Supporting Information

Melt polycondensation of carboxytelechelic polyethylene for the design of degradable segmented copolyester polyolefins

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Figure S1. ¹H NMR of carboxytelechelic PCO. Analysis performed using 500 MHz Bruker spectrometer in CDCl₃ using 128 scans and a 5 s relaxation delay.



Figure S2. SEC trace of carboxy-terminated PCO and table of values from SEC in THF, using dn/dc = 0.110 from literature sources.¹⁸



Figure S3. ¹H NMR of carboxytelechelic PE ($M_n = 3900$ g/mol). Analysis performed using 400 MHz Bruker spectrometer in tetrachloroethane-d₂ at 100 °C using 8 scans and a 1 s delay.

Table S1. Summary of thermogravimetric data of control homopolymers and segmentedcopolymers with varying wt.% PE loading.

Polymer composition	<i>Τ</i> _{d,5%} (°C)	7 _{d, 2nd step} (°С)
Carboxytelechelic polyethylene	435	-
poly(ethylene ₁₀ - <i>co</i> -neopentyl adipate ₉₀)	337	470
poly(ethylene ₄₈ - <i>co</i> -neopentyl adipate ₅₂)	337	450
poly(ethylene ₇₅ - <i>co</i> -neopentyl adipate ₂₅)	340	443
poly(ethylene ₉₅ - <i>co</i> -neopentyl adipate ₅)	434	-
poly(neopentyl adipate)	324	-



Figure S4. DSC trace of carboxytelechelic PE ($M_n = 3900$ g/mol) following reduction of double bonds. Heat/cool/heat cycle, second heat displayed with endothermic transition up.

Sample	λ , long period (Å)	Crystallinity from DSC (%)	Estimated Crystallite thickness (Å)
Commercial HDPE	209	63	132
poly(ethylene ₉₅ - <i>co</i> -neopentyl adipate ₅)	201	53	107
poly(ethylene ₇₅ - <i>co</i> -neopentyl adipate ₂₅)	189	48	91

Table S2. Crystallite thickness calculation originating from DSC-derived % crystallinity in combined with the long period from SAXS.



Figure S5. Melt rheology of various segmented copolymer compositions illustrates differences in complex viscosity when subject to 170 °C at 0.1% strain under air.

Accelerated acid-catalyzed hydrolysis depolymerization of segmented copolyester demonstrates recovery of telechelic prepolymer



Figure S6. ¹H NMR of the original telechelic prepolymer (bottom) compared to recovered polymer following hydrolysis of segmented copolymer (top) reveals good recovery of prepolymer following depolymerization. Analysis was performed using 400 MHz Bruker spectrometer in tetrachloroethane-d₂ at 100 °C using 128 scans and a 1 s delay.

Hydrolysis of the 48 wt.% PE segmented copolymer demonstrated the ability to chemically depolymerize the PE-segmented copolymers described herein. Subjecting a melt-pressed film of the segmented copolymer to hydrochloric acid at reflux in a homogeneous solution of toluene generated a white solid upon cooling. Following filtration and washing with methanol, the above NMR spectrum was obtained (**Figure S6**), revealing a slightly lower integration of the backbone

signal of PE compared to the starting material prepolymer. Partial degradation of the PE backbone at elevated temperatures may be responsible for the slight molecular weight decrease observed. The successful recovery of the PE prepolymer confirms the degradability of the segmented copolyesters.