

Electronic Supporting Information (ESI)

Barbier Polymerization towards Polar Polyolefin Analogue for Polyolefin Modification

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Experimental details

Materials

THF was dried with sodium metal before use, and re-evaporated and purified with benzophenone as an indicator. Chemicals and other common reagents were obtained from commercial suppliers and used without further purification.

Characterization methods

Nuclear magnetic resonance (NMR) spectroscopy. The ^1H and ^{13}C NMR measurements were performed on Bruker-BioSpin AVANCE III HD 400 spectrometer in CDCl_3 using tetramethylsilane as an internal standard.

Gel permeation chromatography (GPC). Number average molecular weight (M_n), Weight average molecular weight (M_w) and polydispersity indices (PDI) of the polymers were estimated on an Agilent 1260 InfinityII equipped with a G7110B isocratic pump and G7162A refractive index detector. Polystyrene standards were utilized, and DMF was used as the eluent at a flow rate of 1.0 mL/min at 50 °C.

Fourier transform infrared (FT-IR) spectroscopy. FT-IR Spectra using KBr pellets were recorded on a TENSOR II FTIR Spectrometre (Bruker, Germany). The spectra were recorded from an accumulation of 16 scans in the range of 4000-400 cm^{-1} and were collected at room temperature. The OPUS v7.5 software auto-corrected the spectral base line and calculated the second derivative spectra.

Field emission scanning electron microscope (FESEM) images (COXEMCOLTD, Korea). FE-SEM was performed at 5 kV and 10 μA , respectively.

Differential scanning calorimetry (DSC) (DSC25, TA Instrument, USA). DSC was performed to investigate the thermal properties of LDPE-HPBP and LDPE with a rate of 10 $^{\circ}\text{C min}^{-1}$. The DSC study was conducted from 0 to 150 $^{\circ}\text{C}$ in a nitrogen atmosphere environment.

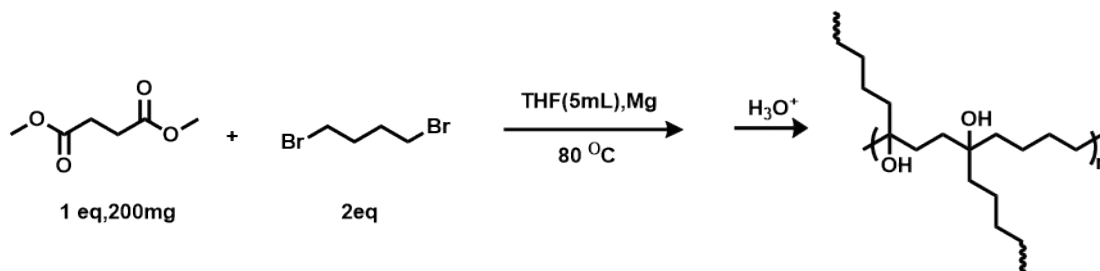
Universal testing machine (CMT6203 2 KN, MTS Systems, China) The tensile-strain tests were conducted on a universal testing machine by using a sample-holding apparatus.

Rheology Test (DHR-2, Waters Corporation, America) Dynamic strain scanning experiments on the system before and after blending.

Synthetic procedures

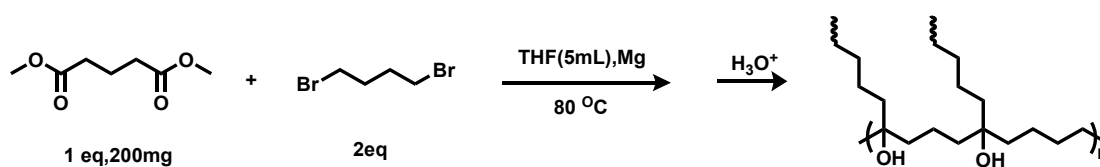
Synthesis of HPBB.

Under nitrogen atmosphere, 5 mL of THF, dimethyl succinate (0.20 g, 1.0 eq.), 1,4-dibromobutane (0.59 g, 2.0 eq.) were added via syringe at room temperature in a flame dried Schlenk tube containing freshly stripped Mg chips (0.16 g, 4.8 eq.) and then transferred to an oil bath at 80 °C. After 24 h of reaction, the hydrolysis was quenched with 20 ml of saturated aqueous ammonium chloride solution. The organic solution was filtered and checked by dichloromethane/water, dried with anhydrous MgSO₄ and concentrated under reduced pressure. The product was purified by precipitation with amount of petroleum ether and dried by vacuum filtration to give 0.14 g of HPBB white powder, yielding 56.7%. ¹H NMR (400 MHz, CDCl₃): δ=5.08-4.83 (broad, -OH, 1H), 2.10-0.97 (broad, -CH₂-, 2H).



Synthesis of HPBP.

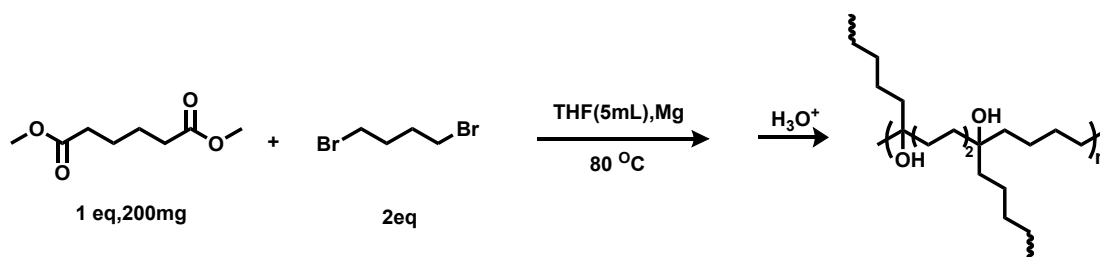
Under nitrogen atmosphere, 5 mL of THF, dimethyl glutarate (0.20 g, 1.0 eq.), 1,4-dibromobutane (0.54 g, 2.0 eq.) were added via syringe at room temperature in a flame dried Schlenk tube containing freshly stripped Mg chips (0.15 g, 4.8 eq.) and then transferred to an oil bath at 80 °C. After 24h of reaction, the hydrolysis was quenched with 20 ml of saturated aqueous ammonium chloride solution. The organic solution was filtered and checked by dichloromethane/water, dried with anhydrous MgSO₄ and concentrated under reduced pressure. The product was purified by precipitation with amount of petroleum ether and dried by vacuum filtration to give 0.21 g of HPBP brown powder, yielding 77.6%. ¹H NMR (400 MHz, CDCl₃): δ=4.99-4.81 (broad, -OH, 1H), 2.02-1.15 (broad, -CH₂-, 2H).



Synthesis of HPBHEX.

Under nitrogen atmosphere, 5 mL of THF, dimethyl adipate (0.2 g, 1.0 eq.), 1,4-dibromobutane (0.49 g, 2.0 eq.) were added via syringe at room temperature in a flame dried Schlenk tube containing freshly stripped Mg chips (0.14 g, 4.8 eq.) and then transferred to an oil bath at 80 °C. After

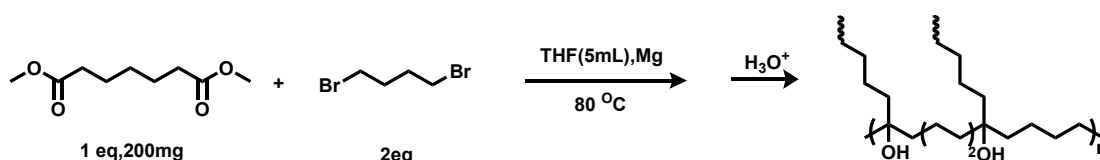
24h of reaction, the hydrolysis was quenched with 20 ml of saturated aqueous ammonium chloride solution. The organic solution was filtered and checked by dichloromethane/water, dried with anhydrous MgSO_4 and concentrated under reduced pressure. The product was purified by precipitation with amount of petroleum ether and dried by vacuum filtration to give 0.20 g of HPBHEX brown powder, yielding 65.2%. ^1H NMR (400 MHz, CDCl_3): δ =4.99-4.81 (broad, -OH, 1H), 2.02-1.15 (broad, - CH_2 -, 2H).



Synthesis of HPBHEP.

Under nitrogen atmosphere, 5 mL of THF, dimethyl pimelate (0.2 g, 1.0 eq.), 1,4-dibromobutane (0.46 g, 2.0 eq.) were added via syringe at room temperature in a flame dried Schlenk tube containing freshly stripped Mg chips (0.12 g, 4.8 eq.) and then transferred to an oil bath at 80 °C. After 24h of reaction, the hydrolysis was quenched with 20 ml of saturated aqueous ammonium chloride solution. The organic solution was filtered and checked by dichloromethane/water, dried with anhydrous MgSO_4 and concentrated under reduced pressure. The product was purified by precipitation with amount of petroleum ether and dried by vacuum

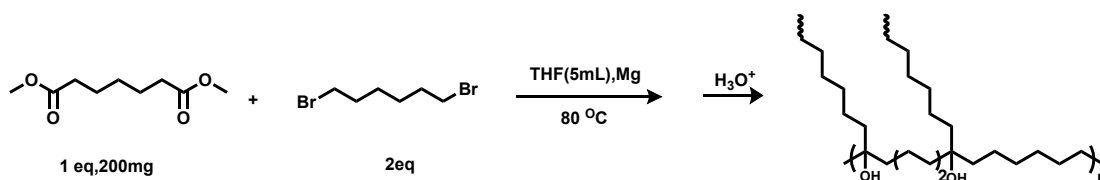
filtration to give 0.10 g of HPBHEP brown powder, yielding 22.8%. ¹H NMR (400 MHz, CDCl₃): δ=4.97-4.76 (broad, -OH, 1H), 1.98-1.02 (broad, -CH₂-, 2H).



Synthesis of HPHB.

Under nitrogen atmosphere, 5 mL of THF, dimethyl adipate (0.2 g, 1.0 eq.), 1,4-dibromohexane (0.67 g, 2.0 eq.) were added via syringe at room temperature in a flame dried Schlenk tube containing freshly stripped Mg chips (0.16 g, 4.8 eq.) and then transferred to an oil bath at 80 °C. After 24h of reaction, the hydrolysis was quenched with 20 ml of saturated aqueous ammonium chloride solution. The organic solution was filtered and checked by dichloromethane/water, dried with anhydrous MgSO₄ and concentrated under reduced pressure. The product was purified by precipitation with amount of petroleum ether and dried by vacuum filtration to give 0.12 g of HPHB yellow powder, yielding 45.6%. ¹H NMR (400 MHz, CDCl₃): δ= 4.95-4.87 (broad, -OH, 1H), 1.81-0.98 (broad, -CH₂-, 2H).

aqueous ammonium chloride solution. The organic solution was filtered and checked by dichloromethane/water, dried with anhydrous MgSO_4 and concentrated under reduced pressure. The product was purified by precipitation with amount of petroleum ether and dried by vacuum filtration to give 0.10 g of HPHHEP brown powder, yielding 18.3%. ^1H NMR (400 MHz, CDCl_3): δ = 4.89-4.79 (broad, -OH, 1H), 1.89-1.09 (broad, - CH_2 -, 2H).



Preparation of Blends

10 wt % of LDPE was dissolved in xylene to form a clear homogeneous solution at 120 °C. Then, 5 wt % of HPBP was dispersed in the solution at this temperature for 2 hours, and further heating at 150 °C for 1 hour, then hot press at a pressure of 5000 kilopascals for 3 minutes, and coated on a demold plate, solvent removed in a vacuum oven at 150 °C to obtain film.

Result and characterization data

Synthetic characterization

Table S1. Barbier polymerization at different temperatures.

	T / °C	Yield/ %	M _w	M _w /M _n
1	60	31.5	6700	1.42
2	70	41.6	5700	1.66
3	80	77.6	5900	2.52

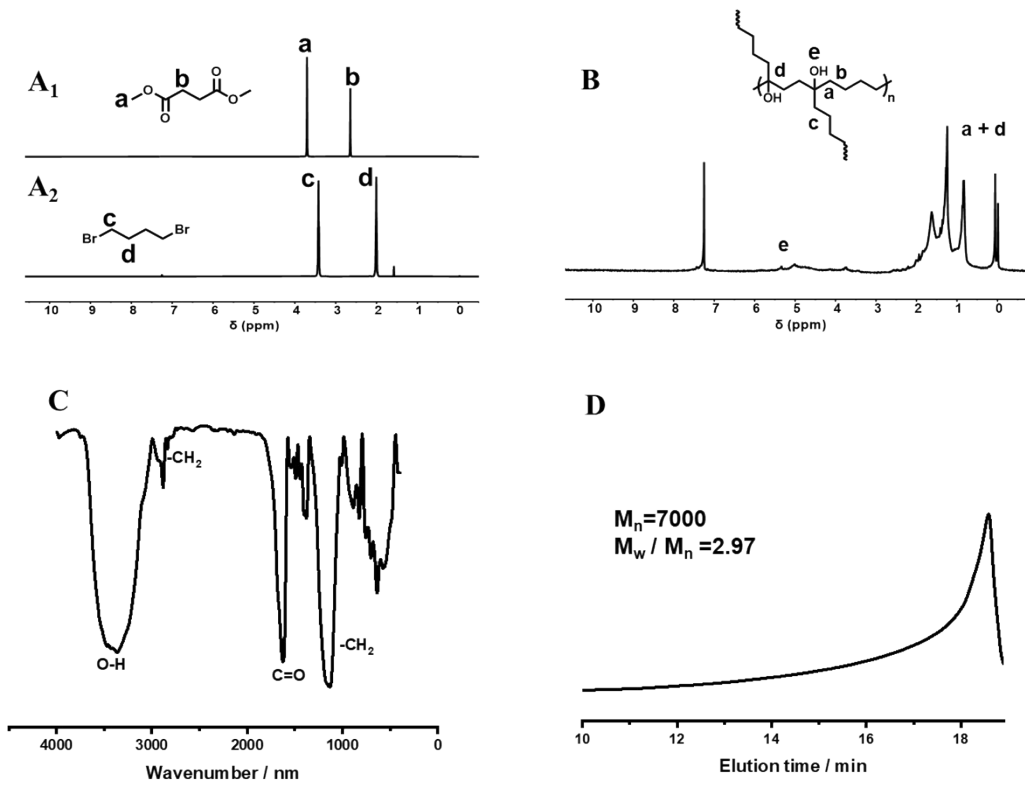


Figure S1. Characterizations of HPBB. ¹H NMR spectra of dimethyl succinate (A₁), 1,4-dibromobutane (A₂) and HPBB (B) in CDCl₃, FT-IR spectrum of HPBB (C), and GPC curve of HPBP in DMF (D).

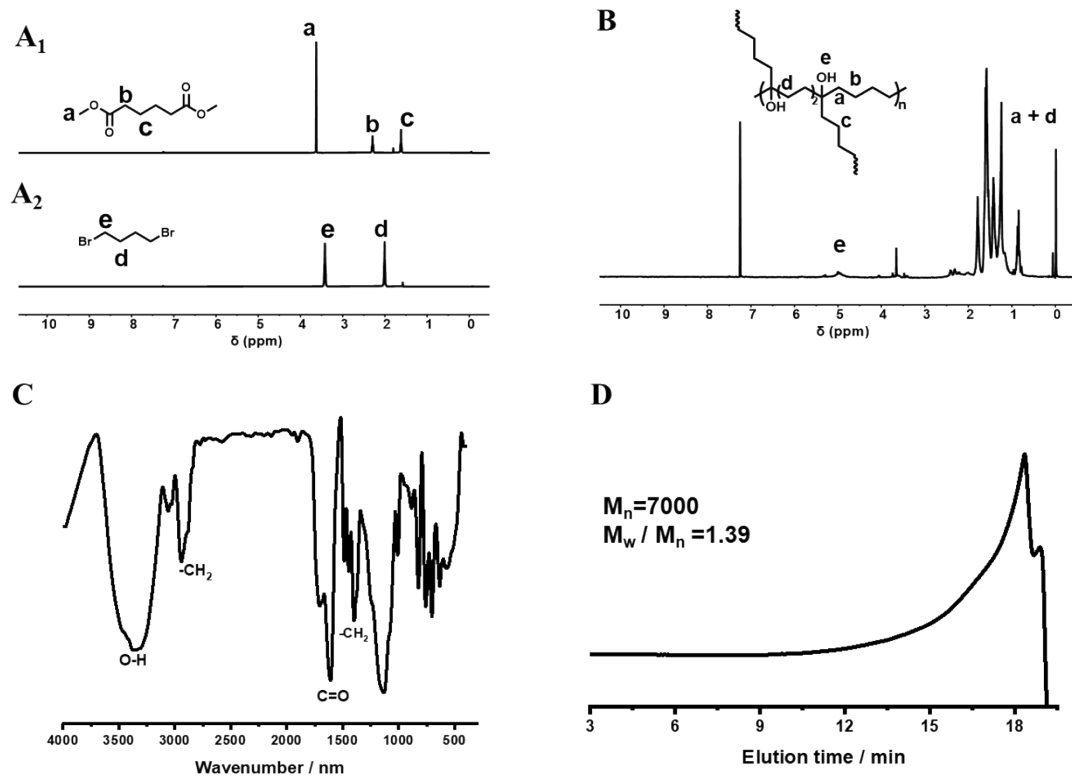


Figure S2. Characterizations of HPBHEX. ^1H NMR spectra of dimethyl adipate (A_1), 1,4-dibromobutane (A_2) and HPBHEX (B) in CDCl_3 , FT-IR spectrum of HPBHEX (C), and GPC curve of HPBP in DMF (D).

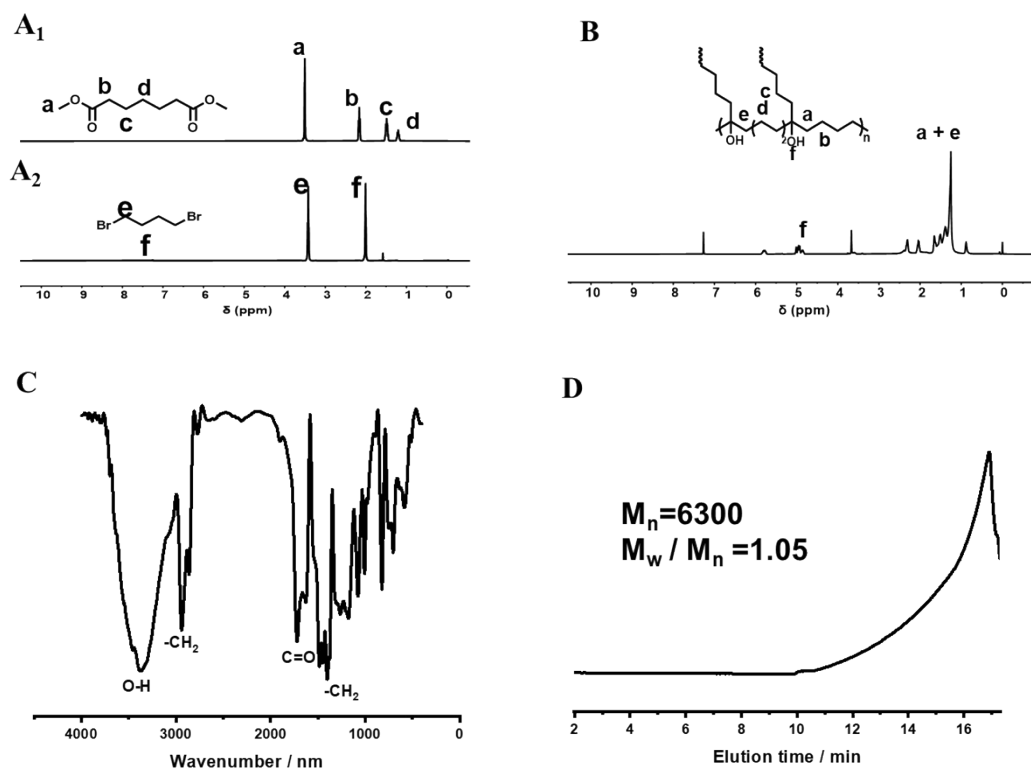


Figure S3. Characterizations of HPBHEP. ¹H NMR spectra of dimethyl pimelate (A₁), 1,4-dibromobutane (A₂) and HPBHEP (B) in CDCl₃, FT-IR spectrum of HPBHEP (C), and GPC curve of HPBP in DMF (D).

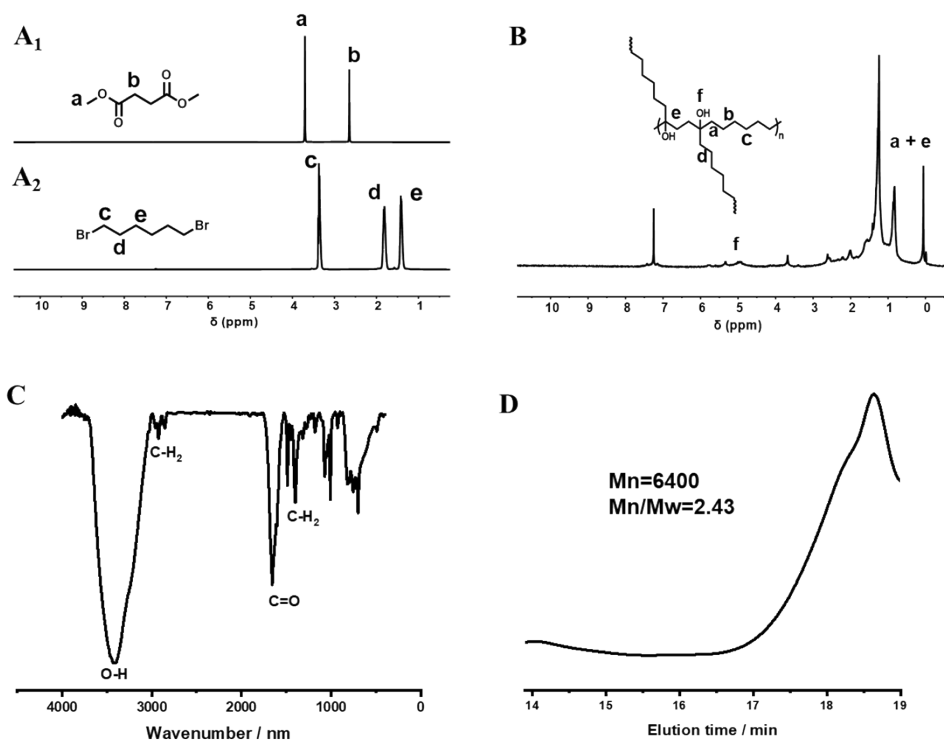


Figure S4. Characterizations of HPHB. ¹H NMR spectra of dimethyl succinate (A₁), 1,4-dibromohexane (A₂) and HPHB (B) in CDCl₃, FT-IR spectrum of HPHB (C), and GPC curve of HPHB in DMF (D).

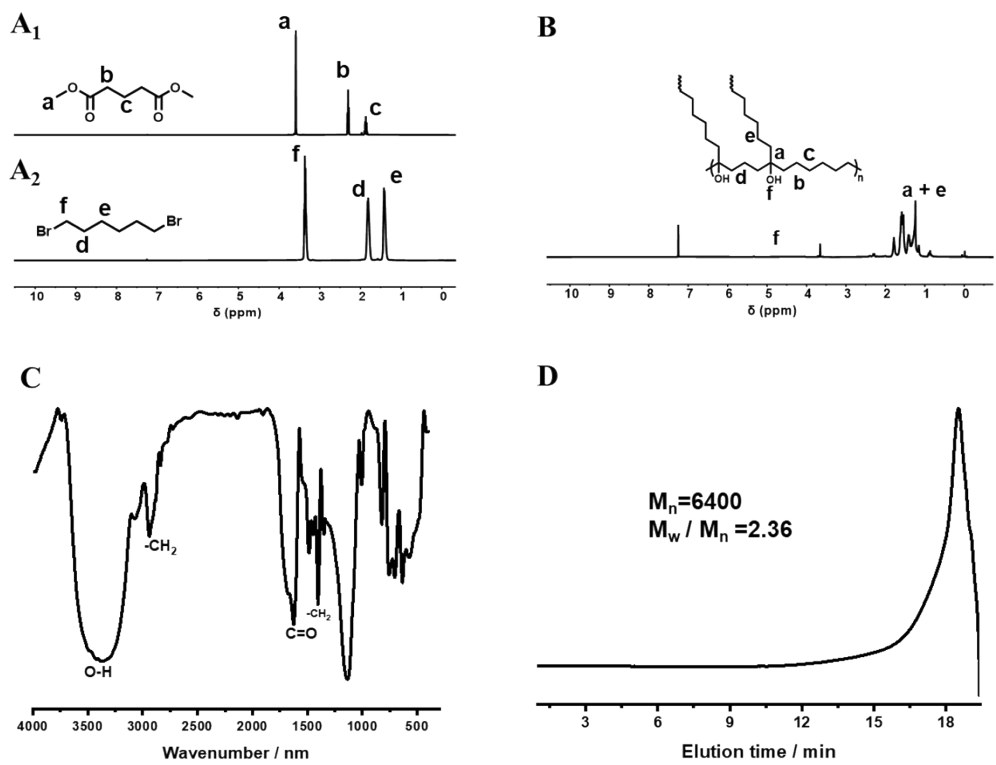


Figure S5. Characterizations of HPHP. ¹H NMR spectra of dimethyl glutarate (A₁), 1,4-dibromohexane (A₂) and HPHP (B) in CDCl₃, FT-IR spectrum of HPHP (C), and GPC curve of HPPB in DMF (D).

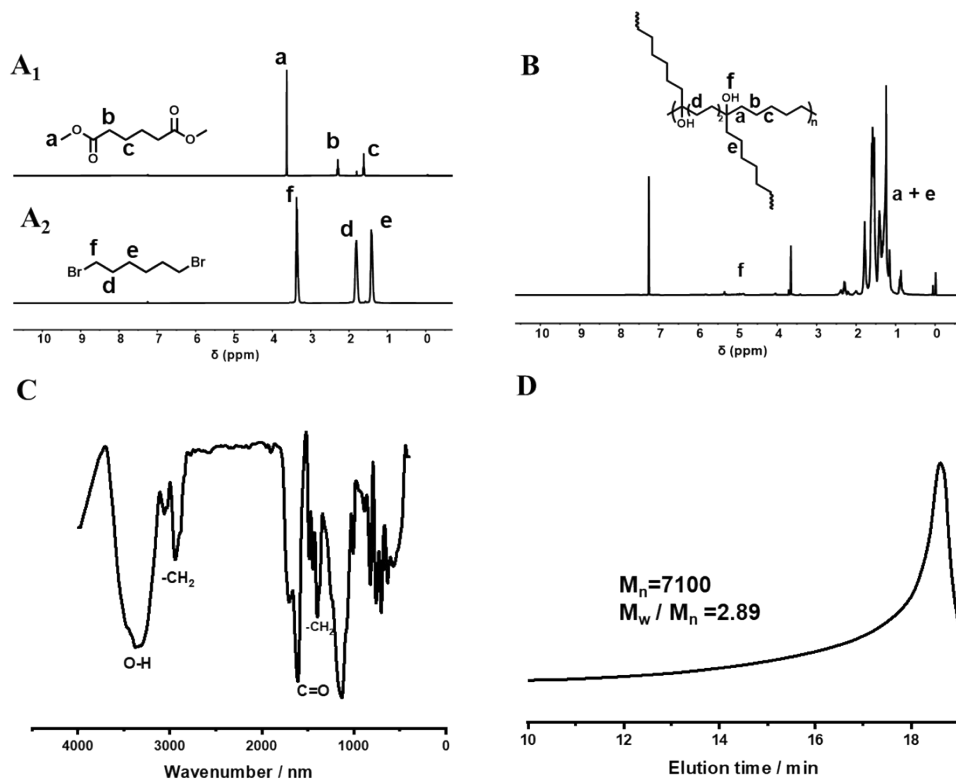


Figure S6. Characterizations of HPHHEX. ¹H NMR spectra of dimethyl adipate (A₁), 1,4-dibromohexane (A₂) and HPHHEX (B) in CDCl₃, FT-IR spectrum of HPHHEX (C), and GPC curve of HPBP in DMF (D).

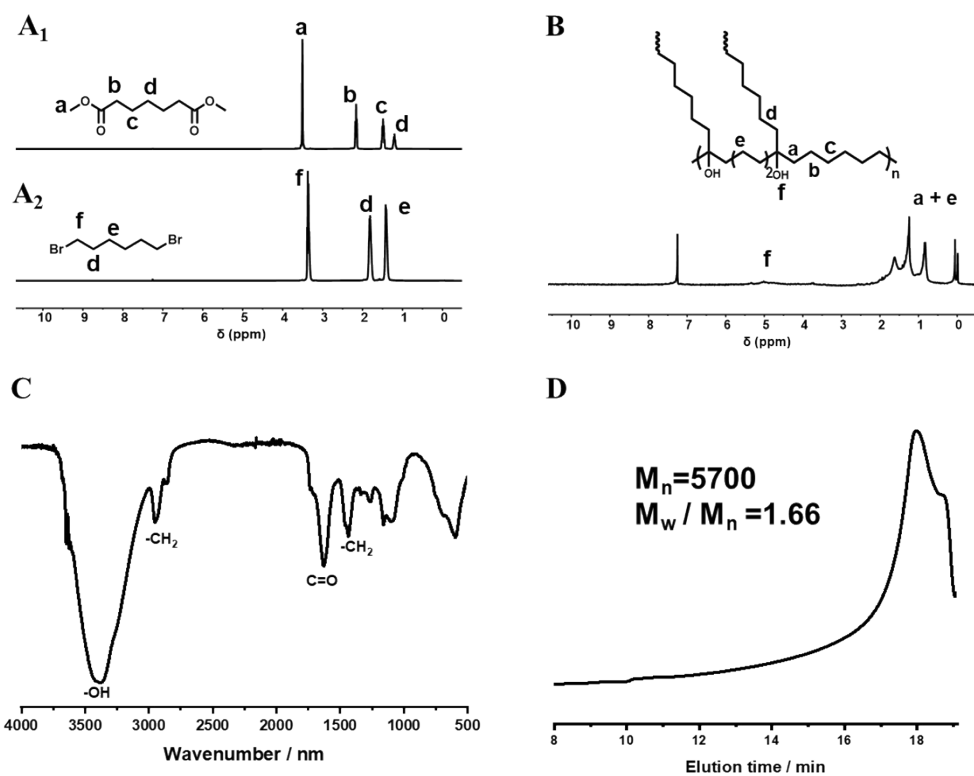


Figure S7. Characterizations of HPHHEP. ¹H NMR spectra of dimethyl pimelate (A₁), 1,4-dibromohexane (A₂) and HPHHEP (B) in CDCl₃, FT-IR spectrum of HPHHEP (C), and GPC curve of HPBP in DMF (D).