

Electronic Supplementary Information

Facile Synthesis of Multi-block Copolymers Containing Poly(ester-amide) Segments with Ordered Side Group Sequence

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Experimental Section

Materials

1, 6-diisocyanohexane (Sigma-aldrich; >98%), undecylenic aldehyde (Alfa Aesar; >95%), poly-(ethylene glycol) (PEG) 1000 (Alfa Aesar), *tert*-butyl isocyanacetate (Sigma-aldrich; >95%), succinic anhydride (>99%, Sinopharm Chem. Reagent Co., Ltd), *o*-nitrobenzaldehyde (Beijing Chemical Works) and anhydrous formic acid (Beijing Chemical Works) were all used as received. Phenylacetaldehyde (Alfa Aesar; >95%) and all the solvents were redistilled before use.

Measurements

Gel permeation chromatography (GPC) was equipped with three Waters Styragel HT columns (HT2, HT3, HT4), a Waters 1525 binary HPLC pump, and a 2414 refractive index detector. Polystyrene was used as the standards. The flow rate was 1.0 mL/min for all measurements. ¹H NMR and ¹³C NMR were recorded on a Bruker ARX-400 spectrometer. Matrix-assisted laser-desorption-ionization time-of-flight mass (MALDI-TOF-MS) spectra was performed on a Bruker Biflex III spectrometer. Calorimetric measurement was performed with a Q100 differential scanning calorimeter (TA Co., Ltd.). The nitrogen was set at 50 mL/min and the program was set to finish two cycles in a temperature range of -80 to 80 °C at heating cooling rate of 10 °C/min. Date of endothermic curve were acquired from the second scan data for each polymer sample. TA Universal Analysis software was applied for date acquisition and processing in the two measurements.

Synthesis of Macromonomer M1

PEG1000 (20.00 g, 20 mmol), succinic anhydride (5.20g, 52 mmol), 4-dimethylamiopyridine (4.88 g, 40 mmol), and triethylamine (4.04 g, 40 mmol) were dissolved in dioxane (200 mL). The reaction system was stirred over night at room temperature. The solution was concentrated and added to 200 mL water, followed by the acidification to pH 3.0 by 5 N HCl. The water phase was extracted with CH₂Cl₂, and the concentrated organic phase was precipitated in diethyl ether (400 mL). The precipitate was collected and dried in vacuum at 35 °C to get the final product **M1** (23.10 g, yield: 96.3 %).

Synthesis of N1

M1 (8.40 g, 7 mmol), *tert*-butyl isocyanacetate (2.37g, 16.8 mmol), and undecylenic aldehyde (2.83 g, 16.8 mmol) were dissolved in 100 mL of CH₂Cl₂. The reaction system was stirred at 30 °C

for 48 h. The solution was concentrated and precipitated in a mixture of diethyl ether and petroleum ether (1:2 v/v) at 0 °C for 3 times. The precipitate was collected and dried in vacuum at 30 °C to get the final product **N1** (12.92g, yield: 95%).

Synthesis of Macromonomer **M2**

Compound **N1** (11.10 g, 6 mmol) was hydrolyzed in 100 mL of HCOOH at 15 °C for 12 h. HCOOH was removed in vacuum. The crude product was purified by precipitation in a mixture of diethyl ether and petroleum ether (1:2 v/v) at 0 °C for 3 times. The precipitate was collected and dried in vacuum at 30 °C to get the final product **M2** (9.91 g, yield: 95%).

Synthesis of **N2**

Macromonomer **M2** (1.74 g, 1 mmol), *tert*-butyl isocynoacetate (338 mg, 2.4 mmol), and *o*-nitrobenzaldehyde (363 mg, 2.4 mmol) were dissolved in 30 mL of CH₂Cl₂. The reaction system was stirred at 30 °C for 48 h. The solution was concentrated and precipitated in a mixture of diethyl ether and petroleum ether (1:2 v/v) at 0 °C for 3 times. The precipitate was collected and dried in vacuum at 30 °C to get the final product **N2** (2.29 g, yield: 94%).

Synthesis of Macromonomer **M3**

Compound **N2** (1.86 g, 0.8 mmol) was hydrolyzed in 30 mL of HCOOH at 15 °C for 12 h. HCOOH was removed in vacuum. The crude product was purified by precipitation in diethyl ether at 0 °C for 3 times. The precipitate was collected and dried in vacuum at 30 °C to get the final product **M3** (1.68 g, yield: 95%).

One Pot Synthesis of **M2**

Macromonomer **M1** (1.20 g, 1 mmol), *tert*-butyl isocynoacetate (0.34g, 2.4 mmol) and undecylenic aldehyde (0.40 g, 2.4 mmol) were dissolved in 20 mL of CH₂Cl₂. The reaction system was stirred at 30 °C for 48 h. Then, the solution was concentrated, and 20 mL of HCOOH was added. The solution was stirred at 15 °C for 12 h, and HCOOH was removed in vacuum. The crude product was purified by precipitation in mixture of diethyl ether and petroleum ether (1:2 v/v) at 0 °C for 3 times. The product was characterized by ¹H NMR and MALDI-TOF-MS spectra.

General Procedure for Multicomponent Polymerization

Take the synthesis of **P2** as an example. Macromonomer **M2** (521.4 mg, 0.3 mmol), 1, 6-diisocyanohexane (40.8 mg, 0.3 mmol) and phenylacetaldehyde (86.5 mg, 0.72 mmol) were dissolved in 1 mL of CH₂Cl₂. The polymerization was performed in an airtight Schlenk flask at 30 °C for 4 days under stirring. The resulted viscous solution was diluted by CH₂Cl₂ (2 mL), precipitated in diethyl ether (50 mL) for three times. The precipitate was collected and dried in vacuum to get the final product **P2** (589.9 mg, yield: 93%).

For the synthesis of **P3**, the polymer was precipitated in a mixture of tetrahydrofuran and diethyl

ether (1:2 v/v) because **M3** was not soluble in diethyl ether.

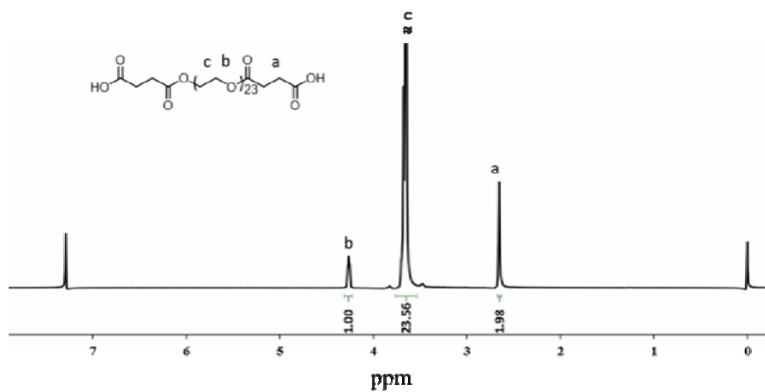


Fig. S1 ^1H NMR spectrum of **M1** in CDCl_3 .
(The integration ratio of protons **a** to **b** is 2 to 1, and the calculated M_n is 1230.)

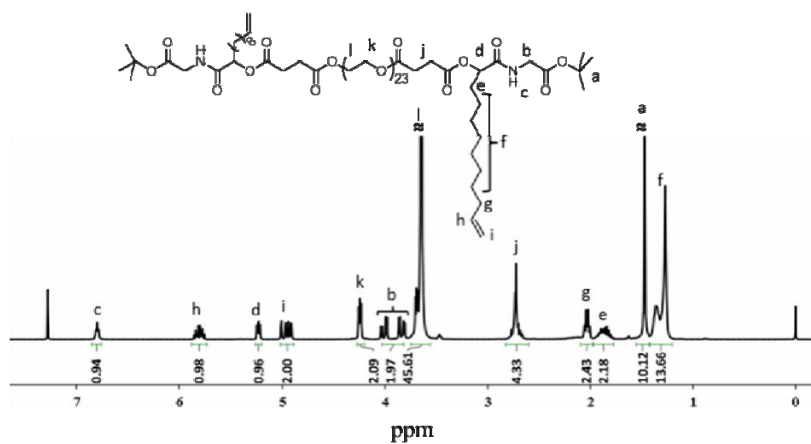


Fig. S2 ^1H NMR spectrum of **N1** in CDCl_3 .

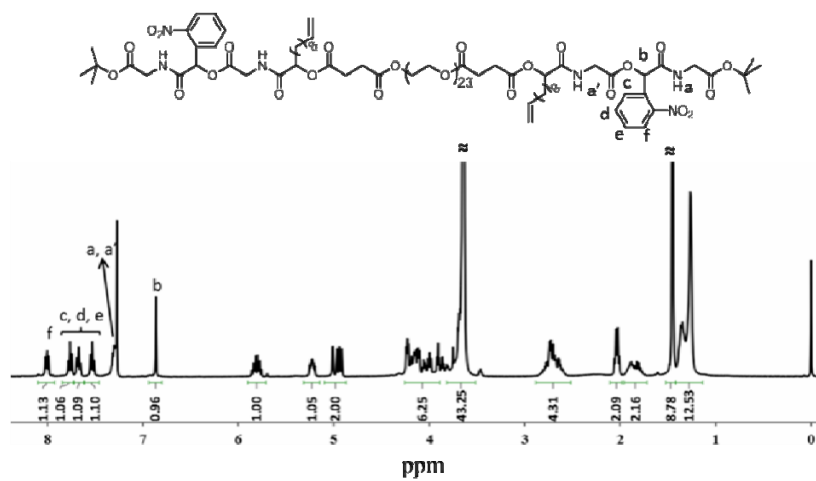


Fig. S3 ^1H NMR spectrum of **N2** in CDCl_3 .

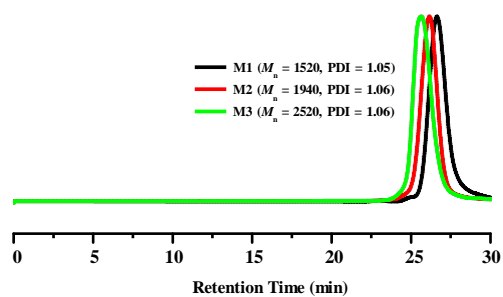


Fig. S4 GPC curves of macromonomers **M1**, **M2**, and **M3**.

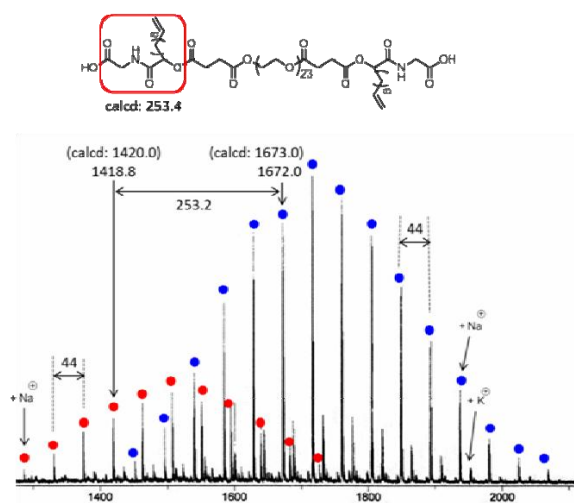


Fig. S5 MALDI-TOF-MS spectrum of the product from the one pot synthesis of **M2**. (**M2**) • and • (side products resulted from the break of the ester bond formed *via* PR).

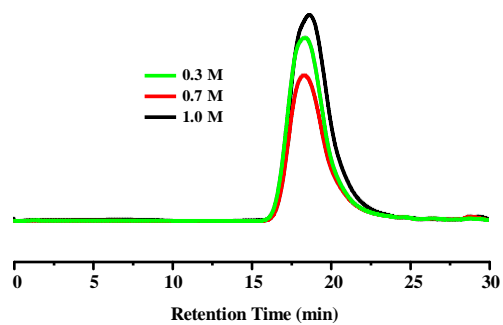


Fig. S6 GPC traces of **P1**.

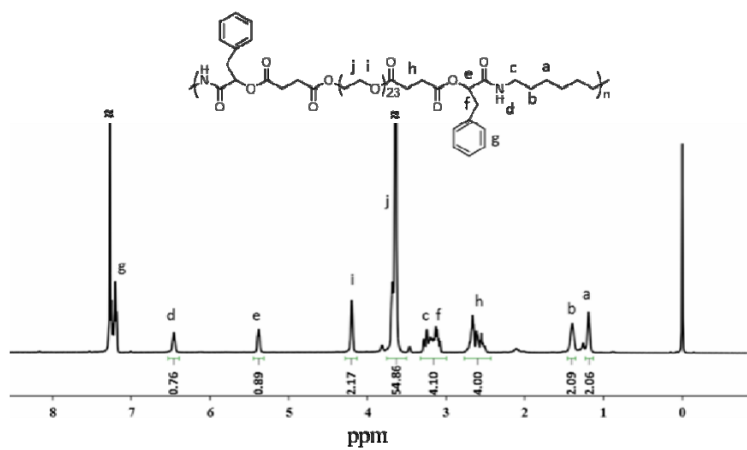


Fig. S7 ¹H NMR spectrum of **P1-A** in CDCl₃.

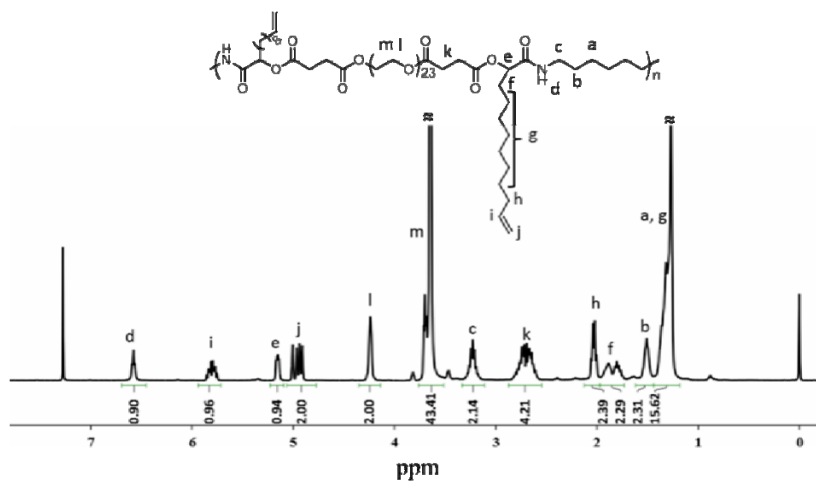


Fig. S8 ¹H NMR spectrum of **P1-D** in CDCl₃.

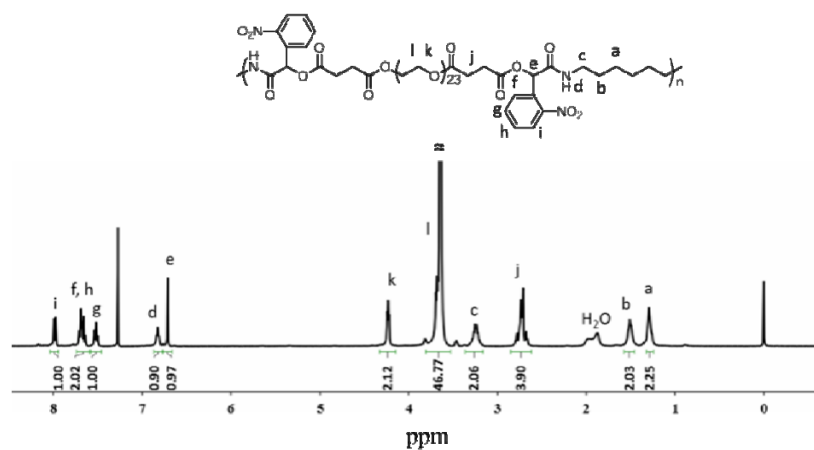


Fig. S9 ¹H NMR spectrum of **P1-E** in CDCl₃.

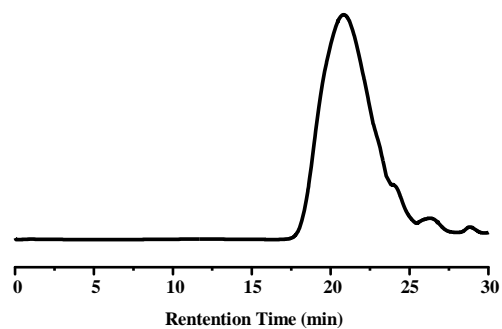


Fig. S10 GPC trace of **P1-D**.

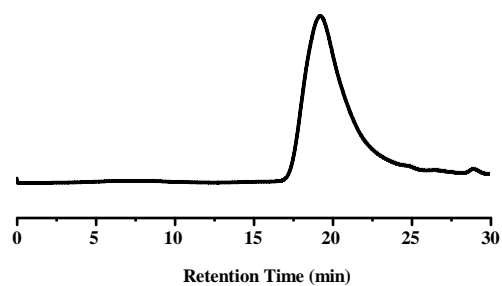


Fig. S11 GPC trace of **P1-E**.

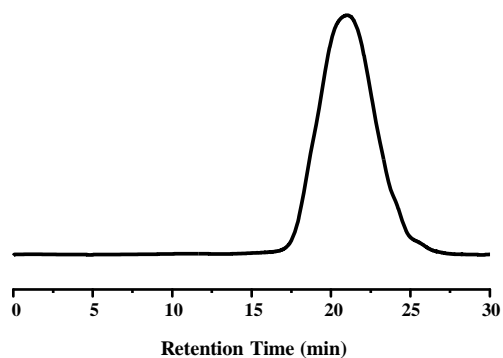


Fig. S12 GPC trace of **P2**.

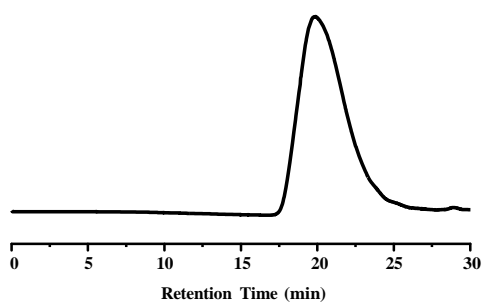


Fig. S13 GPC trace of **P3**.

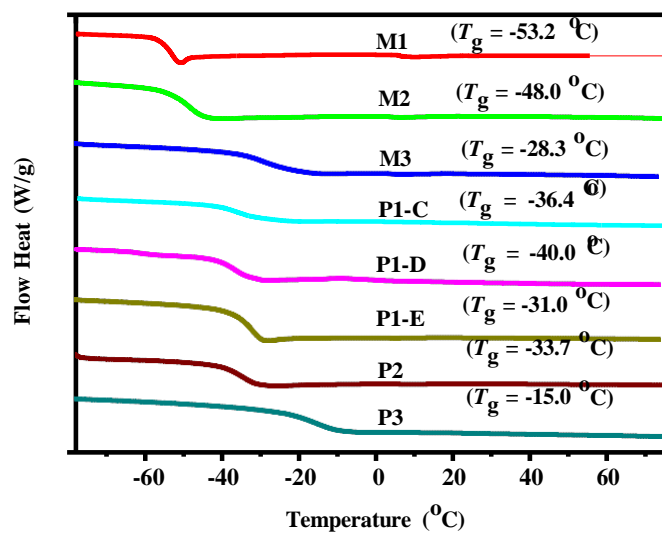


Fig. S14 DSC thermograms of macromonomers and polymers.