Supplementary Information

Synthesis and characterization of biobased (co)polyesters derived from cyclic monomers: camphoric acid and 1,4-cyclohexanedimethanol

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Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy

The ^{1}H-NMR spectrum of PCHC is shown in the manuscript (Figure 1). The spectra of PEC, POC, PCHC, P(CHC-*co*-EC), P(CHC-*co*-OC), and CHDM are shown below (Figure S1-S5). The alphabet with primes (e.g. a') denotes the corresponding hydrogen atom at the end of polyester chains. The peak at 7.26 ppm is the residual solvent peak of $CDCl_3$.

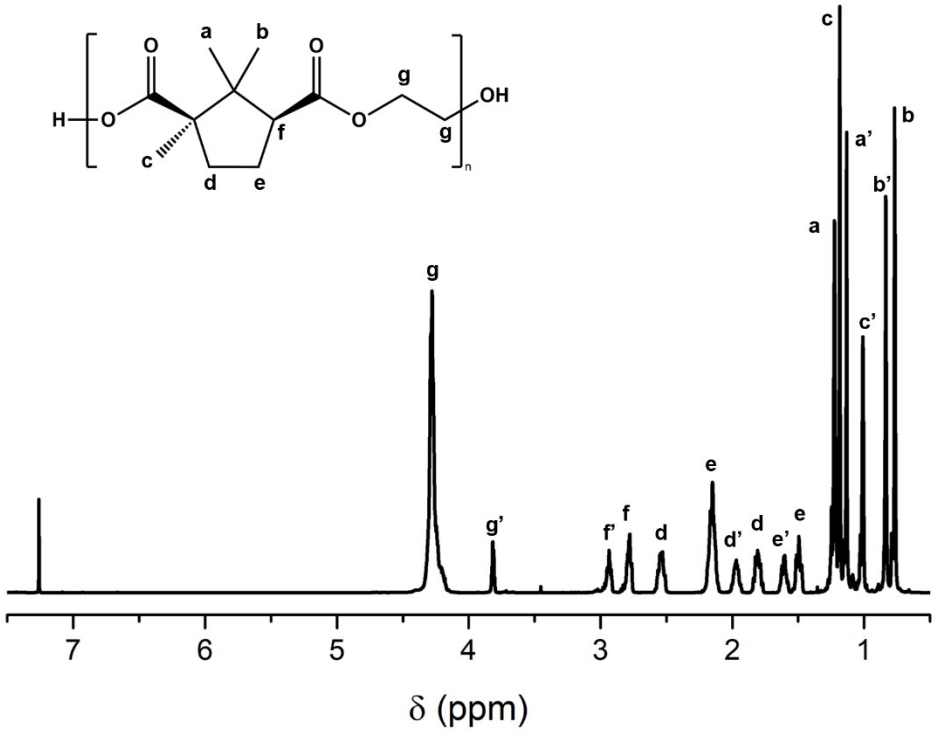


Figure S1. ^{1}H-NMR spectrum of PEC.

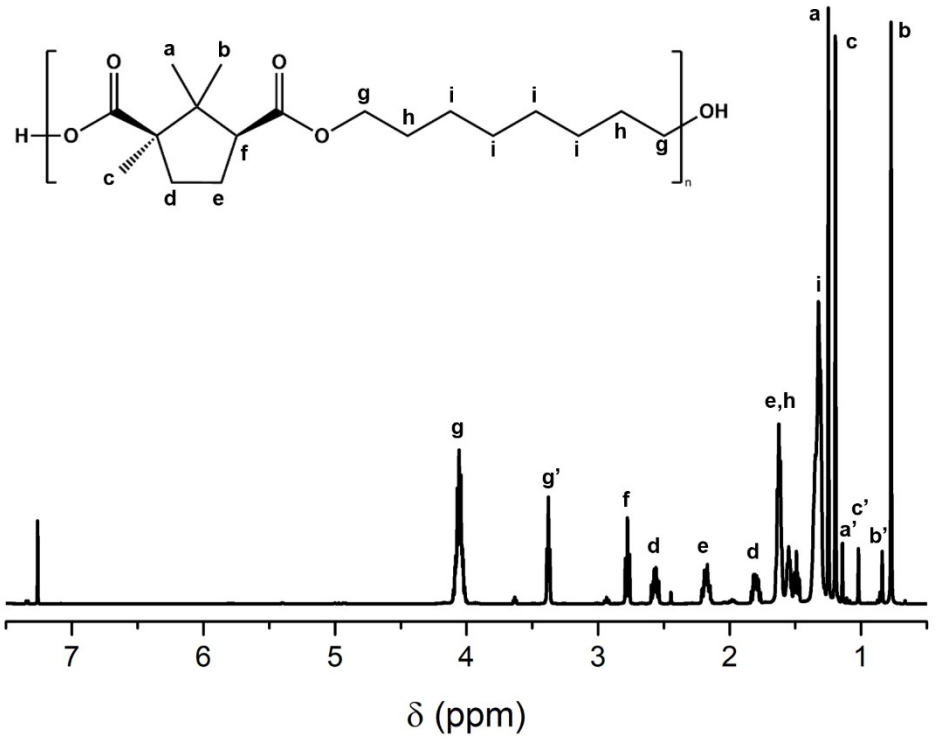


Figure S2. ^{1}H-NMR spectrum of POC.

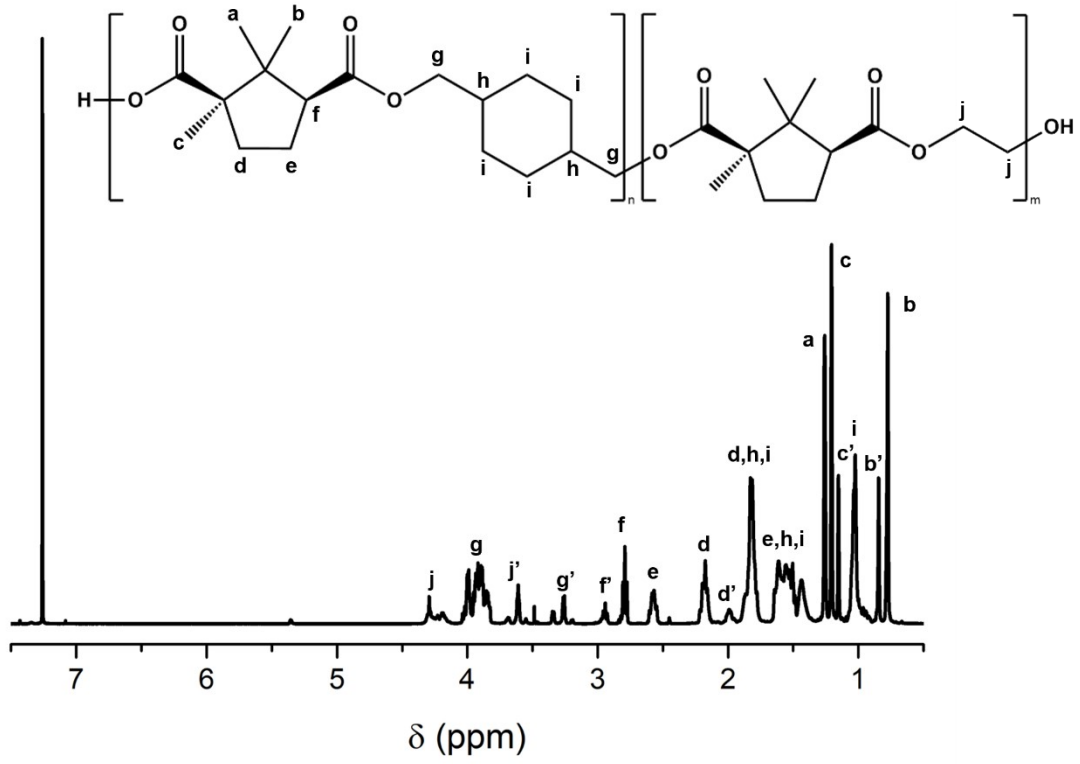


Figure S3. ^{1}H-NMR spectrum of P(CHC-*co*-EC).

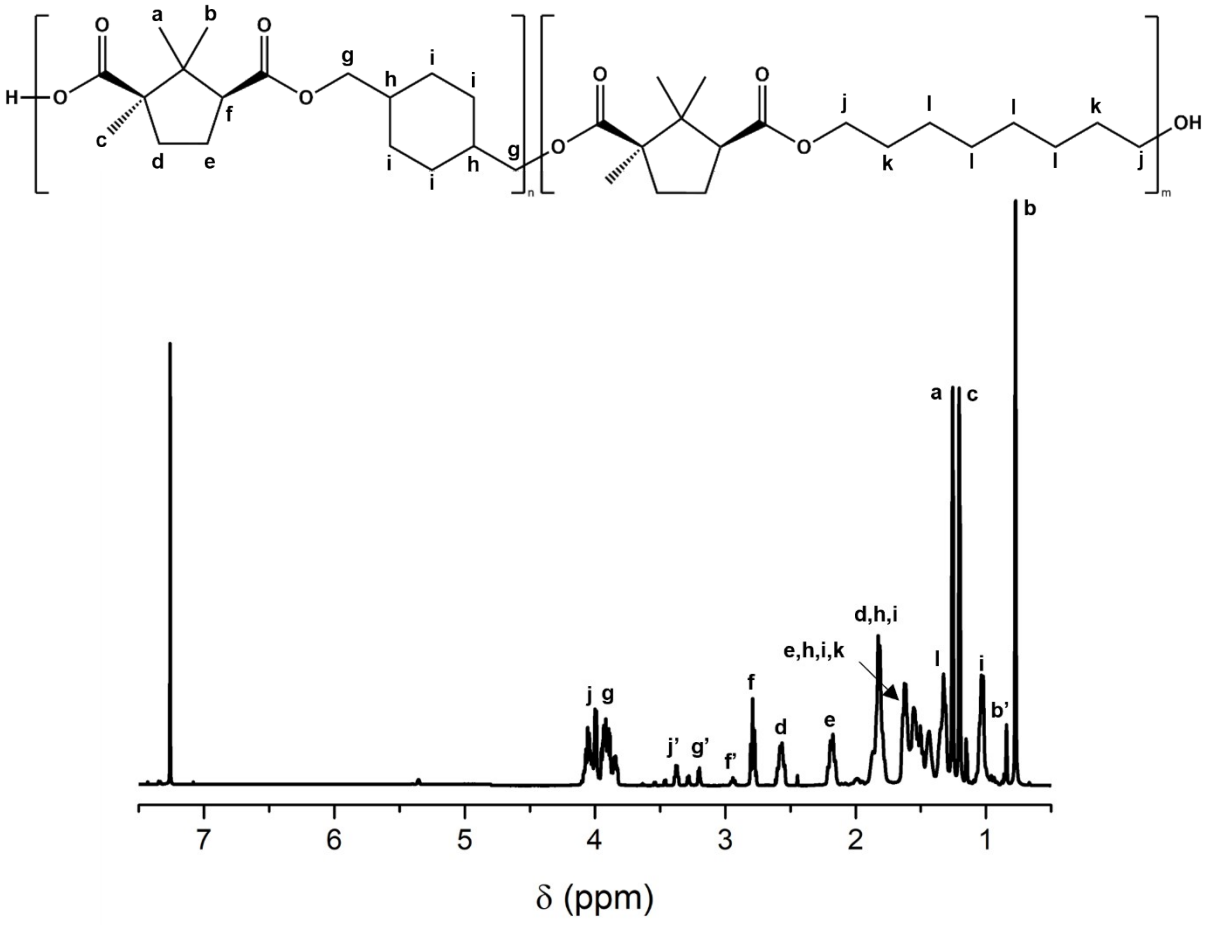


Figure S4. ^{1}H-NMR spectrum of P(CHC-*co*-OC).

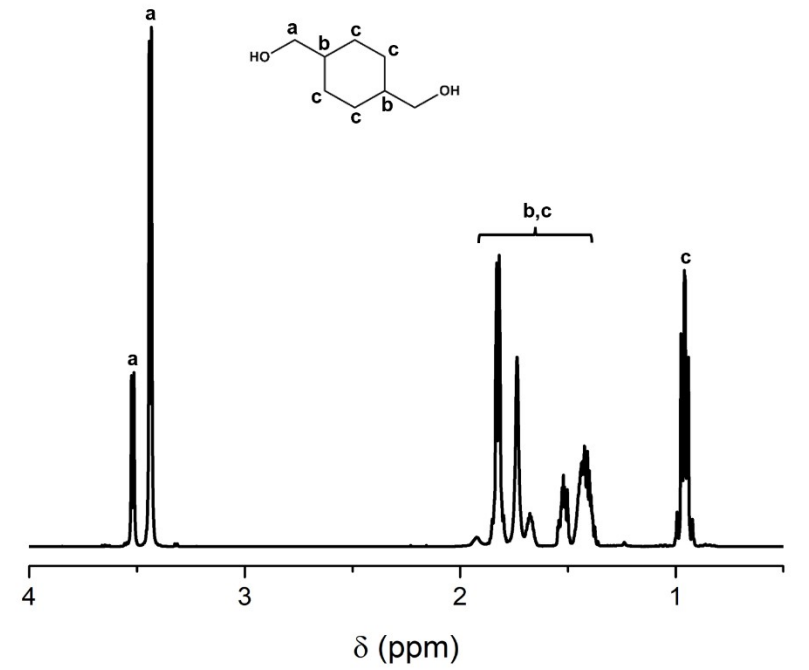


Figure S5. ^{1}H-NMR spectrum of CHDM. 3.51 ppm (d, CH_2OH, cis), I = 1.00; 3.43 ppm (d, CH_2OH, trans), I = 3.00.

Kinetics study

Table S1. Kinetics study of polymerization of camphoric acid and CHDM

Time (h)	$\bar{M}_{w}$ [a] (g/mol)	$\bar{M}_{n}$ [a] (g/mol)	Đ	$\bar{M}_{n}$ [b] (g/mol)
1	600	500	1.2	800
2	900	700	1.3	1,200
3	1,300	800	1.6	1,700
6	6,000	2,600	2.3	4,500
9	8,200	3,500	2.3	6,700
22	12,100	5,000	2.4	7,100
24	13,200	5,300	2.5	7,600
26	12,000	5,000	2.4	7,700

[a] Molecular weights were determined by SEC in chloroform.
[b] Molecular weights were determined by ^{1}H NMR.

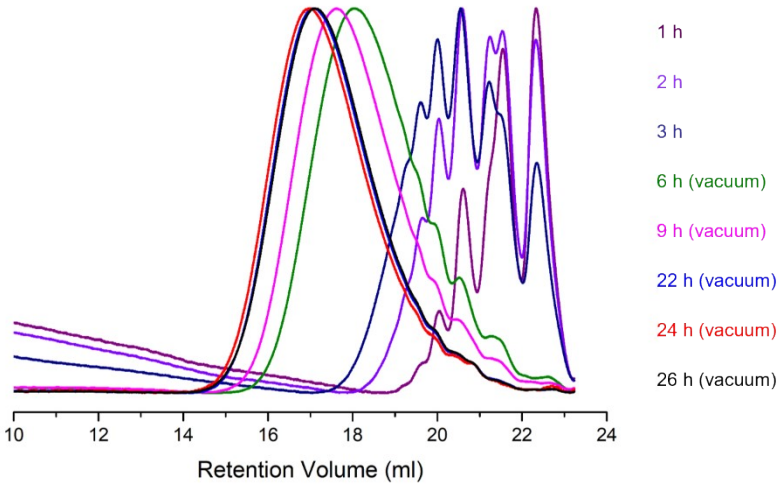


Figure S6. SEC chromatograms of the mixture from the *p*-TSA-catalyzed polycondensations of camphoric acid and CHDM in bulk, carried out at 180 °C for the first 3 h under nitrogen and increased gradually to 200 °C under dynamic vacuum until 2 mmHg was reached.

Size exclusion chromatography (SEC)

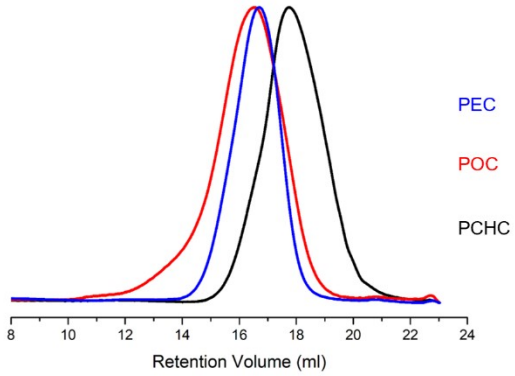


Figure S7. SEC chromatograms of PEC, POC, and PCHC

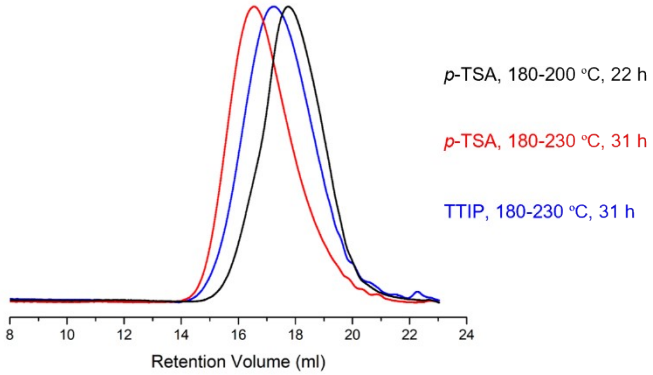
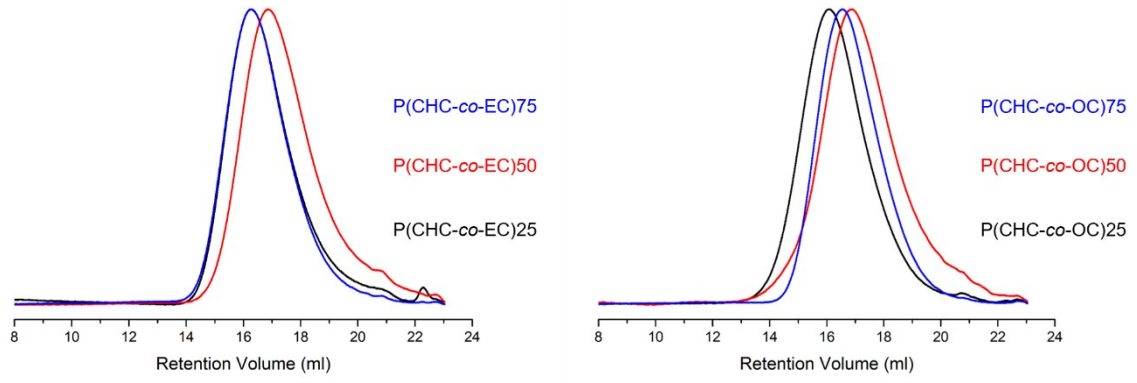


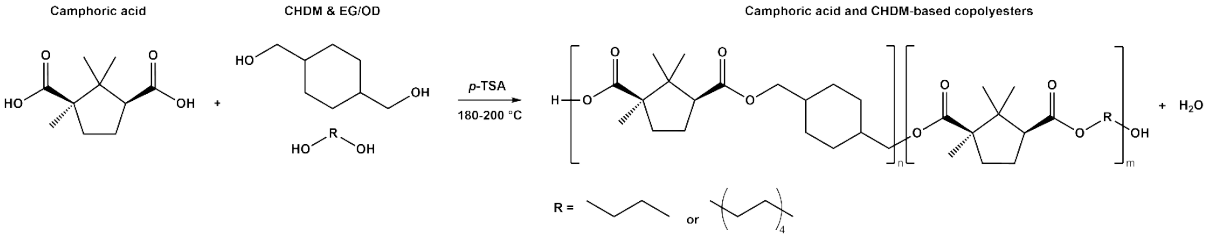
Figure S8. SEC chromatograms of PCHC from variation of polymerization conditions



(a) (b)

Figure S9. SEC chromatograms of (a) P(CHC-*co*-EC) and (b) P(CHC-*co*-OC).

Reaction scheme



Scheme S1. Polymerization reaction of camphoric acid and CHDM-based copolyesters.

In P(CHC-*co*-EC), X_{CHC} and X_{EC} are calculated using the equation:

$$X_{CHC} = \frac{I_{\delta(3.80-4.10)}}{I_{\delta(4.10-4.55)} + I_{\delta(3.80-4.10)}} \quad (1)$$

$$X_{EC} = \frac{I_{\delta(4.10-4.55)}}{I_{\delta(4.10-4.55)} + I_{\delta(3.80-4.10)}} \quad (2)$$

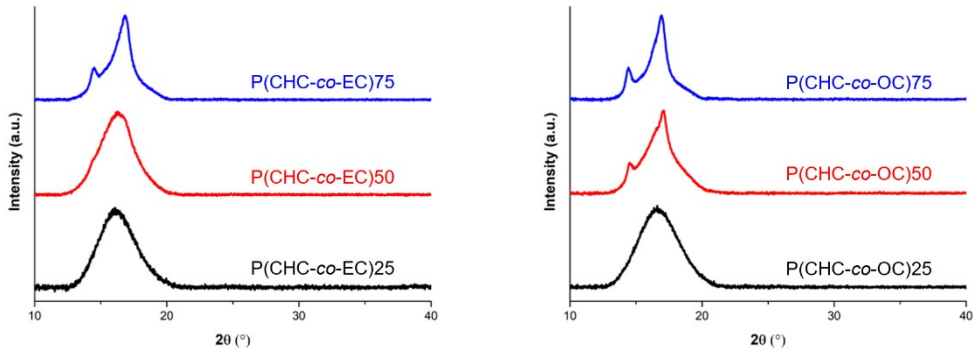
In P(CHC-*co*-OC), X_{CHC} and X_{OC} are calculated using the equation:

$$X_{CHC} = \frac{I_{\delta 3.80-4.04}}{I_{\delta 4.04-4.22} + I_{\delta 3.80-4.04}} \quad (3)$$

$$X_{OC} = \frac{I_{\delta 4.04-4.22}}{I_{\delta 4.04-4.22} + I_{\delta 3.80-4.04}} \quad (4)$$

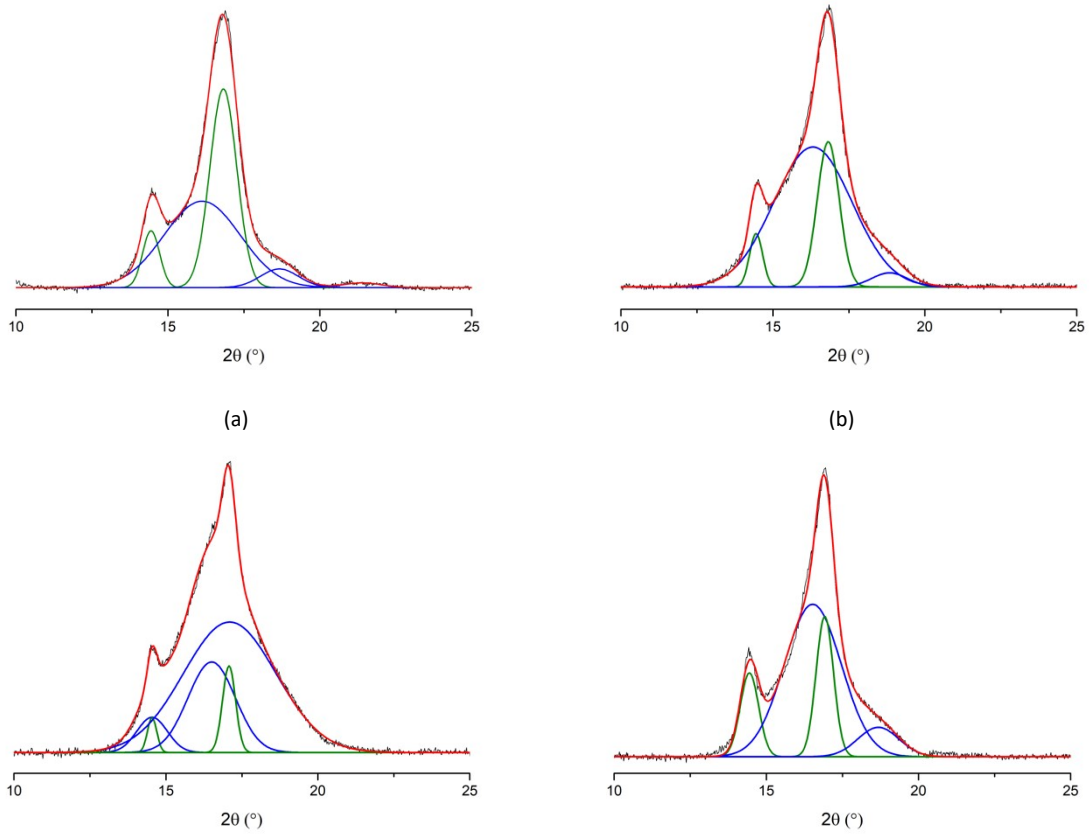
All $I_{\delta(x-y)}$ values represent the integral from δ = x ppm to δ = y ppm of ^{1}H-NMR spectra of the respective copolymers. $I_{\delta(3.80-4.10)}$ represents the integral of proton peaks 3.99 ppm (m, 2H, ester-**CH_2**-cyclohexane, cis) and 3.89 ppm (m, 2H, ester-**CH_2**-cyclohexane, trans). $I_{\delta(4.10-4.55)}$ represents the integral of proton peak 4.29 ppm (m, 4H, ester-**CH_2**-**CH_2**-ester). $I_{\delta(3.80-4.04)}$ represents the integral of proton peaks 4.00 ppm (m, 2H, ester-**CH_2**-cyclohexane, cis) and 3.92 ppm (m, 2H, ester-**CH_2**-cyclohexane, trans). $I_{\delta(4.04-4.22)}$ represents the integral of proton peak 4.06 ppm (m, 4H, ester-**CH_2**-CH_2-$(CH_2)_4$-CH_2-**CH_2**-ester).

Wide-Angle X-Ray Diffraction (WAXD) spectra



(a) (b)

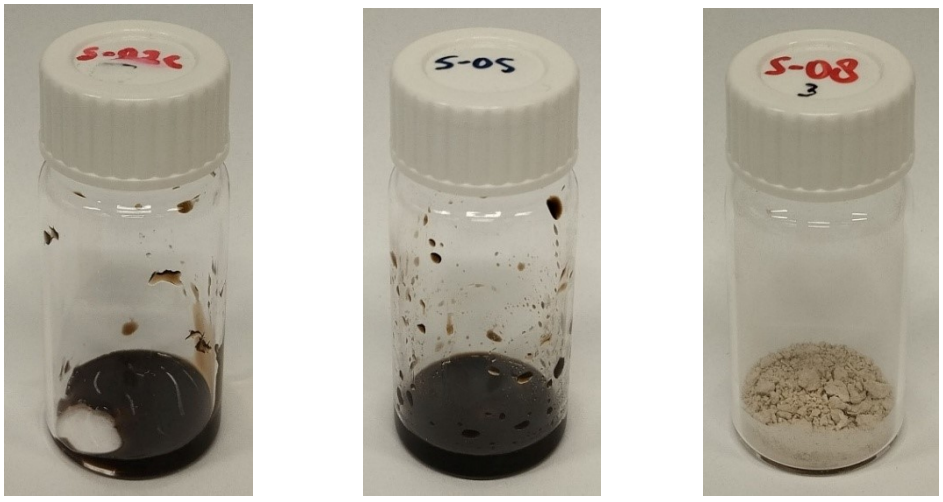
Figure S10. Wide-angle X-ray diffraction (WAXD) results of (a) P(CHC-*co*-EC) and (b) P(CHC-*co*-OC).



(a) (b)

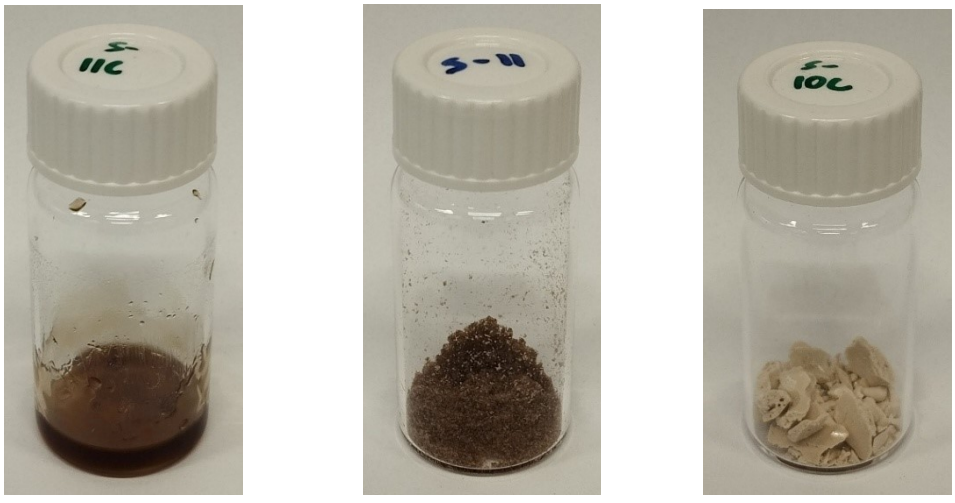
(c) (d)

Figure S11. Multi-peak fitting of WAXD spectra of (a) PCHC, (b) P(CHC-*co*-EC)75, (c) P(CHC-*co*-OC)50, and (d) P(CHC-*co*-OC)75. Blue lines represent amorphous peaks. Green lines represent crystalline peaks. Red lines represent the cumulative fit peaks.



(a) (b) (c)

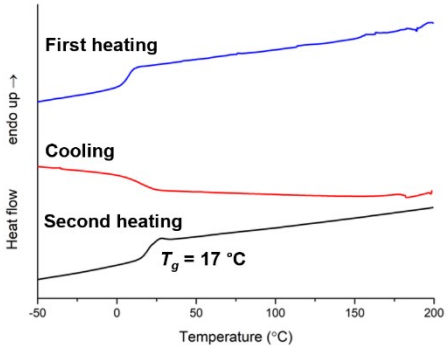
Figure S12. Product appearance of (a) PEC, (b) POC, and (c) PCHC.



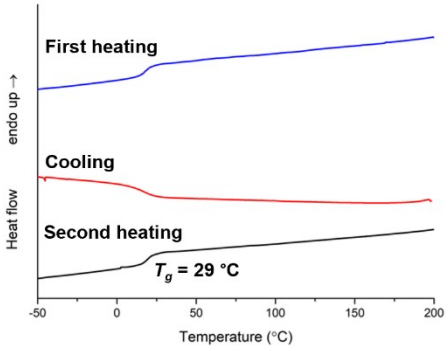
(a) (b) (c)

(d) (e) (f)

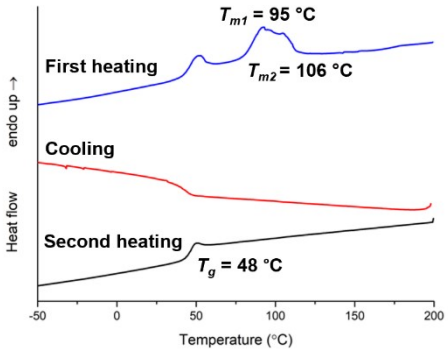
Figure S13. Product appearances of (a) P(CHC-*co*-EC)25, (b) P(CHC-*co*-EC)50, (c) P(CHC-*co*-EC)75, (d) P(CHC-*co*-OC)25, (e) P(CHC-*co*-OC)50, and (f) P(CHC-*co*-OC)75.



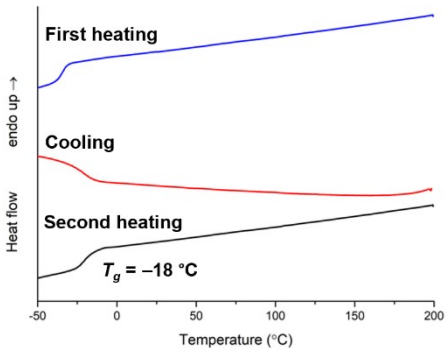
(a)



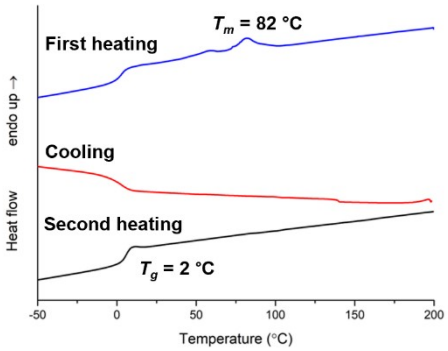
(b)



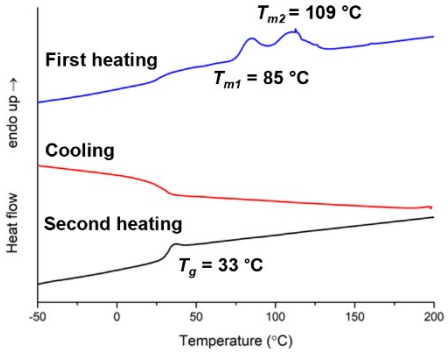
(c)



(d)



(e)



(f)

Figure S14. DSC thermograms of (a) P(CHC-*co*-EC)25, (b) P(CHC-*co*-EC)50, (c) P(CHC-*co*-EC)75, (d) P(CHC-*co*-OC)25, (e) P(CHC-*co*-OC)50, and (f) P(CHC-*co*-OC)75.

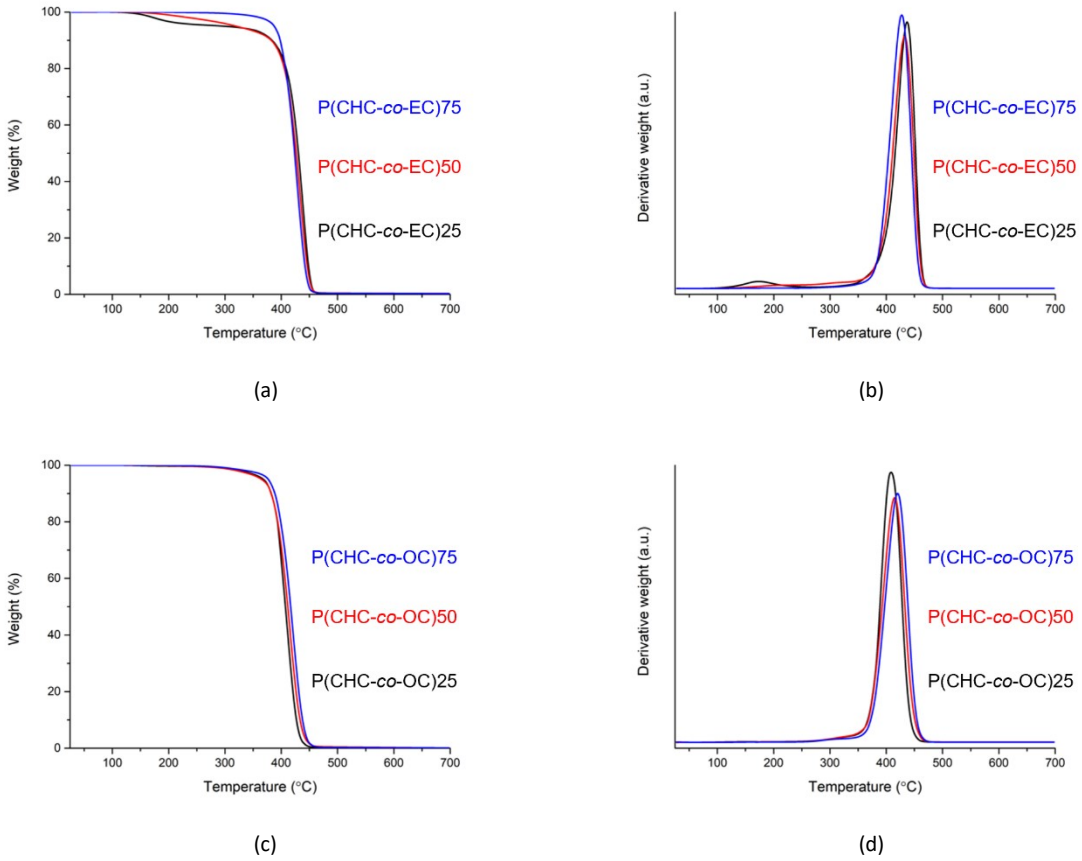


Figure S15. (a) TGA results of P(CHC-*co*-EC)s, (b) Derivative weight loss curves versus temperature of P(CHC-*co*-EC)s, (c) TGA results of P(CHC-*co*-OC)s, and (d) Derivative weight loss curves versus temperature of P(CHC-*co*-OC)s.

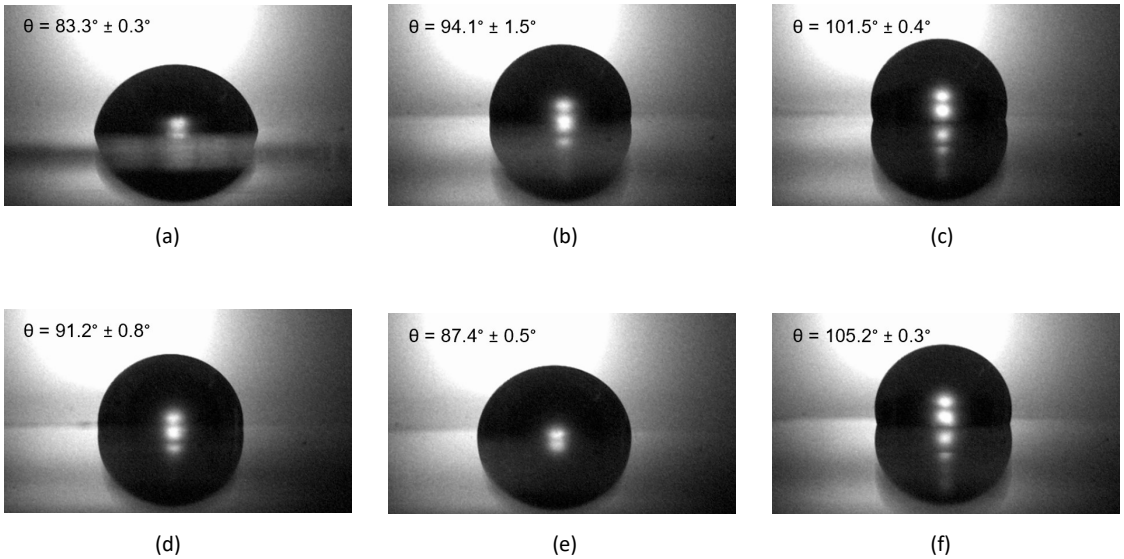


Figure S16. Drop profile and water contact angle value of copolyesters: (a) P(CHC-*co*-EC)25, (b) P(CHC-*co*-EC)50, (c) P(CHC-*co*-EC)75, (d) P(CHC-*co*-OC)25, (e) P(CHC-*co*-OC)50, and (f) P(CHC-*co*-OC)75.