed using the Gromacs program suite with the general amber force field (GAFF2) force field and AM1-BCC atomic charge. The force field parameters of these different polymers were generated using the AuToFF web server. The initial simulation boxes of dimensions 40×40×40 Å<sup>3</sup> packed with five polymer chains of forty degrees of polymerization were constructed using Gromacs tool suites. These structures were first relaxed by energy-minimizing calculations and then annealed from 900 to 298.15 K with a time step of 1 ps during 10 ns to reach the equilibrium state. A Velocity-rescale thermostat with a relaxation constant of 1 ps was used to control the temperature at 298.15 K. Berendsen's barostat with an isothermal compressibility constant of  $4.5 \times 10^{-5}$  was used to control the pressure at  $1.01325 \times 10^{5}$ Pa. Periodic boundary conditions were applied in all directions. The particle-mesh Ewald (PME) method with a cut-off distance of 10 Å was applied to treat the electrostatic interactions and the van der Waals forces. Following the energy-minimization and equilibration steps, a 50 ns MD simulation was performed at constant NPT ensemble, and the trajectory was saved every 1 ps. Finally, the free volumes of these systems were obtained from trajectory data for

the last 10 ns. The mean square radius of rotation of these polymers was also calculated to confirm the system was in equilibrium.

The tensile strength and elongation at break were measured at a stretching rate of 50 mm min<sup>-1</sup> on a Sansi Universal Testing Machine (CMT, Shenzhen, China) at room temperature. At least five measurements were conducted for each sample, and the results were reported as averaged values.

The haze and transparency were analyzed by the WGT-S transparency-haze meter. The PBC<sub>x</sub>S films (100 $\mu$ m) were prepared by melt-pressed molding at 140 °C.

The liquid extract of the PBC<sub>20</sub>S film was used to culture mouse fibroblast L929, and the cytotoxicity of the material was evaluated by the cell counting kit 8 (CCK-8). L929 ( $5\times10^4$  cell ml<sup>-1</sup>) cells were seeded (100 µL well<sup>-1</sup>) in a 96-well plate (Corning), and the plates were preincubated in a humidified incubator for 24 hours to allow cells to adhere to the well walls. The sterile PBC<sub>20</sub>S film was soaked in a cell growth medium for 24 hours, and then the extract and the cell culture solution were mixed at 0:10, 4:6, and 8:2 ratios to prepare a new cell growth medium. After 24 or 48 hours of treatment, each well's absorbance at 450 nm was measured using a microplate reader. Each group was tested three times in parallel, and cell viability was estimated. Calcein-AM (living cell/green) and propidium iodide (PI) (dead cell/red) kits were used to detect the fluorescent staining of live and dead cells. L929 cells ( $5\times10^4$  cells ml<sup>-1</sup>) were inoculated in a 48-well plate (Corning) and treated with different proportions of extracts. The morphology of cells was observed under a fluorescence microscope. At 24 and 48 hours, L929 cells were injected with 5 µL of Annexin-V-FITC and propidium iodide (PI) to distinguish cells in different apoptosis cycles. After incubation for 10–15 minutes, flow cytometry was used to analyze the treated cells. The parallel test was done three times, and the final results were analyzed by flowjo 10.0.2 software.

Barrier properties to  $O_2$  and  $H_2O$  were tested through a manometric method using a permeance testing device (Labthink VAC-V2). All melt-pressed membranes of polyesters were cut into circular discs with a thickness of 0.5 mm and a diameter of 50 mm. Each measurement was continuously monitored until a stable oxygen permeability rate was reached.

The water contact angles of PBC<sub>x</sub>S films were measured by an optical contact angle tester (JC2000D2H, China).

The PBC<sub>x</sub>S films were immersed in water for 0-120 min, and the water absorption was calculated by weighing the mass of the PBC<sub>x</sub>S films.

The solvent-resistant test of the materials was performed at the ambient condition by soaking samples in 10 mL of different solvents (including EtOH, ACN, TOL, DMSO, MeOH, H<sub>2</sub>O, ACE, HCl (1M), DMF, PE and EtOAc for 7 days. Then, the insoluble sample was dried at 80 °C under vacuum for 24 hours to a constant weight ( $M_2$ ). The weight retention (%) of the samples was calculated by using the following equation:

Weight Retention (%) = 
$$\frac{M_2}{M_1} \times 100\%$$

(6)

Where  $M_1$  is the original weight of the sample.

The height profile and surface roughness of copolyester films were scanned by an atomic force microscope (AFM, Multimode 8, Germany) and a laser scanning confocal microscope (LSMC, LSM800, Germany).

The purity of r-SA, r-SA-MIX and r-BDO was characterized by liquid chromatograph (LC) with Finnigan TSQ Quantum. The recycled liquid was tested by gas chromatograph (GC) with Agilent 7890B using methanol as solvent, and the test condition was to keep the temperature at 60 °C for 3 minutes and increase to 240 °C at 20 °C per minute.

Various 3D architectures were flexibly fabricated by using an FDM printer (Dr. INVIVO 4D, Rokit Healthcare Co., Ltd., Korea) equipped with an air pressure control system and a barrel heating module. Before printing, the target model was established using the 3ds MAX software and sliced into layers using the NewCreatorK software. Then, the material was cut into pieces and put in a barrel. The printing parameters were set as follows: printing temperature: 130 °C.

The micro-type twin-screw mixing extruder is used to extrude at 130 °Cand the winding machine is used to pull the spinning. The injection spline was produced by a micro-injection molding machine at 130 °C, 800 bar.

#### **Results and Discussion**

In <sup>1</sup>H NMR spectra (**Figure S2a, Figure S3–S7**) signals,  $H_a$  and  $H_b$  show peaks at 4.14 and 1.72 ppm of the BDO, the peaks of the camphoric ring, and those of the  $H_e$ ,  $H_f$ , and  $H_d$  signals relate to the protons of the three methyl groups at 1.28, 1.22, and 0.80 ppm, respectively. Simultaneously, with the increased content of the CA, the intensity of  $H_e$  and  $H_f$  gradually increases. Furthermore,  $H_g$  and  $H_c$  peak at 2.81 and 2.65 ppm, respectively, coming from the protons on the carbon atom adjacent to the carboxylic group of CA and SA. Finally, the multiple signals  $H_h$ ,  $H_{h'}$ ,  $H_i$ , and  $H_{i'}$  of the methylene protons of the ring were placed at the same distance from each other at 2.48, 2.22, 1.87, and 1.53 ppm, respectively.<sup>6</sup>

However, due to the similarity of the ATR-FTIR spectra of SA and CA, the ATR-FTIR spectra of PBC<sub>x</sub>S and PBS copolyesters are coincident (**Figure S2b**), and the peak at 2975 cm<sup>-1</sup>, 1712 cm<sup>-1</sup>, and 1150 cm<sup>-1</sup> are assigned to the stretching vibrations of C-H, C=O, and the in-plane deformation vibration of C-O-C bonds.



Figure S2. a) <sup>1</sup>H NMR, b) ATR-FTIR spectra of PBC<sub>x</sub>S and PBS.



Figure S3. <sup>1</sup>H NMR spectra of  $PBC_5S$ 



Figure S4. <sup>1</sup>H NMR spectra of PBC<sub>10</sub>S



Figure S5. <sup>1</sup>H NMR spectra of PBC<sub>15</sub>S

Figure S6. <sup>1</sup>H NMR spectra of PBC<sub>20</sub>S



Figure S7. <sup>1</sup>H NMR spectra of PBS



**Figure S8.** a) DSC cooling and b)  $2^{nd}$  heating scans of PBC<sub>x</sub>S and PBS, c)  $T_g$  of PBC<sub>x</sub>S copolyesters and PBS by DSC.



**Figure S9.** a) WAXS curves of thermal annealing PBC<sub>x</sub>S and PBS, b) *X*<sub>c</sub> testing plots.



**Figure S10.** a–b) TGA curves of PBC<sub>x</sub>S and PBS.



**Figure S11.** GPC chromatogram of PBC<sub>x</sub>S and PBS.



Figure S12. Cross model equation is applied to fit the relaxation spectra.



**Figure S13.** a–e) Storage modulus (G') and loss modulus (G'') versus frequency of PBC<sub>x</sub>S and PBS.



**Figure S14.** The AFM image for the surface and height profile of  $PBC_xS$  and PBS films.



Figure S15. a) Water absorption of film  $PBC_{20}S$  films, b) water resistance of  $PBC_{20}S$  films.



Figure S16. Weight retention of PBC<sub>20</sub>S films.

## **Chemical recycling**

## <sup>1</sup>H NMR (400 MHz, DMSO-d6)

 $\delta$  12.13 (s, 2H), 2.42 (s, 4H).

## <sup>13</sup>C NMR (100 MHz, DMSO-*d6*)

δ 174.04, 29.23.



**Figure S17.** a) <sup>13</sup>C NMR spectra of standard SA (STD-SA) and r-SA obtained from PBC<sub>x</sub>S recycling experiment, b) <sup>13</sup>C NMR spectra of STD-SA and r-SA-MIX obtained from recycling experiments in PBC<sub>x</sub>S, PP, and PE mixtures.



Figure S18. a–b) <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of STD-SA



Figure S19. a–b) <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of r-SA.



Figure S20. a–b) <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of r-SA-MIX.



Figure S21. FT-IR spectra of STD-SA, r-SA and r-SA-MIX

## <sup>1</sup>H NMR (400 MHz, DMSO-d6)

 $\delta$  4.49–4.28 (m, 2H), 3.46–3.28 (m, 4H), 1.52–1.34 (m, 4H).

## <sup>13</sup>C NMR (100 MHz, DMSO-d6)

δ 61.22, 29.60.



**Figure S22.** a) <sup>1</sup>H NMR spectra and b) <sup>13</sup>C NMR spectra of standard BDO (STD-BDO) and recycle BDO (r-BDO).



Figure S23. a–b)<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of STD-BDO.



Figure S24. a–b)<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of r-BDO.

(a)



Figure S25. GC trace of STD-BDO and r-BDO obtained from recycling experiment.



Figure S26. <sup>1</sup>H NMR spectra of r-PBC<sub>10</sub>S.



**Figure S27.** Stress-strain curves of  $r-PBC_{10}S$  and  $PBC_{10}S$ .

Complex	Samples $f^{a)}$ (mol%) $F^{b)}$ (mol%) $f_{SA}$ $f_{CA}$ $F_{SA}$ $F_{CA}$ $[\eta]$ (		F <sup>b)</sup> (mol%)		[m] (d)	M. (a. m. al-1)	$\Lambda (a m al^{-1})$	
Samples .			. [/] (ur g -)	<i>wi</i> n (g moi -)	<i>w</i> <sub>w</sub> (g moi -)	ΓIJ		
PBS	100	0	100	0	1.81	6.2×10 <sup>4</sup>	8.6×10 <sup>4</sup>	1.4
PBC₅S	95	5	95.2	4.8	1.82	5.4×10 <sup>4</sup>	8.4×10 <sup>4</sup>	1.5
PBC <sub>10</sub> S	90	10	90.5	9.5	1.76	5.8×10 <sup>4</sup>	8.3×10 <sup>4</sup>	1.4
PBC <sub>15</sub> S	85	15	85.5	14.5	1.78	6.0×10 <sup>4</sup>	8.3×10 <sup>4</sup>	1.4
PBC <sub>20</sub> S	80	20	82.0	18.0	1.75	5.4×10 <sup>4</sup>	7.4×10 <sup>4</sup>	1.3

**Table S1.** Composition and molecular weight of  $PBC_xS$  and PBS.

<sup>a)</sup> the molar ratio of SA/CA feed. <sup>b)</sup> actual molar ratio of SA/CA in the copolyesters.

**Table S2.** Thermal properties and crystallinity for  $PBC_xS$  and PBS.

Complex	Tg	T <sub>m</sub>	∆H <sub>m</sub> (J	T <sub>c</sub>	∆H <sub>c</sub> (J	T <sub>5%</sub>	T <sub>max</sub>	$X_c^{a)}$
Samples	(°C)	(°C)	g-1)	(°C)	g <sup>-1</sup> )	(°C)	(°C)	(%)
PBS	-36.9	113.3	80.1	72.4	65.4	333.3	410.4	80.2
PBC₅S	-32.6	112.4	74.6	70.3	62.2	329.4	405.9	71.8
$PBC_{10}S$	-31.2	110.9	71.9	66.9	61.9	326.7	402.4	65.4
PBC <sub>15</sub> S	-30.2	108.9	67.6	59.2	59.2	327.3	398.6	63.7
PBC <sub>20</sub> S	-29.4	103.4	58.4	42.2	53.9	326.2	402.2	40.3

<sup>a)</sup> Crystallinity degree ( $X_c$ ) calculated by the deconvolution of amorphous and crystalline peaks in WXRD patterns using the peak separation software.

Samples	$\eta_0$ (Pa.s)
PBS	2260.2
PBC₅S	4290.6
PBC <sub>10</sub> S	7320.3
PBC <sub>15</sub> S	13334.2
PBC <sub>20</sub> S	19514.6

Samples	τ <sub>3</sub> (ns)	I <sub>3</sub> (%)	<i>R</i> (nm)	<i>V<sub>f</sub></i> (nm³)	<i>f</i> <sub>V</sub> (%)	F <sub>V</sub> (%) <sup>a)</sup>
PBS	2.16	13.2	0.299	0.1119	1.47708	24.61
PBC₅S	2.11	13.2	0.294	0.1064	1.40448	-
PBC <sub>10</sub> S	2.08	13.0	0.292	0.1042	1.35460	-
PBC <sub>15</sub> S	2.09	12.8	0.292	0.1042	1.33376	-
PBC <sub>20</sub> S	2.04	12.7	0.288	0.1000	1.27000	17.45

**Table S4.** Summary of Ps lifetime components and corresponding pore sizes of  $PBC_xS$  and PBS.

<sup>a)</sup> The free volume calculated via Materials Studio software.

Samples	Tensile strength (MPa)	Elongation break (%)	Elastic modulus (MPa)
PBS	33.4±2.4	288.9±53.5	409.5±19.3
PBC <sub>5</sub> S	35.0±0.8	397.6±12.6	380.0±13.5
PBC <sub>10</sub> S	38.8±0.9	470.4±13.3	359.9±11.1
PBC <sub>15</sub> S	40.6±0.4	498.4±42.8	338.5±39.3
PBC <sub>20</sub> S	33.9±1.6	557.9±20.8	369.7±34.0
PP <sup>7</sup>	24.2	200.0	900
PE <sup>8</sup>	~34.0	420.0	-
HDPE <sup>9</sup>	20.4	460.0	1130±10
LLDPE <sup>10</sup>	20.7	460.0	270±10
PC-18 <sup>11</sup>	~18.0	350.0	~680
PE-18 <sup>11</sup>	~22.0	470.0	~1030
PE510 <sup>12</sup>	11.9	436.0	358±30
PBTF <sup>13</sup>	38.8	194.0	1957.9±36.3
PBAT <sup>8, 12</sup>	21.4	400.0	68
PBT <sup>14</sup>	34.4	5.0	-

**Table S5.** Mechanical properties of  $PBC_xS$ , PBS and other polyesters.

Samples	Transmittance (%)	Haze (%)
PBS	75.5	91.1
PBC₅S	76.4	83.0
PBC <sub>10</sub> S	83.2	61.3
PBC <sub>15</sub> S	85.6	52.0
PBC <sub>20</sub> S	90.5	48.9

**Table S6.** Transmittance and haze of  $PBC_xS$  and PBS films.

## Gas barrier properties

Complete 3)	<i>P</i> O <sub>2</sub>		WVTR	<i>P</i> (H <sub>2</sub> O) <sup>c)</sup>		
Samples "	(barrer) <sup>b)</sup>	ыгр	(g m <sup>-2</sup> day <sup>-1</sup> ) <sup>c)</sup>	(g cm cm <sup>-2</sup> s <sup>-1</sup> Pa <sup>-1</sup> )	Чпа	
PBAT <sup>15</sup>	0.76	1.0	-	- 3.52E-13		
PLA <sup>15</sup>	0.25	3.0	-	1.10E-13	3.20	
PCC <sup>16</sup>	0.09	8.4	-	4.40E-13	0.80	
PHB <sup>17, 18</sup>	0.10	7.6	16.10	-	1.64	
PE <sup>19, 20</sup>	1.58	0.5	7.90	-	3.34	
PCL <sup>21</sup>	0.72	1.1	-	5.10E-13	0.69	
PDePD25 <sup>22</sup>	0.40	1.9	-	3.00E-12	0.12	
PDelP <sup>22</sup>	0.90	0.8	-	2.25E-12	0.16	
PE510 <sup>12</sup>	0.84	0.9	-	1.29E-13	2.73	
PBS	0.15	5.1	20.65	2.80E-13	1.26	
PBC₅S	0.14	5.4	19.01	1.88E-13	1.87	
$PBC_{10}S$	0.12	6.3	18.73	1.82E-13	1.93	
$PBC_{15}S$	0.11	6.9	13.56	1.76E-13	2.00	
PBC <sub>20</sub> S	0.09	8.4	12.76	1.70E-13	2.07	

**Table S7.** Gas permeability coefficients for PBC<sub>x</sub>S and other materials.

<sup>a)</sup> The test was performed at 0.1 MPa. <sup>b)</sup> O<sub>2</sub> permeability coefficient, at 23 °C, 50% relative humidity 1 barrer=10<sup>-10</sup> cm<sup>3</sup> cm cm<sup>-2</sup> s<sup>-1</sup> cm Hg<sup>-1</sup>). <sup>c)</sup> H<sub>2</sub>O permeability coefficient, at 37 °C, 90% relative humidity.

Samples	Water contact angle (°)	
PBS	66.3±0.3	
PBC₅S	69.1±0.9	
PBC <sub>10</sub> S	70.3±0.4	
PBC <sub>15</sub> S	72.2±0.5	
PBC <sub>20</sub> S	74.5±1.0	

**Table S8.** Water contact angle of  $PBC_xS$  and PBS films.

Samples	R <sub>a</sub> (nm)	<i>R<sub>q</sub></i> (nm)	<i>S<sub>a</sub></i> (μm)
PBS	7.13	9.19	0.966
PBC₅S	6.90	8.97	0.766
PBC <sub>10</sub> S	5.82	7.41	0.442
PBC <sub>15</sub> S	5.50	7.36	0.414
PBC <sub>20</sub> S	4.52	5.91	0.389

**Table S9.** Surface roughness of  $PBC_xS$  and PBS films.

**Table S10**. Summary of the Weight retention (%) of PBC<sub>20</sub>S films after being soaked in different solvents for 7 days.

Samples	EtOH	ACN	TOL	DMSO	MeOH	H <sub>2</sub> O	ACE	HCI	DMF	PE	EtOAc
Weight retention (%)	100.0	100.0	99.9	99.9	99.3	99.5	100.0	100.0	99.7	99.2	98.8

#### References

1 T. Stassin, R. Verbeke, A. J. Cruz, S. Rodríguez-Hermida, I. Stassen, J. Marreiros, M. Krishtab, M. Dickmann, W. Egger, I. F. J. Vankelecom, S. Furukawa, D. De Vos, D. Grosso, M. Thommes, R. Ameloot, *Adv. Mater.*, 2021, **33**, 2006993.

- 2 W.-J. Wang, Z. Ye, H. Fan, B.-G. Li and S. Zhu, *Polymer.*, 2004, **45**, 5497-5504.
- 3 G. Dlubek, K. Saarinen, H. M. Fretwell, J. Polym. Sci., 1998, **36**, 1513.
- 4 V. P. Shantarovich, I. B. Kevdina, Y. P. Yampolskii, A. Y. Alentiev, *Macromolecules.*, 2000, **33**, 7453.
- 5 X. Liu, H.-H. Wu, W. Xu, Y. Jiang, J.-H. Zhang, B.-J. Ye, H.-J. Zhang, S.-F. Chen, M.-H. Miao, D.-H. Zhang, *Adv. Mater.*, 2024, **36**, 2308434.
- G. Guidotti, G. Burzotta, M. Soccio, M. Gazzano, V. Siracusa, A. Munari, N. Lotti, *Polymers-basel.*, 2021,
  13, 2707.
- 7 V. N. Hristov, S. T. Vasileva, M. Krumova, R. Lach, G. H. Michler, *Polym. Composite.*, 2004, **25**, 521.
- E. C. Quinn, A. H. Westlie, A. Sangroniz, M. R. Caputo, S. Xu, Z. Zhang, M. Urgun-Demirtas, A. J. Müller,
  E. Y. X. Chen, *J. Am. Chem. Soc.*, 2023, **145**, 5795.
- 9 M. Eck, S. T. Schwab, T. F. Nelson, K. Wurst, S. Iberl, D. Schleheck, C. Link, G. Battagliarin, S. Mecking, *Angew. Chem. Int. Ed.*, 2023, **62**, e202213438.
- 10 Y. Zhao, E. M. Rettner, K. L. Harry, Z. Hu, J. Miscall, N. A. Rorrer, G. M. Miyake, *Science.*, 2023, **382**, 310.
- 11 M. Haussler, M. Eck, D. Rothauer, S. Mecking, *Nature.*, 2021, **590**, 423.
- 12 L. Zhou, L. Wu, P. Qin, B.-G. Li, Polym. Degrad. Stabil., 2021, 187, 109546.
- 13 S. Tian, Y. Du, P. Wang, T. Chen, J. Xu, H. Yu, B. Guo, ACS. Sustain. Chem. Eng., 2023, **11**, 6652.
- 14 T.-H. Zhao, W.-Q. Yuan, Y.-D. Li, Y.-X. Weng, J.-B. Zeng, *Macromolecules.*, 2018, **51**, 2027.
- 15 H. Hu, R. Zhang, Y. Jiang, L. Shi, J. Wang, W. B. Ying, J. Zhu, ACS. Sustain. Chem. Eng., 2019, 7, 4255.
- 16 T. Dong, X. Yun, M. Li, W. Sun, Y. Duan, Y. Jin, J. Appl. Polym. Sci., 2015, 132.
- 17 C. Thellen, M. Coyne, D. Froio, M. Auerbach, C. Wirsen, J. A. Ratto, J. Polym. Environ., 2008, 16, 1.
- 18 O. Akin, F. Tihminlioglu, J. Polym. Environ., 2018, 26, 1121.
- 19 J. H. Jagannath, S. Nadanasabapathi, A. S. Bawa, J. Appl. Polym. Sci., 2006, 99, 3355
- 20 E. Jacquelot, E. Espuche, J. F. Gérard, J. Duchet, P. Mazabraud, J. Polym. Sci. Pol. Phys., 2006, 44, 431.
- 21 F. Wu, M. Misra, A. K. Mohanty, Prog. Polym. Sci., 2021, 117, 101395.
- 22 X. Liu, N. Desilles, B. Jiang, C. Chappey, L. Lebrun, *Polymer.*, 2022, **247**, 124790.