Supporting Information

One-Pot Synthesis of Semicrystalline/Amorphous Multiblock Copolymers via Divinyl-Terminated Telechelic Polyolefins

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General Information:

All experimental setups were carried out in a glovebox under nitrogen atmosphere or under dry argon using standard Schlenk line techniques. All glassware was oven-dried or flame-dried. Ethylene (polymer grade, 99.9%) and Ar were purchased from Praxair and purified by passing through Agilent moisture and oxygen traps. Toluene for hydrogenation, in situ ethenolysis and polymerization was dried using a column solvent purification system. Unless specifically mentioned, all chemicals are commercially available and were used as received.

High temperature ^{1}H NMR spectra were recorded on Bruker 500 MHz spectrometer in tetrachloroethane-d2. Gel permeation chromatography (GPC) analysis of polymers was performed on a Polymer Laboratory high temperature GPC system (Model PL-220) equipped with a refractive index detector. Samples were run at 150 °C in spectrophotometric grade 1,2,4-trichlorobenzene as the mobile phase, stabilized with BHT (0.5 g BHT / 4 L solvent) at a flow rate of 1 mL/min. Molecular weights and polydispersity were calculated by using a universal calibration from narrow polystyrene standards in the range of 580 to 7.5 million. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC (Model Q-20) under a nitrogen flow. Samples with a minimum mass of 4 mg were prepared in hermetically sealed aluminum pan and analyzed between -85 to 150 °C at a rate of 10 °C/min. Scanning electron microscopy (SEM) images were obtained using FEI XL30 Sirion FEG digital electron scanning microscope. The cross-sections were prepared by first breaking tensile specimens in liquid nitrogen, and sputtering with 5 nm Au/Pd on top prior to measurements. For comparison, the cross-sections were also chemically etched in toluene at room temperature for 20 min, and depositing 5 nm Au/Pd on the fractured surface. Monotonic and step-cycle tensile tests were carried out with dog-bone specimens at room temperature. For stress-strain plots, representative curves were chosen from at least five data sets per sample. The gauge length of each specimen was 7 mm long and has a cross section that is 2 mm wide and 0.4-0.6 mm thick. The crosshead speed of the tensile machine was kept at 5 mm/min for all the testings. The elastic recovery is defined as the strain recovered upon unloading divided by the maximum strain reached during the step.

Preparation of Starting Polymers via Partial Hydrogenation of Polybutadienes

To prepare the starting semicrystalline polybutadiene **S** (purchased from Sigma-Aldrich, Mn = 200 KDa, Đ = 1.79, 1.29 g), Wilkinson's catalyst (53.7 mg, 0.058 mmol), and triphenylphosphine (51.2 mg, 0.195 mmol) in 165 mL toluene were added into a Parr reactor equipped with a temperature probe, pressure gauge, and a paddle wheel stirrer. The reactor was sealed tightly before taking it outside the glovebox. The reaction mixture was stirred at 75 °C for 2.5 h to ensure the starting polymer completely soluble in toluene. Then the reactor was charged with 200 psi of H_2. High-temperature NMR was used to monitor the reaction and control 1,4-inserted butadiene content. After 1.8 h， the pressure in this system was released and the reactor was disassembled. The reaction solution was precipitated into 500 mL methanol. The mixture was stirred at room temperature for 1 hour. The polymer was filtered and dried under high vacuum overnight. An off-white solid was obtained in 95% yield. Fig. S1 shows the ^{1}H NMR of the resulting product in tetrachloroethane-d2 at 120 °C.

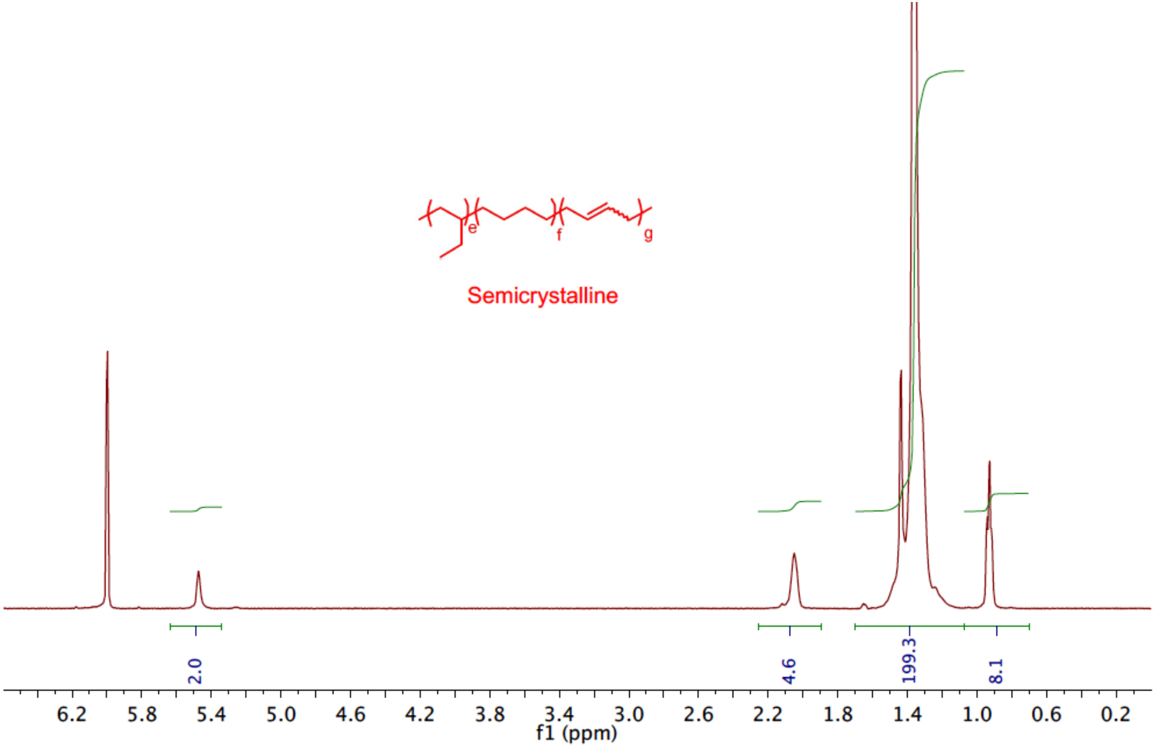

Fig. S1. ^{1}H NMR spectrum of the starting semicrystalline polymer **S** in tetrachloroethane-d2 at 120 °C.

The starting amorphous **A1** was prepared from polybutadiene (purchased from Polymer Source, Mn = 55 KDa, Đ = 1.81) using the similar procedure as described previously for partial hydrogenation of **S**, but the reactions were run at 60 °C for 4.3 h. A colorless, viscous material was obtained in 90% yield.

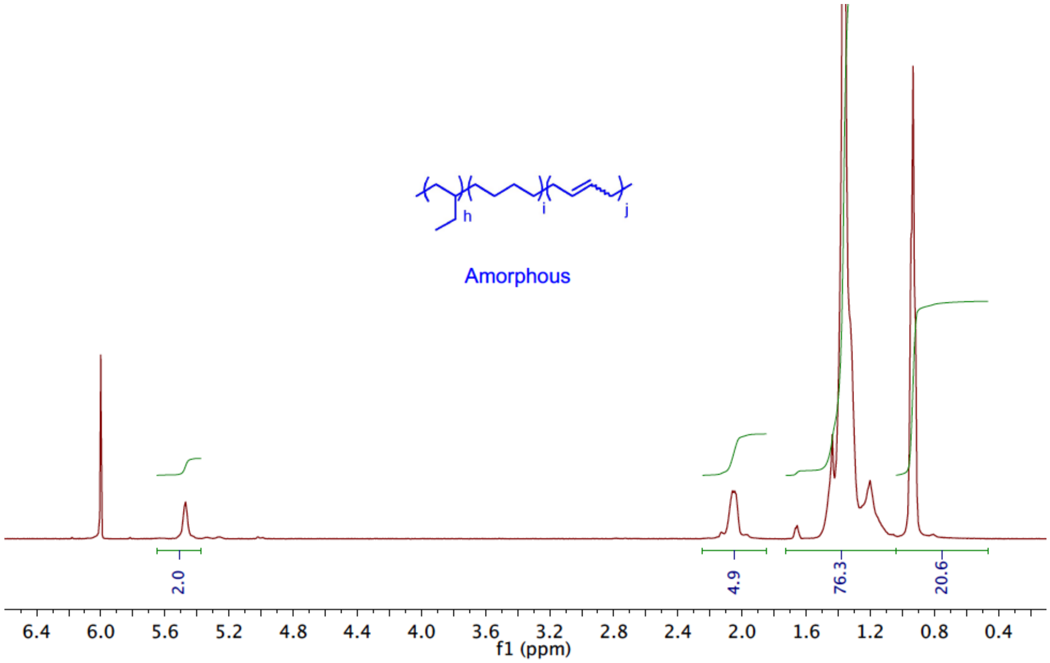

Fig. S2. ^{1}H NMR spectrum of the starting amorphous polymer **A1** in tetrachloroethane-d2 at 120 °C.

The starting amorphous **A2** was prepared from polybutadiene (purchased from Polymer Source, Mn = 197 KDa, Đ = 1.59) using the similar procedure as described previously for partial hydrogenation of **S**, but the reactions were run at 60 °C for 4.2 h. A colorless, viscous material was obtained in 94% yield.

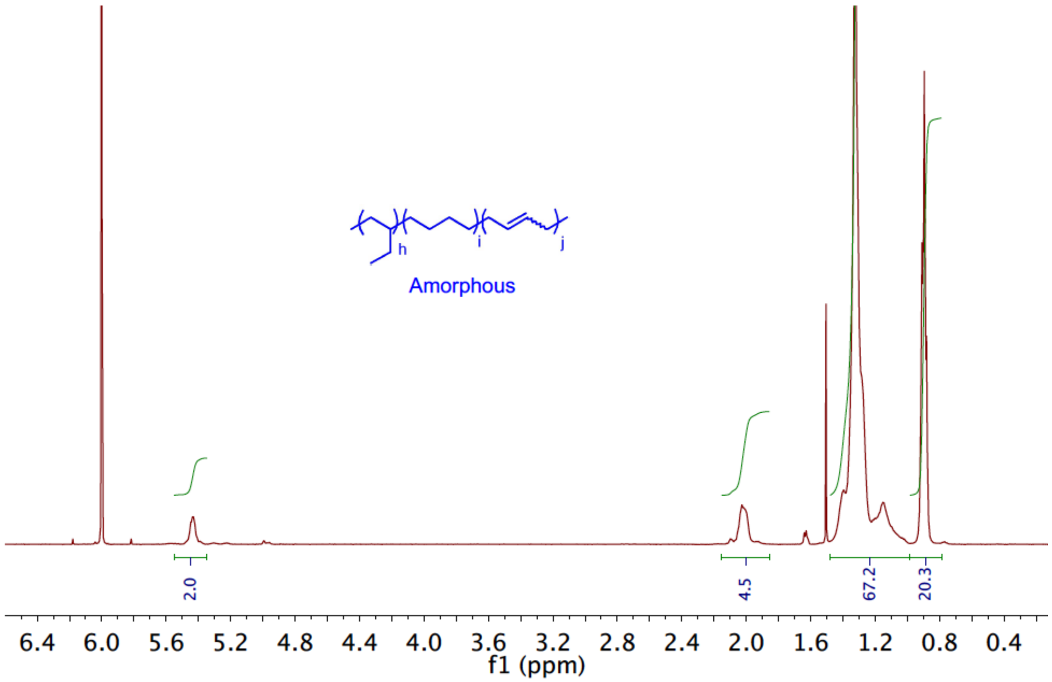

Fig. S3. ^{1}H NMR spectrum of the starting amorphous polymer **A2** in tetrachloroethane-d2 at 120 °C.

One-pot Synthesis of Random Semicrystalline/Amorphous Multiblock Copolymers

A mixture of **S** (318 mg) and **A1** (318 mg), tricyclohexylphosphine[3-phenyl-1H-inden-1-ylidene][1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]ruthenium(II) dichloride (2.2 mol% relative to 1,3-butadiene unsaturation in the starting polymers) and toluene (concentration: 30 g polymer$_{S+A}$ /L toluene) were added to a thick-wall pressure vessel. This assembly was tightly closed inside the glovebox and taken outside to heat up to 90 °C. The reactor was charged with 25 psi of ethylene gas. After the reaction was stirred for 2 h, an aliquot was taken out for high-temperature ^{1}H NMR and GPC analysis. A new portion of catalyst (1.0 mol% relative to 1,3-butadiene unsaturation in the starting polymers) was added into the reaction mixture under Ar. The solvent was sparged with Ar until dryness (about 30 min), and the evaporated solvent was trapped with a cold flask in an ice bath. The reaction residue was re-dissolved in a minimum amount of toluene, and re-precipitated in methanol, filtered and dried under vacuum overnight.

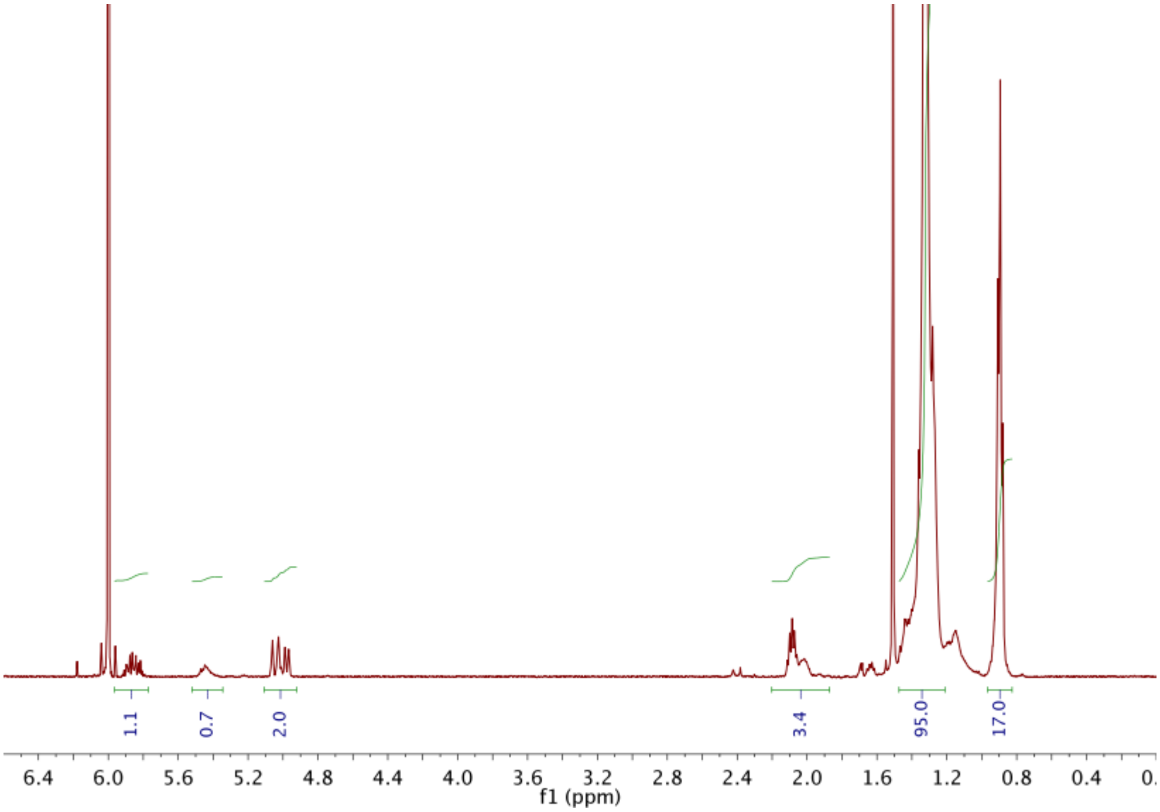

Fig. S4. Representative ^{1}H NMR spectrum of an aliquot of the reaction mixture after ethenolysis in tetrachloroethane-d2 at 120 °C.

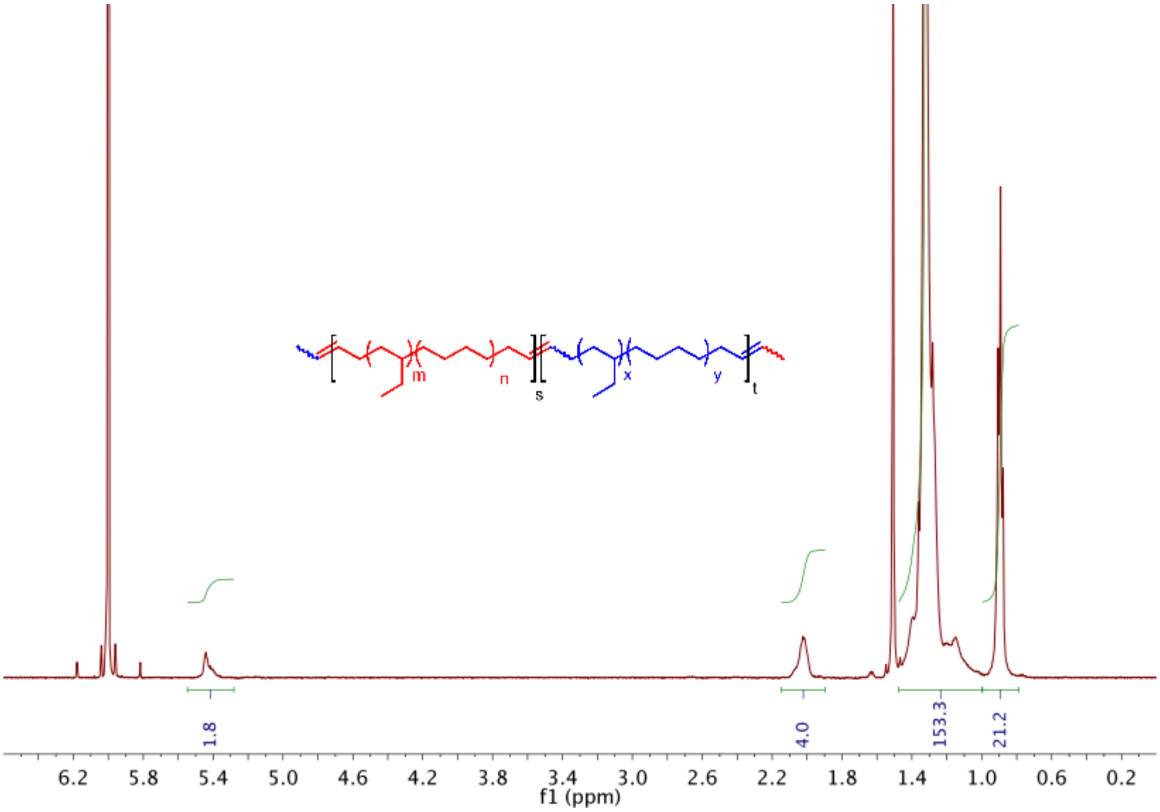

Fig. S5. Representative ^{1}H NMR spectrum of the ADMET product in tetrachloroethane-d2 at 120 °C.

Table S1. Composition of P(S-A) multiblock copolymers.

Polymer	1-Butene[a] (mol%)	Tetramethylene[a] (mol%)	1,3-Butadiene[a] (mol%)
P(S-A1)	31	65	4
P1(S-A2)	32	63	5
P2(S-A2)	28	67	5

[a] Determined by ^{1}H NMR spectroscopy.

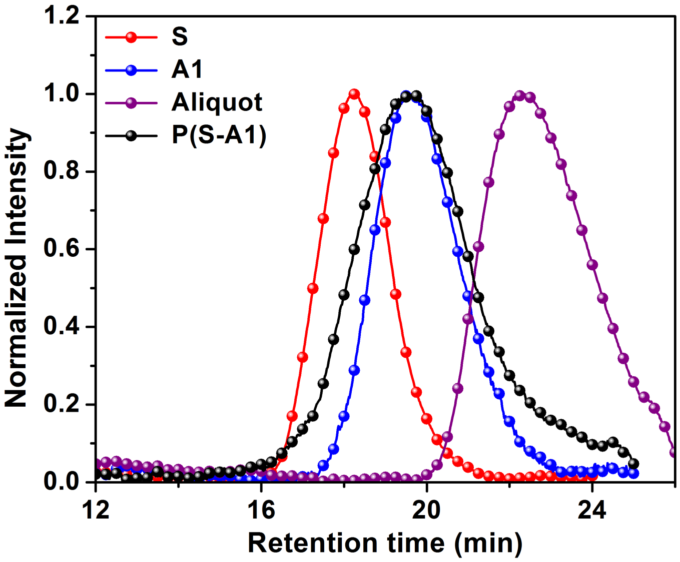

Fig. S6. GPC traces for the starting semicrystalline polymer **S**, the starting amorphous one **A1**, an aliquot of the reaction mixture after ethenolysis, and their ADMET product **P(S-A1).**

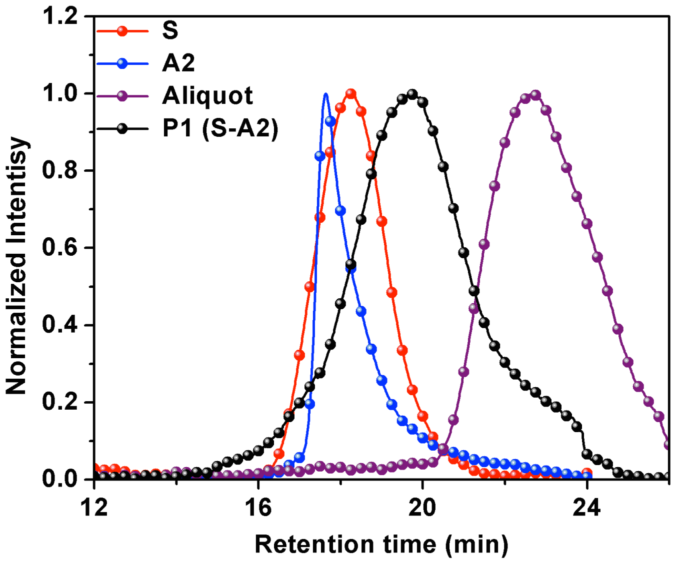

Fig. S7. GPC traces of the starting semicrystalline polymer **S**, the starting amorphous one **A2**, an aliquot of the reaction mixture after ethenolysis, and their ADMET product **P1(S-A2)**.

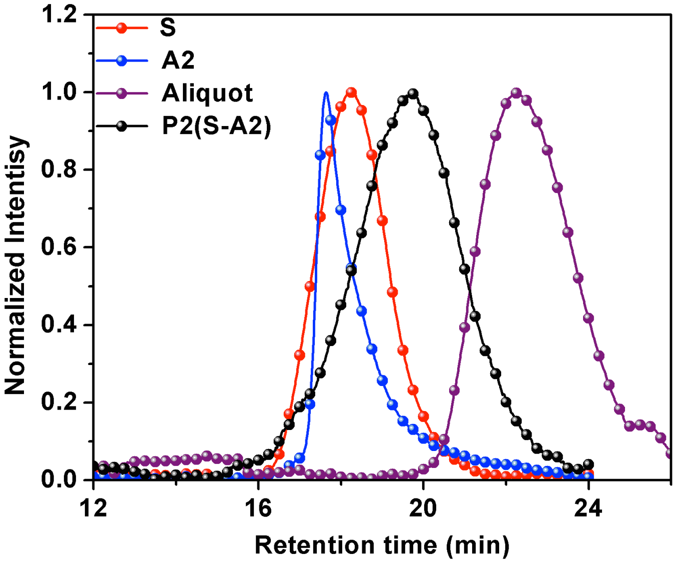

Fig. S8. GPC traces of the starting semicrystalline polymer **S**, the starting amorphous one **A2**, an aliquot of the reaction mixture after ethenolysis, and their ADMET product **P2(S-A2)**.

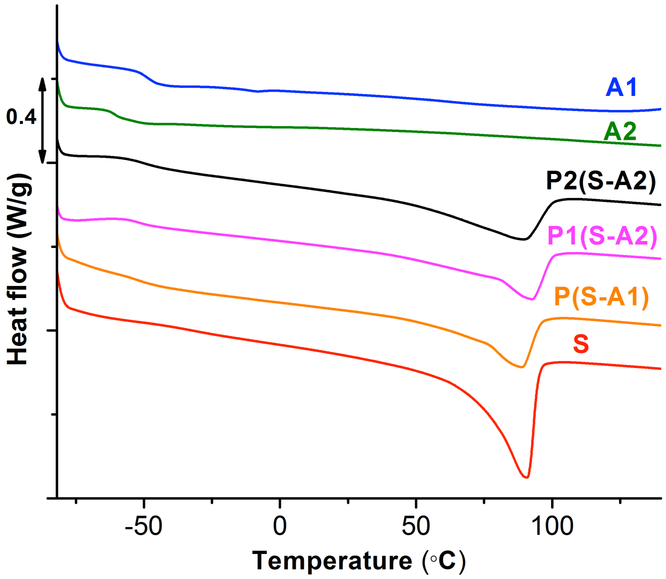

Fig. S9. DSC heating curves of the starting semicrystalline polymer **S**, the starting amorphous polymers **A1** and **A2**, and their ADMET product **P(S-A1)**, **P1(S-A2)**, and **P2(S-A2)**.

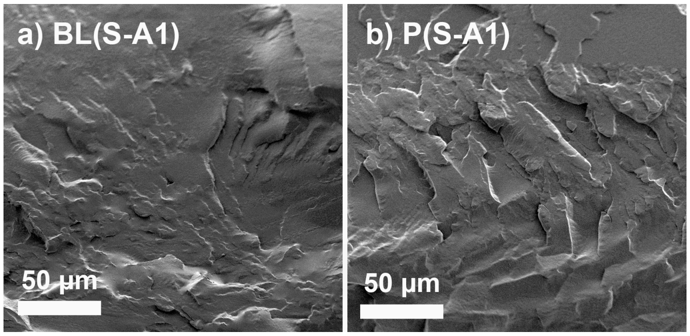

Fig. S10. SEM images of the cross-section of tensile specimens for **BL (S-A1)** (a) and **P (S-A1)** (b) before toluene etching.

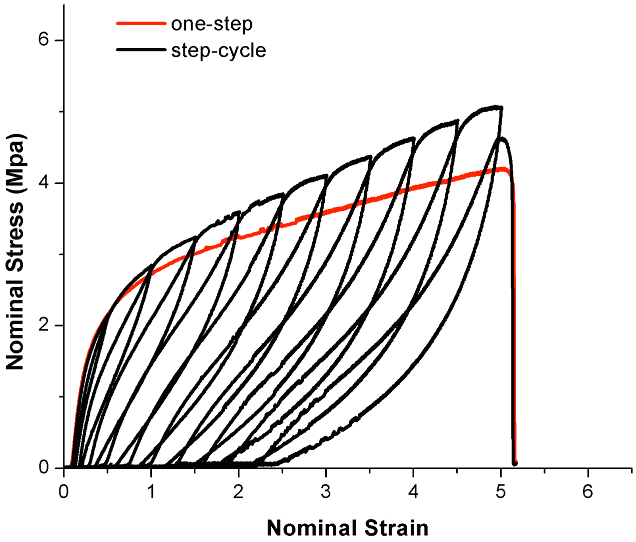

Fig. S11. Monotonic and cyclic tensile testing data for **P1(S-A2)**.

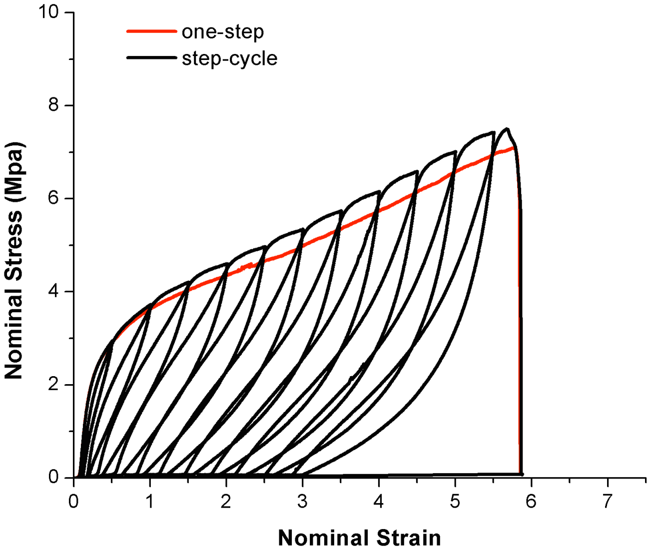

Fig. S12. Monotonic and cyclic tensile testing data for **P2(S-A2)**.