

Supporting Information

High performance long chain polyesters via melt copolymerization of cutin-inspired monomers

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Supplemental Characterization Data

Table S1: Physico-chemical characteristics of copolymers and homopolymers

Name	Young's modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Toughness J/m ³	M_C (g/mol)	Swelling ratio (%)	Insoluble fraction (wt %)
(1) PAA	296 ± 22	1.4 ± 0.4	2.2 ± 0.4	21.8 ± 4.6	28 ± 8	5100	419.2	88.5
(2) P(AA _{0.7} -co-HHA _{0.3})	493 ± 67	4.1 ± 0.5	10.1 ± 2.1	268.4 ± 43.6	2430 ± 430	18000	450.0	88.3
(3) P(AA _{0.5} -co-HHA _{0.5})	892 ± 24	5.1 ± 0.3	9.8 ± 1.6	271.2 ± 35.7	2610 ± 370	11000	77.1	86.1
(4) P(AA _{0.3} -co-HHA _{0.7})	872 ± 58	5.3 ± 0.6	10.8 ± 1.5	266.1 ± 32.1	2730 ± 350	4300	74.3	85.1
(5) PHHA	1727 ± 57	5.3 ± 0.6	8.1 ± 0.8	7.1 ± 1.1	47 ± 7	N.A.	N.A.	N.A.
LDPE	292 ± 13	4.9 ± 0.3	11.5 ± 0.8	348.8 ± 45.2	3050 ± 390	N.A.	N.A.	N.A.

Table S2. Summary of solid state ¹³C NMR spectroscopic analysis.

Sample	%Conversion primary O-H	%Conversion secondary O-H
P(AA)	56	39
P(AA _{0.5} -co-HHA _{0.5})	79	49
P(HHA)	100	n.a.

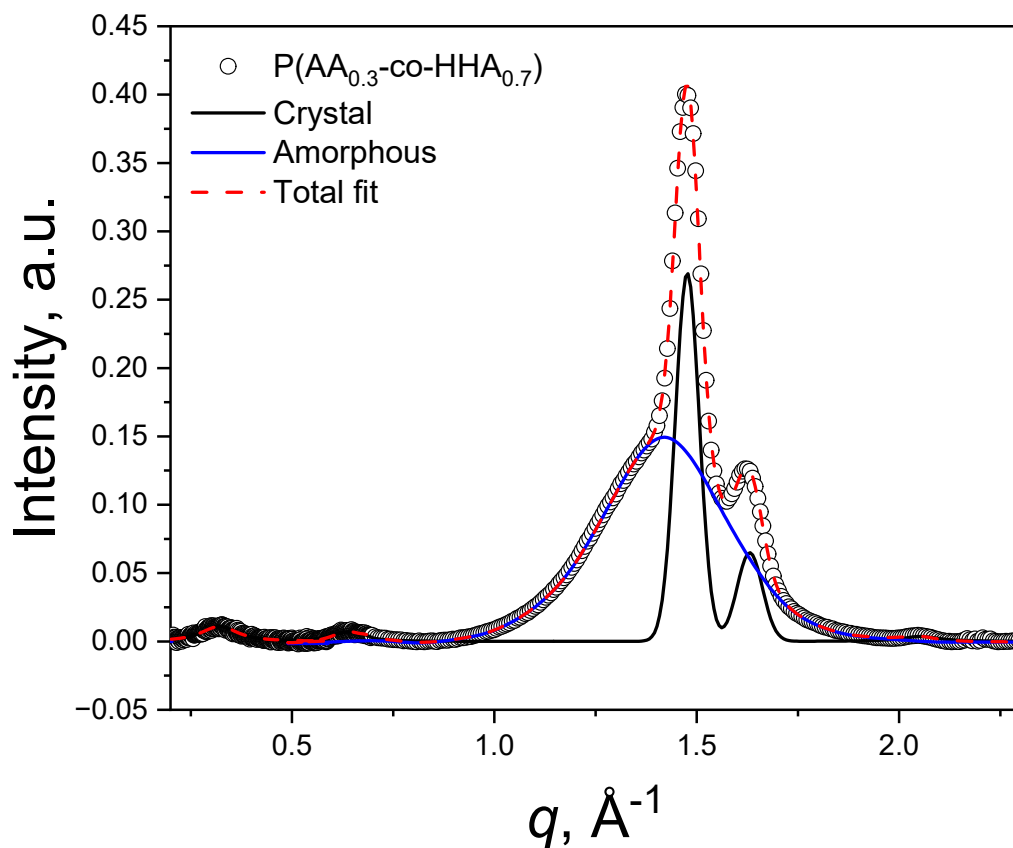


Figure S1. Exemplified peak deconvolution of the WAXS data for P(AA_{0.3}-co-HHA_{0.7}), where the choice of the fit was Voight functions.

Table S3. Results of the fitting of the WAXS data and corresponding crystallinity obtained from the fitting for studied polymers.

	PHHA	P(AA _{0.3} -co-HHA _{0.7})	P(AA _{0.5} -co-HHA _{0.5})	P(AA _{0.7} -co-HHA _{0.3})	PAA
Total crystalline peak area	11.3	5.9	4.6	4.2	4.8
Total amorphous peak area	8.2	9.3	11.3	12.3	14.9
Total WAXS area	19.5	15.2	15.9	16.5	19.7
% crystallinity	57.9	38.8	28.9	25.5	24.4

Table S4: Lamellar long periods from SAXS experiments.

Name	Lamellar long period, Lp
PHHA	134.7 Å
P(AA _{0.3} -co-HHA _{0.7})	119.4 Å
P(AA _{0.5} -co-HHA _{0.5})	154.4 Å
P(AA _{0.7} -co-HHA _{0.3})	132.3 Å
PAA	173.3 Å

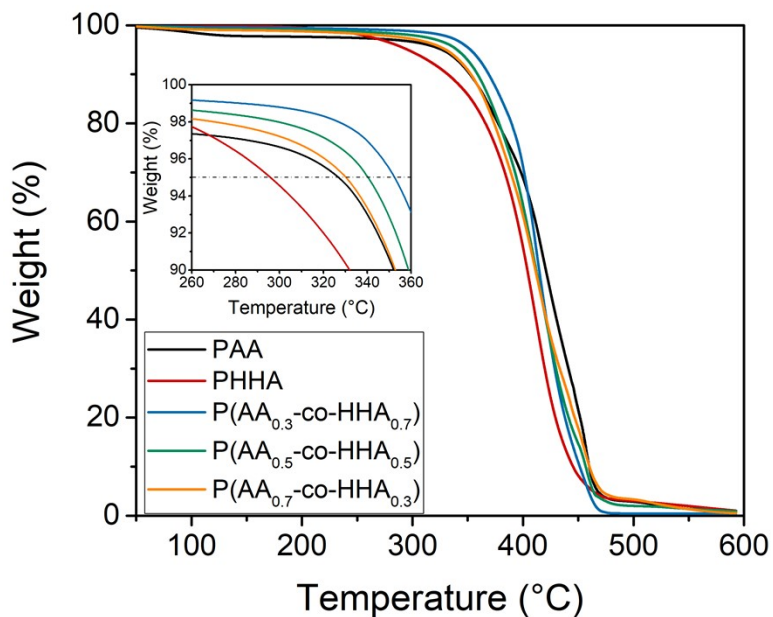


Figure S2. TGA results for all co-polymer and homopolymers. The inset contains zoomed-in area to better illustrate the onset of thermal degradation.

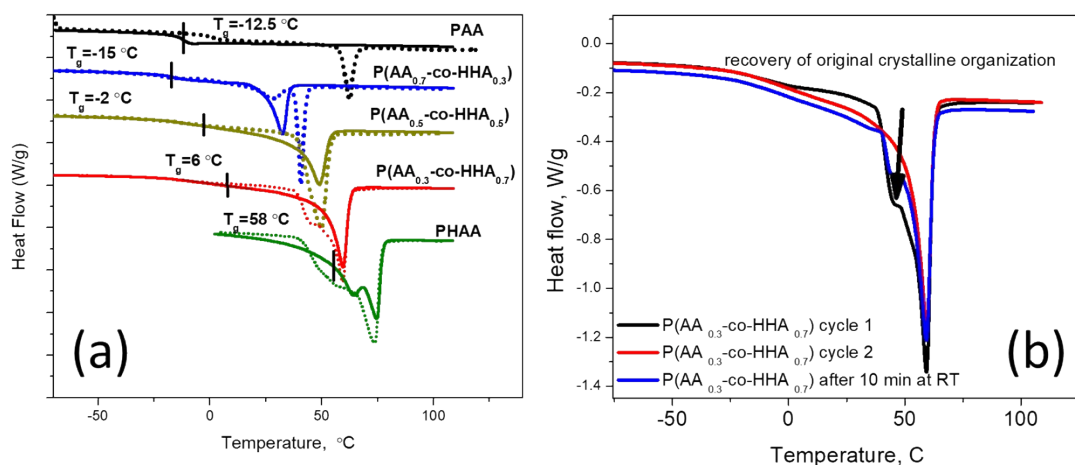


Figure S3. DSC a) first (dotted line) and second (solid line) heating cycles b) DSC of $P(\text{AA}_{0.3}\text{-co-HHA}_{0.7})$, which demonstrates the transient nature of the crystalline phase obtained after the cooling in DSC instrument.

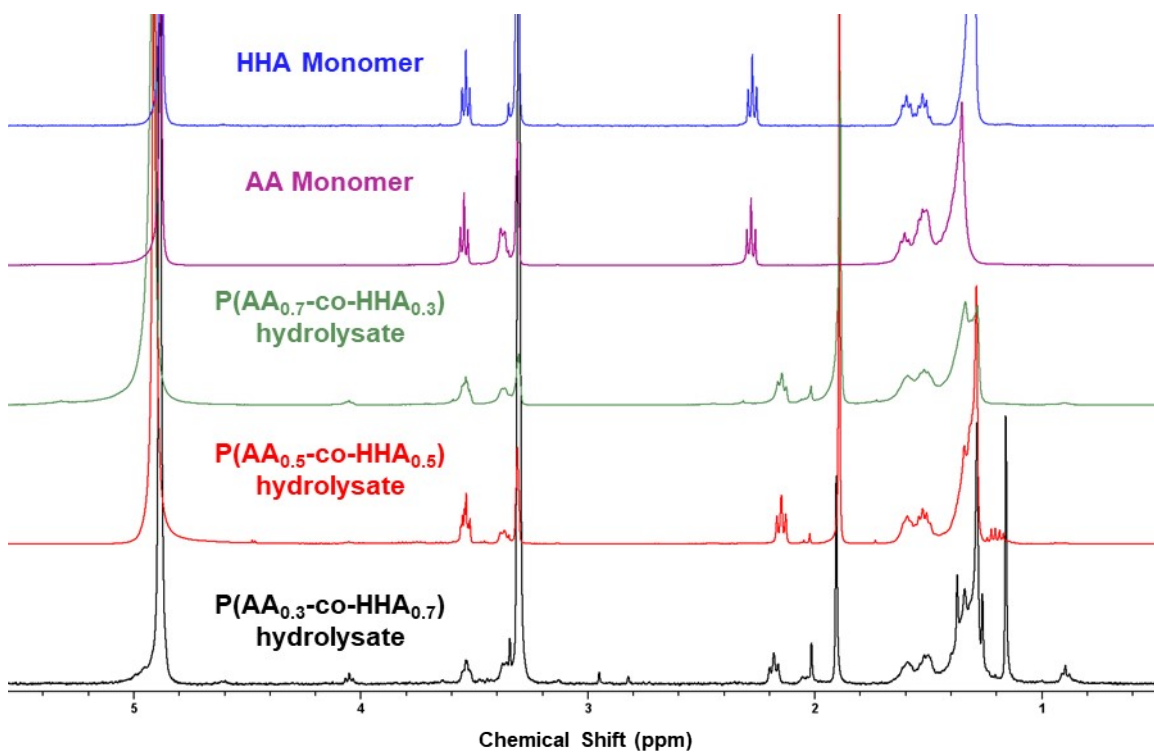


Figure S4. ^1H NMR spectra in MeOD of HHA and AA monomers and the crude samples obtained via hydrolysis of the various copolymers.

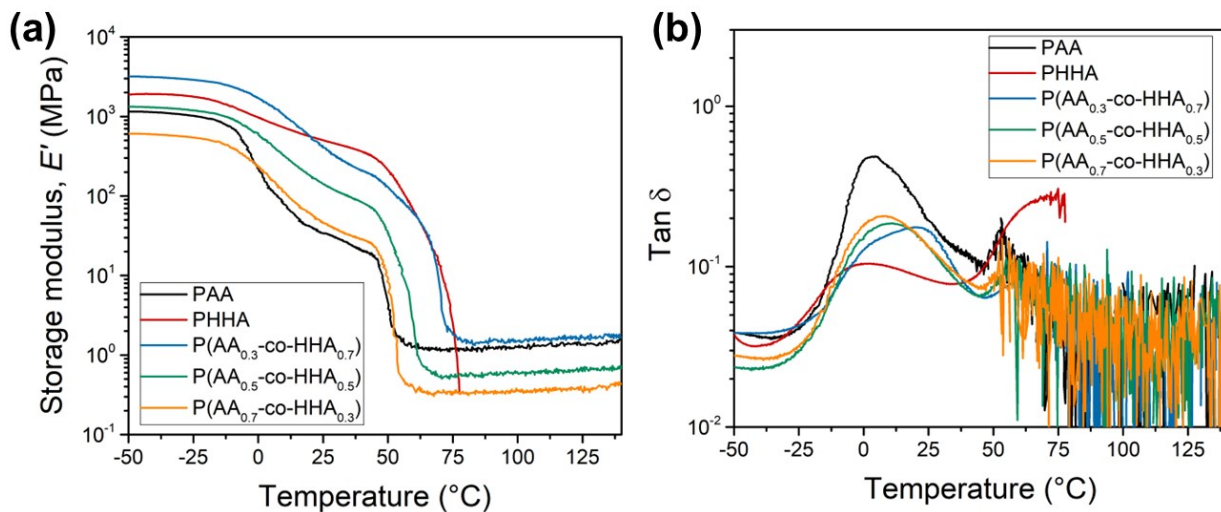


Figure S5. DMA results a) storage modulus b) tan delta.

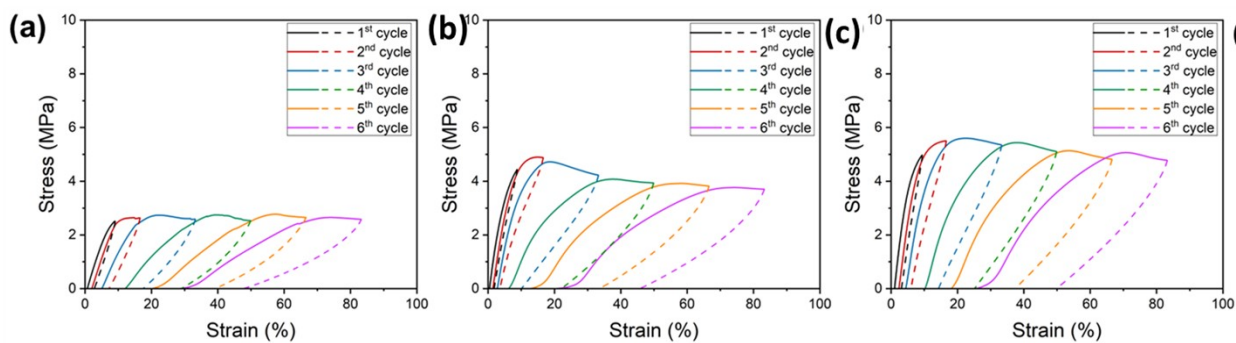


Figure S6 Cyclic DMA tests for a) $\text{P}(\text{AA}_{0.7}\text{-co-HHA}_{0.3})$; b) $\text{P}(\text{AA}_{0.5}\text{-co-HHA}_{0.5})$; and c) $\text{P}(\text{AA}_{0.3}\text{-co-HHA}_{0.7})$ tested at 25 $^{\circ}\text{C}$.

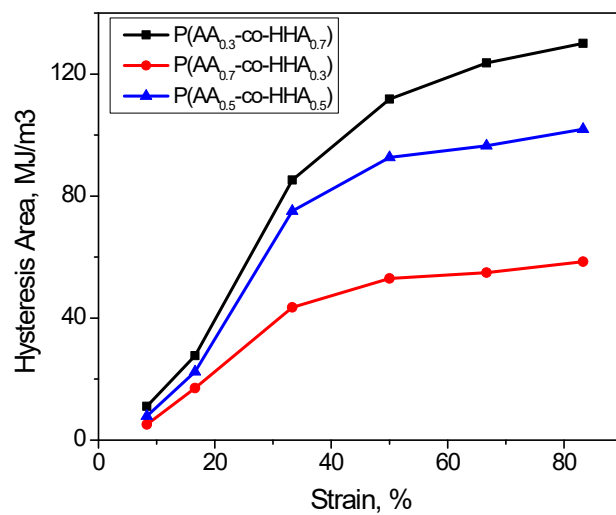


Figure S7. Plots of hysteresis area vs. applied max strain for copolymers.

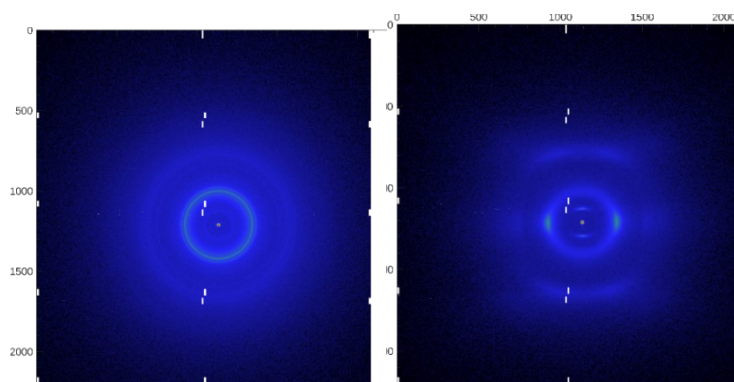


Figure S8. 2D WAXS images of P(AA_{0.5}-co-HHA_{0.5}) at the condition of pristine and 200% stretching.