Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis of Novel Polyether with Abundant Reactive Sites and Diverse Skeletons Based on Ring Opening Reaction of D-A Cyclopropane

Shuai Wu[†,‡,#], Jun-Fang Li[†], Xiu-Li Sun[†], Xiao-Yan Wang*[,†] and Yong Tang*[,†]

[†]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

[‡]School of Physical Science and Technology, ShanghaiTech University, 393 Middle Huaxia Road, Shanghai 201210, China

[#]University of Chinese Academy of Sciences, No.19(A) Yuquan Road, Beijing 100049, China

*E-mail: tangy@sioc.ac.cn; wangxiaoyan@sioc.ac.cn

Contents

1. Supplementary Experimental Procedures

(1) General Information

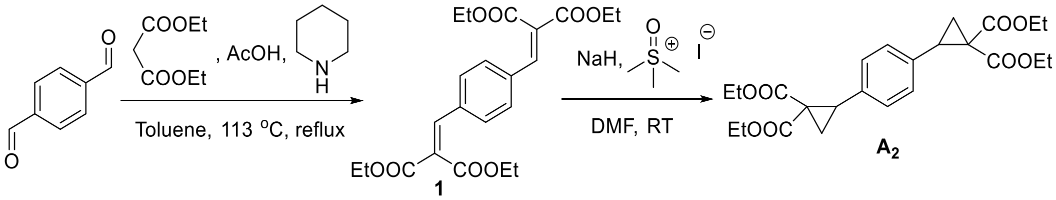
Unless stated otherwise, all manipulations with air- and moisture-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, or in an inert gas (N_2)-filled glovebox. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz spectrometer and Agilent Technologies 400 MHz spectrometer. The molecular weight and polydispersity index (Đ) were measured by gel permeation chromatography (GPC). GPC was performed on a Waters (USA) 1515 gel permeation chromatograph equipped with a Waters 2414 refractive-index detector with three commercial columns (Waters Styragel) connected in series. The analysis was undertaken at 25 °C with purified high-performance-liquid-chromatography-grade THF as the eluent at a flow rate of 1 mL/min. Calibration was performed with standard PS. MALDI-TOF MS was conducted using a Shimadzu Axima Performance MALDI-TOF/TOF mass spectrometer, equipped with a nitrogen laser delivering 2 ns laser pulses at 337 nm with positive ion TOF detection performed using an accelerating voltage of 20 kV. Solutions in tetrahydrofuran (50 μL) of dithranol as a matrix (saturated solution), silver acetate as the cationization agent (1.0 mg mL^{-1}) and sample (1.0 mg mL^{-1}) were mixed, and 0.7 μL of the mixture was applied to the target plate. Thermal transition temperatures of polymers were measured by differential scanning calorimetry (DSC) using a TA Instruments Q2000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected with the heat/cool/heat cycle at a rate of 10 °C/min, and processed with TA Q series software. Thermogravimetric analyses (TGA) were performed with a heating rate of 10 °C/min in nitrogen.

The conversion of hydroxy and the molecular weight ($M_{\mathrm{n,NMR}}$) for the A_2/B_2 system were determined by ^{1}H NMR spectra of the resultant polymers and calculated according to the formulas $\mathrm{Conv.(OH)} = (1 - I_g/I_c) \times 100\%$, $M_{\mathrm{n,NMR}} = I_c/2I_g \times [\mathrm{Mr}(A_2) + \mathrm{Mr}(B_2)]$, where I_g and I_c are the peak integral of proton marked as "g" and "c", respectively; Mr(A_2) and Mr(B_2) are the relative molecular mass of monomer A_2 and B_2, respectively. The conversion of hydroxy and the molecular weight ($M_{n,NMR}$) for the AB system were determined by ^{1}H NMR spectra of the resultant polymers and calculated according to the formulas Conv.(OH) = $(1 - I_g/I_c) \times 100\%$, $M_{n,NMR} = I_c/I_g \times$ Mr(AB), where I_g and I_c are the peak integral of proton marked as “g” and “c”, respectively; Mr(AB) is the relative molecular mass of monomer AB.

The B_2 monomer (diols), including 1,4-phenylenedimethanol (I) (Aladdin; purity >98%), 2,3,5,6-tetrafluoro-1,4-benzenedimethanol (II) (Energy; purity 97%) and 1,8-octanediol (III) (TCI; purity 98%), were used as received.

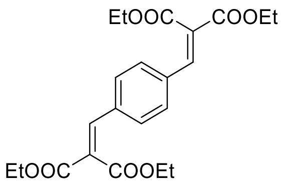
(2) The Procedure for Synthesis of Monomers

The Synthesis of A_2 Monomer[1]



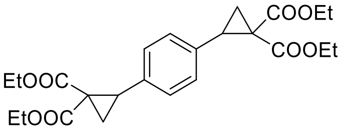
A 5 L three-necked bottle was connected with a reflux water separator and a mechanical stirring device. A thermometer was used for temperature detection. Terephthalaldehyde (402.3 g, 3000 mmol), toluene (2 L) and diethyl malonate (1138 mL, 7500 mmol) were added into the bottle and stirred, to which piperidine (24.3 mL, 300 mmol) and acetic acid (19.3 mL, 300 mmol) were injected, subsequently. While stirred at a high speed, the reaction mixture was heated up until the solution began to reflux. The internal temperature of the reaction system is about 113 ºC. Every 8 hours, a small amount of the reaction solution sample was taken and concentrated. The residue was subjected to ^{1}H NMR detection. After the reaction finished, the mixture was cooled down. Before the temperature dropped to room temperature, the solution was poured into a 5 L beaker, which was stirred at a high speed. Subsequently, small white solid particles gradually precipitated. After solid-liquid separation, the solid was beaten with petroleum ether to obtain product **1** (880 g) as white powder with a yield of 70%.

A 100 mL Schlenk bottle was purged with argon gas at high temperature three times and then filled with argon gas. Before adding the reagents, the bottle was placed in an ice bath, to which trimethyl sulfoxide (2.64 g, 12.0 mmol), sodium hydride (60 %, 480 mg, 12 mmol) and DMF (50 mL) were added. After the mixture gradually dissolved, white solid **1** was added into the bottle. One hour later, the reaction was detected by TLC. After the reaction was finished, the reaction solution was neutralized with saturated aqueous ammonium chloride solution, and then extracted with ether. The organic phase was dried and beaten using methanol, giving product **A_2** as white solid or colorless crystal with a yield of 56%.



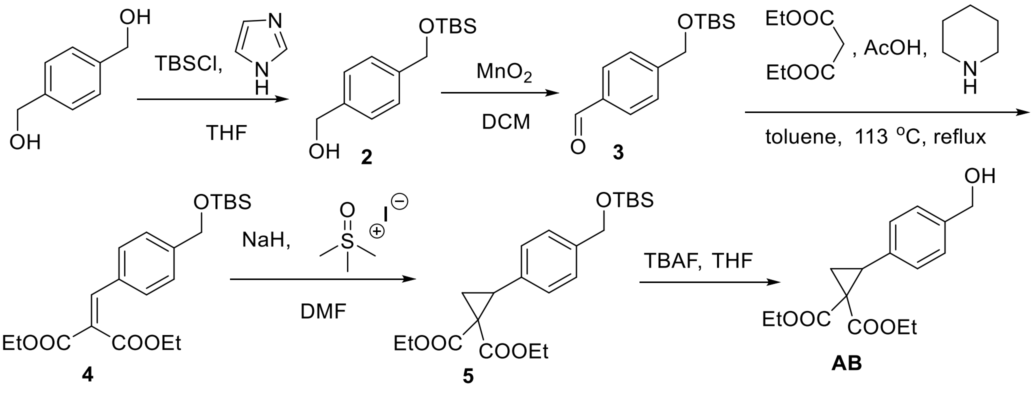
White solid **1** (70%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 2H), 7.45 (s, 4H), 4.35 (q, J = 7.2

Hz, 4H), 4.31 (q, *J* = 7.2 Hz, 4H) 1.33 (t, *J* = 7.2 Hz, 6H) 1.28 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 163.8, 140.7, 134.8, 129.7, 127.5, 61.9, 61.8, 14.1, 13.9; IR: ν(cm^{-1}) = 2976, 2936, 2869, 1719, 1626, 1514, 1487, 1466, 1443, 1421, 1396, 1379, 1368, 1298, 1262, 1200, 1173, 1113, 1097, 1064, 1011, 999, 961, 900, 867, 847, 798, 774, 760, 702, 608, 573, 521, 445, 417; HRMS(ESI): [M+Na]$^+$ calcd for $C_{22}H_{26}O_8Na$, 441.15; Found, 441.15.



White solid **A$_2$** (56%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (s, 4H), 4.32–4.13 (m, 4H), 3.93–3.74 (m, 4H), 3.15 (dd, *J* = 9.2, 8.0 Hz, 2H), 2.11 (dd, *J* = 8.0, 5.1 Hz, 2H), 1.67 (dd, *J* = 9.2, 5.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H), 0.94 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 166.5, 133.8, 128.3, 61.7, 61.1, 37.4, 31.8, 18.8, 14.1, 13.8; IR: ν(cm^{-1}) = 2979, 2935, 1712, 1519, 1461, 1446, 1371, 1322, 1276, 1214, 1186, 1133, 1095, 1062, 1020, 987, 933, 878, 855, 835, 759, 709, 683, 667, 603, 571, 545, 517, 500, 444, 417; HRMS(ESI): [M+Na]$^+$ calcd for $C_{24}H_{30}O_8Na$, 469.18; Found, 469.18.

The Synthesis of AB Monomer[2]



A 250 mL and a 100 mL Schlenk bottle were purged with argon gas three times at high temperature and then filled with argon gas. 1,4-benzenedimethanol (9.67 g, 70 mmol), imidazole (4.08 g, 60 mmol) and THF (100mL) were added into 250 mL bottle. After the solid was dissolved, the bottle was placed in an ice bath. T-butyldimethylsilyl chloride (TBSCl, 7.54 g, 50 mmol) and THF (20 mL) were added into 100 mL Schlenk bottle. The TBSCl solution was dropwise added into 250 mL Schlenk bottle by a syringe. At the same time, a large amount of white solid generated during the dropping.

After the reaction was finished, solid and liquid was separated through a sand core funnel. Then the solvent was removed through reducing pressure. 1,4-benzenedimethanol (white needle-like crystal) was precipitated by adding a small amount of DCM. After the solid-liquid separation, the solvent of liquid was removed in vacuo. Column chromatography (eluent is PE:EA:Acetone 20:1:1) gave product **2** as colorless oily liquid (6.19 g), with a yield of 49%.

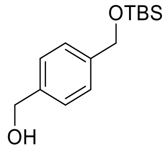
Oily liquid **2** (6.14 g, 24.33 mmol) and DCM (100 mL) were added into a 250 mL flask. Then MnO_2 was added into the flask. A small amount of heat and gas would be released from the reaction system, so it is necessary to be connected to the double-row exhaust pipe. After the raw material was almost completely consumed, the liquid and solid was separated by the sand core funnel containing silica gel. The solvent of liquid was removed in vacuum to obtain a colorless oily liquid **3**.

A 1 L three-necked bottle was connected to a reflux water separator. A thermometer was used for temperature detection. Schlenk system was connected for replacing argon gas. Oily liquid **3** (32 g, 128 mmol), toluene (500 mL) and diethyl malonate (23 mL, 153 mmol) were added into the bottle and stirred. Then piperidine (3.47 mL, 38 mmol) and acetic acid (2.17 mL, 38 mmol) were injected. While stirred at a high speed, the mixture was heated up until the solution began to reflux. After the raw material was almost completely consumed, the heater was turned off. The solvent of the reaction solution was removed under reduced pressure. Finally, through further purification by column chromatography (eluent PE:EA 500:1), the colorless oily liquid **4** (49.0 g) was obtained with a yield of 97 %.

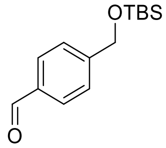
A 1000 mL Schlenk bottle was purged with argon gas three times at high temperature and then filled with argon gas, which was placed in an ice bath. Trimethyl sulfoxide (29.5 g, 134 mmol), sodium hydride (60 %, 5.36 mg, 134 mmol) and DMF (350 mL) were added into the bottle. After the solid gradually dissolved, **4** (colorless oil) was added into the bottle. After the reaction finished, the solution was neutralized with saturated aqueous ammonium chloride solution, and then extracted with ether and saturated sodium chloride solution. The organic phase was dried and filtered to obtain the crude product. Finally, through further purification by column chromatography (eluent PE:EA 200:1) the colorless oily liquid **5** (48.5 g) with a yield of 96%.

A 100 mL Schlenk bottle was purged with argon gas three times at high temperature and then filled with argon gas. Oily liquid **5** (4.0 g, 9.8 mmol), TBAF (3.7 g, 10.8 mmol) and THF (50 mL) were added into the bottle. After an hour, the progress of the reaction was detected by TLC (PE:EA

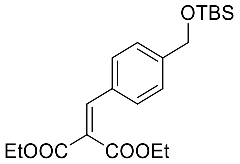
4:1). While the raw material was completely consumed, the reaction solution was extracted with ethyl acetate and saturated sodium chloride solution. The organic phase was dried and concentrated. Finally, through further purification by column chromatography (eluent PE:EA:acetone 20:1:1), the colorless oily liquid **AB** (2.37 g) was obtained with a yield of 83%.



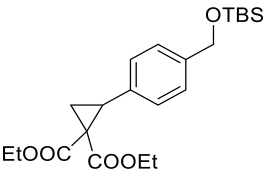
Colorless liquid **2** (49%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 2H), 7.26 (s, 2H), 4.73 (s, 2H), 0.94 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 139.5, 126.8, 126.1, 64.7, 25.9, 18.3, -5.3; IR: ν(cm^{-1}) = 3338, 2953, 2928, 2884, 2856, 1514, 1471, 1462, 1420, 1373, 1361, 1253, 1212, 1086, 1005, 938, 833, 814, 774, 666, 590, 565, 484; HRMS(ESI): $[M+NH_4]^+$ calcd for $C_{14}H_{28}O_2NSi$, 270.19; Found, 270.19.



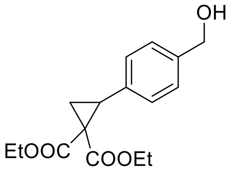
Colorless liquid **3** (>95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.84 (d, J = 7.8 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 4.81 (s, 2H), 0.95 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 148.6, 135.3, 129.8, 126.1, 64.4, 25.9, 18.3, -5.4; IR: ν(cm^{-1}) = 2954, 2929, 2885, 2856, 2732, 1702, 1608, 1578, 1471, 1462, 1424, 1388, 1375, 1361, 1301, 1290, 1254, 1208, 1164, 1106, 1088, 1015, 1005, 938, 834, 812, 775, 703, 668, 640, 620, 572, 479; HRMS(ESI): $[M+H]^+$ calcd for $C_{14}H_{23}O_2Si$, 251.15; Found, 251.15.



Colorless liquid **4** (97%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 164.1, 144.3, 141.9, 141.8, 131.3, 129.4, 126.1, 125.6, 64.3, 61.5, 61.4, 25.8, 18.2, 14.0, 13.8, -5.4; IR: ν(cm^{-1}) = 2955, 2930, 2886, 2857, 1725, 1630, 1611, 1570, 1512, 1463, 1446, 1377, 1313, 1295, 1254, 1198, 1179, 1092, 1062, 1018, 1007, 937, 835, 814, 775, 709, 668, 641, 582, 549, 498; HRMS(ESI): $[M+Na]^+$ calcd for $C_{21}H_{32}O_5NaSi$, 415.19; Found, 415.19.



Colorless oil **5** (96%); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.21 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.69 (s, 2H), 4.33 – 4.14 (m, 2H), 3.92 – 3.77 (m, 2H), 3.20 (dd, *J* = 9.3, 8.0 Hz, 1H), 2.16 (dd, *J* = 8.0, 5.1 Hz, 1H), 1.69 (dd, *J* = 9.3, 5.1 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.92 (s, 9H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 166.6, 140.5, 133.1, 128.3, 125.8, 64.6, 61.6, 61.0, 37.4, 31.9, 25.8, 18.7, 18.3, 14.0, 13.6, -5.3; IR: ν(cm^{-1}) = 2980, 2956, 2930, 2899, 2857, 1723, 1518, 1464, 1445, 1371, 1321, 1275, 1210, 1189, 1128, 1087, 1032, 1020, 990, 939, 835, 775, 712, 684, 666, 638, 593, 566, 537, 460; HRMS(ESI): [M+Na]$^+$ calcd for $C_{22}H_{34}O_5NaSi$, 429.21; Found, 429.21.



Colorless oil **AB** (83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 4.65 (d, J = 4.8 Hz, 2H), 4.33–4.15 (m, 2H), 3.86 (p, J = 7.1 Hz, 2H), 3.21 (dd, J = 9.2, 8.0 Hz, 1H), 2.16 (dd, J = 8.0, 5.2 Hz, 1H), 1.70 (dd, J = 9.2, 5.2 Hz, 1H), 1.60 (t, J = 5.7 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.8, 166.6, 140.0, 134.1, 128.8, 126.7, 64.9, 61.7, 61.1, 37.4, 31.9, 18.8, 14.1, 13.7; IR: ν(cm^{-1}) = 3475, 2982, 2937, 2873, 1717, 1518, 1466, 1445, 1393, 1372, 1322, 1275, 1212, 1191, 1133, 1095, 1017, 854, 840, 762, 701, 605, 537; HRMS(ESI): [M+Na]$^+$ calcd for $C_{16}H_{20}O_5Na$, 315.12; Found, 315.12.

(3) General Polymerization Procedure

The polymerization of monomers A_2 and B_2

A dried Schlenk tube was placed in the glove box, to which was added a desired amount of catalyst and ligand. The tube was removed from the glove box and connected to the dual-manifold line. The fully dried monomers A_2 and B_2 (solid, poorly soluble) were added into another dried Schlenk tube, which were freeze-dried to maintain the reaction system anhydrous and oxygen-free. A certain amount of solvent was injected into two Schlenk tubes to dissolve the reactants. At the same time, the tubes were placed in the oil bath at a desired temperature. Then the catalyst solution was injected into the monomer solution to start the reaction. After the desired time, the reaction was stopped, and a small amount of ethyl acetate was added into the reaction system. Then the metal ions were removed through a sand core funnel containing alumina. The solvent was removed under reduced pressure. The polymer was obtained and subjected to subsequent tests.

The polymerization of monomer AB

A dried Schlenk tube was placed in the glove box, to which was added a desired amount of catalyst and ligand. The tube was removed from the glove box and connected to the dual-manifold line. The fully dried monomers AB (liquid) was added into another dried Schlenk tube, which was freeze-dried to maintain the reaction system anhydrous and oxygen-free. A certain amount of solvent was injected into two Schlenk tubes to dissolve the reactants. At the same time, the tubes were placed in the oil bath at a desired temperature. Then the monomers solution was injected into the catalyst solution to start the reaction. After the desired time, the reaction was stopped, and a small amount of ethyl acetate was added into the reaction system. Then the metal ions were removed through a sand core funnel containing alumina. After the solvent was removed under reduce pressure, the polymer was obtained and subjected to subsequent tests.

(4) General Procedure of Transformation Reactions

Hydrolysis of Polyether

The polyether of A_2/B_2 monomers (136 mg, 0.93 mmol ester groups) and THF (5 mL) were added into the 50 mL reaction flask. The aqueous solution of potassium hydroxide (50 mg/mL, 7 mL, 6.25 mmol potassium hydroxide) was injected into the reaction system and stirred. The flask was placed in oil bath at 80 °C. After three days, THF was removed under reduced pressure. Hydrochloric acid was added into the reaction solution, which was stirred to neutralize the potassium hydroxide. After neutralization process, yellow solid precipitated and mostly adsorbed on the magnetic stirrer. After solid-liquid separation, the obtained solid was put in dilute hydrochloric acid and stirred to remove the inorganic salt, and then washed with ethyl acetate to remove the residue of acidic impurities. Finally, the solid was fully dried in vacuum to obtain 125 mg of a yellow solid. The solid was subjected to ^1H NMR spectroscopy test using deuterated dimethyl sulfoxide as a solvent, and the conversion of functional group was calculated to be 98%.

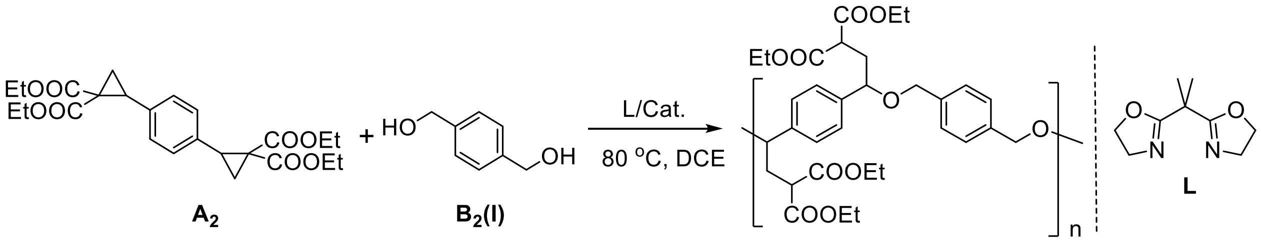
Transesterification of Polyether

The polyether of A_2/B_2 monomers (116.8 mg, 0.8 mmol ester groups) and zinc acetate (14.7 mg, 0.4 mmol) were added into the 25 mL reaction flask. Diethylene glycol monomethyl ether (1 mL) was injected into the reaction system and stirred. The flask was placed in oil bath at 80 °C. After three days, diethylene glycol monomethyl ether in the reaction solution was removed under reduced pressure at high temperature. The solid was put into water and stirred to remove the inorganic salt. After solid-liquid separation, the obtained solid was fully dried in vacuum. The solid was subjected to ^1H NMR spectroscopy test using deuterated chloroform as a solvent, and the conversion of functional group was calculated to be 86%.

2. Supplementary Results of Polymerization

(1) The Polymerizations of A_2 and B_2 under Different Conditions

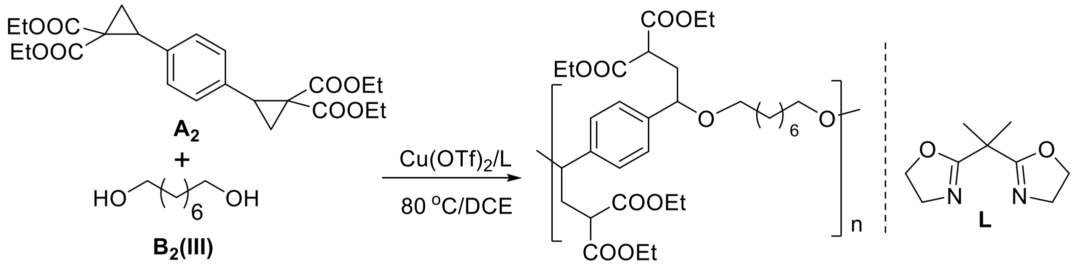
Table S1. The polymerization of A_2 and B_2(I) using different metal catalysts[a]



Entry	Cat.	Conv.[b] (cyclopropane)	Conv.[b] (OH)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	PDI[c]
1	$Cu(OTf)_2$	100%	94%	5.2	16.4	3.1
2	$GaCl_3$	0	0	No Reaction		
3	$CuBr_2$	0	0	No Reaction		
4	$ZnBr_2$	0	0	No Reaction		
5	$Cu(NTf)_2$	100%	82%	4.1	25.7	6.6
7	AgOTf	0	0	No Reaction		
8	$Cu(AcO)_2$	0	0	No Reaction		

[a]Conditions: 2.5 mL DCE, 0.05 mmol Cat., 0.06 mmol ligand, c(A_2 or B_2(I)) = 0.4 M, oil bath 80 °C, 24 h. [b]Determined by ^{1}H NMR. [c]Determined by GPC.

Table S2. The polymerizations of A_2 and B_2(III) under different conditions[a]

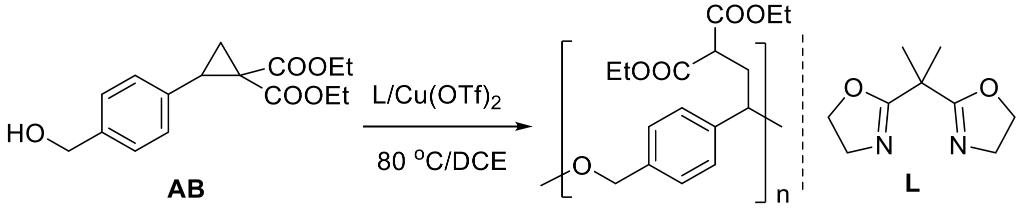


Run	c(Cat.) (M)	Conv.[b] (cyclopropane)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	PDI[c]
1	0.02	100%	3.1	13.9	4.4
2	0.008	100%	2.3	5.4	2.3
3	0.004	100%	1.6	3.0	1.8
4[d]	0.008	100%	1.5	3.1	2.0

[a] Conditions: 2.5 mL DCE, n($Cu(OTf)_2$)/n(L) = 1/1.2, c(A_2 or B_2(III)) = 0.4 M, oil bath 80 °C, 24 h. [b] Determined by ^1H NMR. [c] Determined by GPC. [d] c(A_2 or B_2(III)) = 0.2 M.

(2) The NMR Tracking Experiments for the Polymerization of AB Monomer

Table S3. The NMR tracking experiments for the polymerization of AB monomer[a]



Entry	Time (min)	Conv.[b] (cyclopropane)	Conv.[b] (OH)	$M_{n,NMR}$[c] (kg/mol)	[Cyclo]/[OH][d]
1	5	16.3%	16.7%	0.35	0.98
2	10	36.0%	33.3%	0.44	0.96
3	20	54.8%	52.4%	0.61	0.95
4	30	69.0%	65.5%	0.85	0.90
5	45	82.1%	78.7%	1.37	0.84
6	60	89.0%	85.5%	2.02	0.76
7	90	96.0%	91.9%	3.60	0.49
8	120	98.0%	93.8%	4.68	0.32
9	150	99.0%	93.9%	4.82	0.16
10	180	100%	94.4%	5.20	0
11	240	100%	94.4%	5.23	0
12	360	100%	94.4%	5.26	0

[a]Conditions: 2 mL DCE, 1.6 mmol monomers, 0.04 mmol Cat., 0.048 mmol ligand, oil bath 80 °C. [b]Determined by ^{1}H NMR. [c]Molecular weight by ^{1}H NMR. [d]The number ratio of propane group and hydroxyl group in the system, determined by ^{1}H NMR.

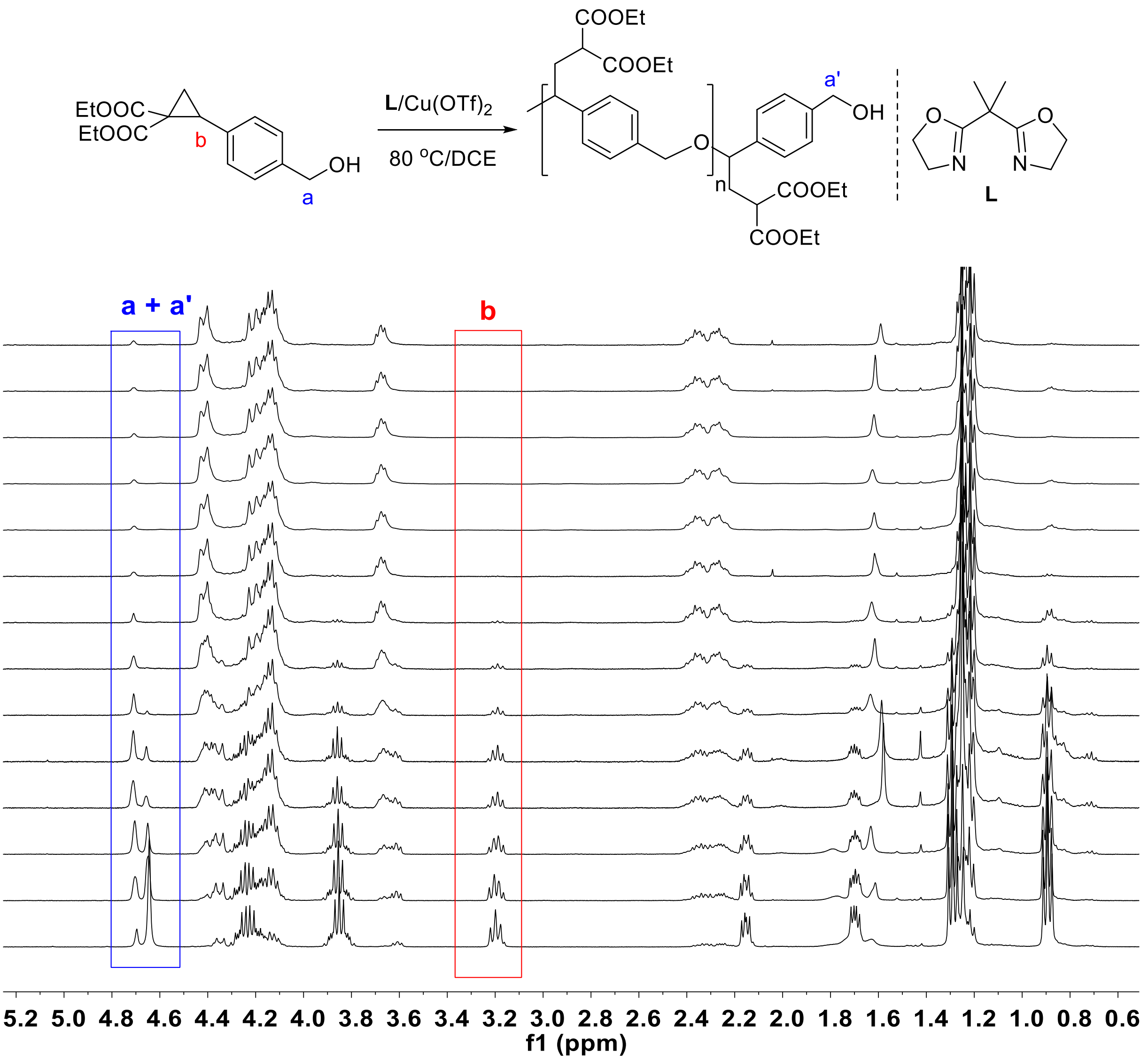


Figure S1. ^{1}H NMR spectra (CCl_3D, 30 °C) tracing the polymerization of AB monomer. Conditions: 2 mL DCE, 1.6 mmol monomers, 0.04 mmol Cat., 0.048 mmol ligand, oil bath 80 °C.

3. Supplementary Characterizations of Polymer

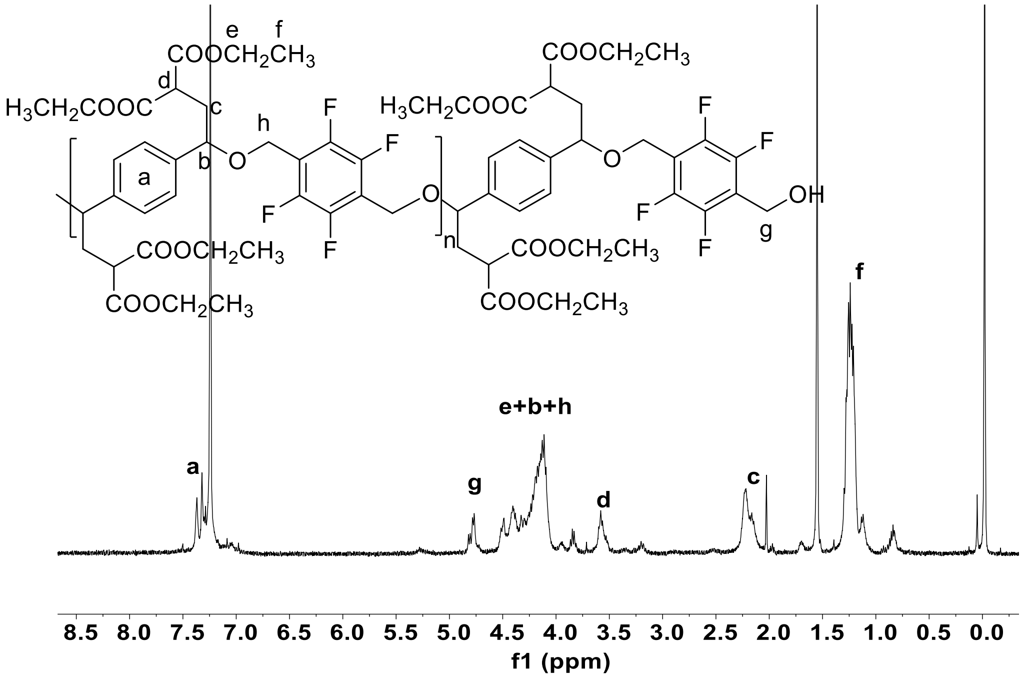


Figure S2. ^{1}H NMR spectrum (CCl_3D, 30 °C) of the polymer of A_2 with $B_2(II)$ (Table 1, run 2). Note: the small peaks that could not be definitely assigned might be due to the inclusion of the low molecular weight components in the polymer product.

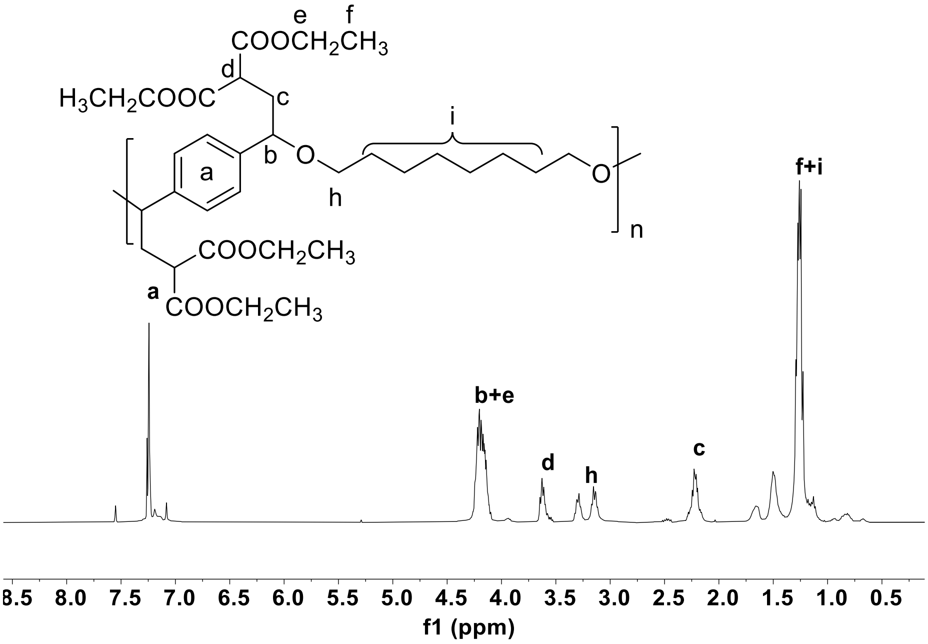


Figure S3. ^{1}H NMR spectrum (CCl_3D, 30 °C) of the polymer of A_2 with $B_2(III)$ (Table 1, run 3). Note: the small peaks that could not be definitely assigned might be due to the inclusion of the low molecular weight components in the polymer product.

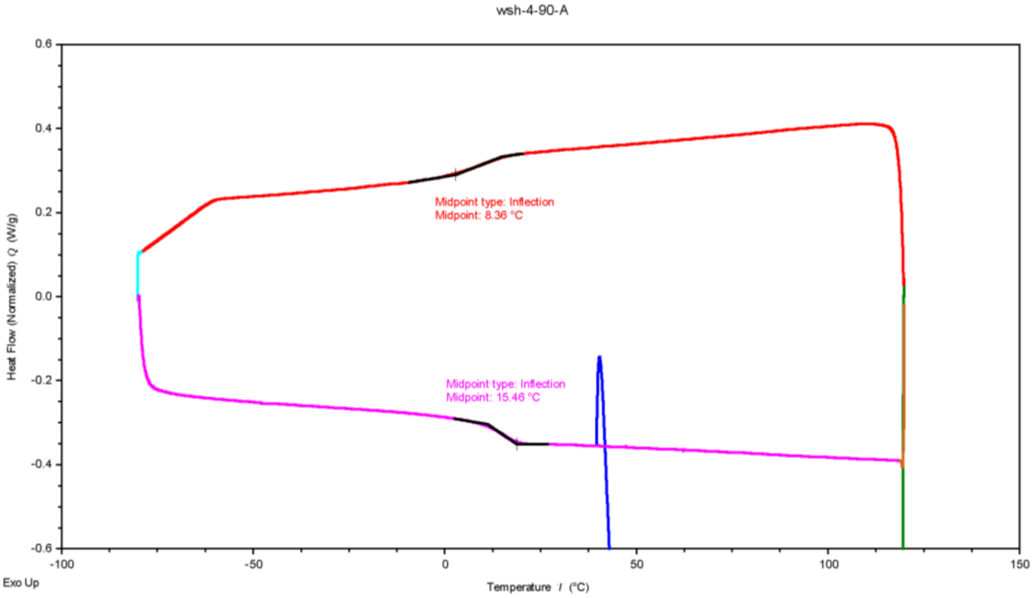


Figure S4. DSC curve of the polymer of A_2 with B_2(I) (Table 1, run 1).

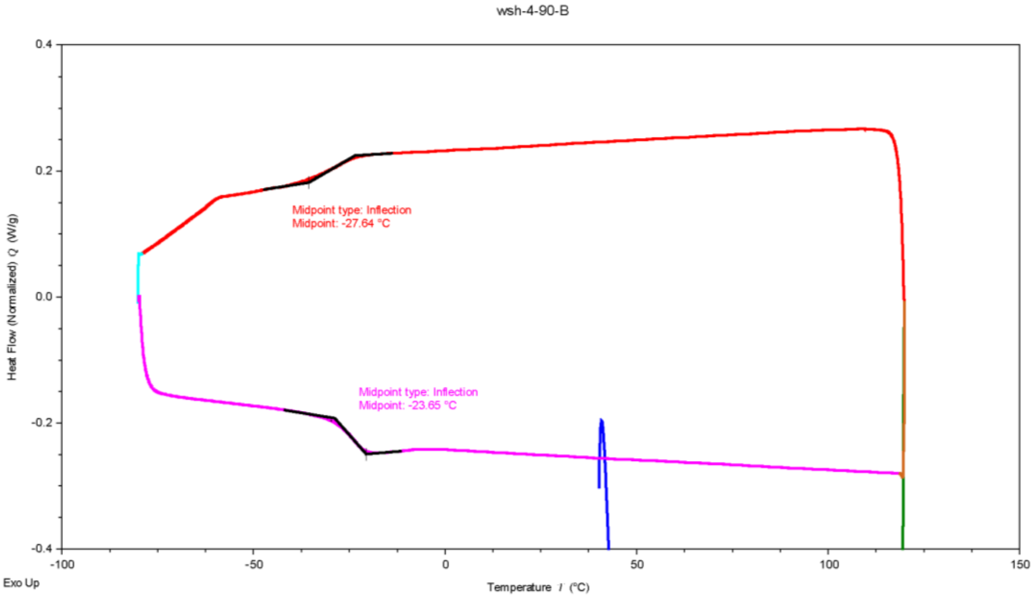


Figure S5. DSC curve of the polymer of A_2 with B_2(III) (Table 1, run 3).

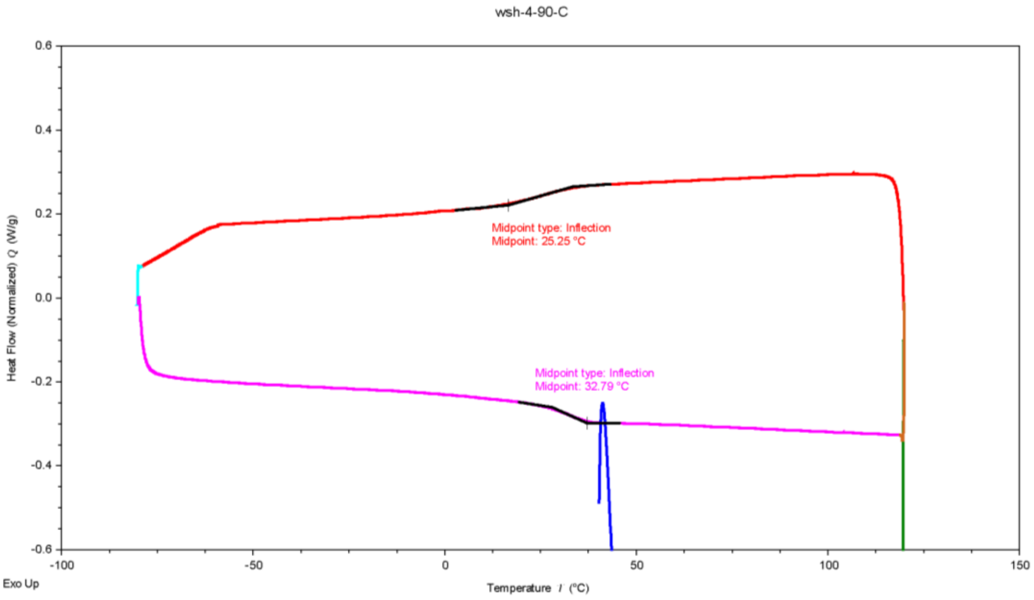


Figure S6. DSC curve of the polymer of A_2 with B_2(II) (Table 1, run 2).

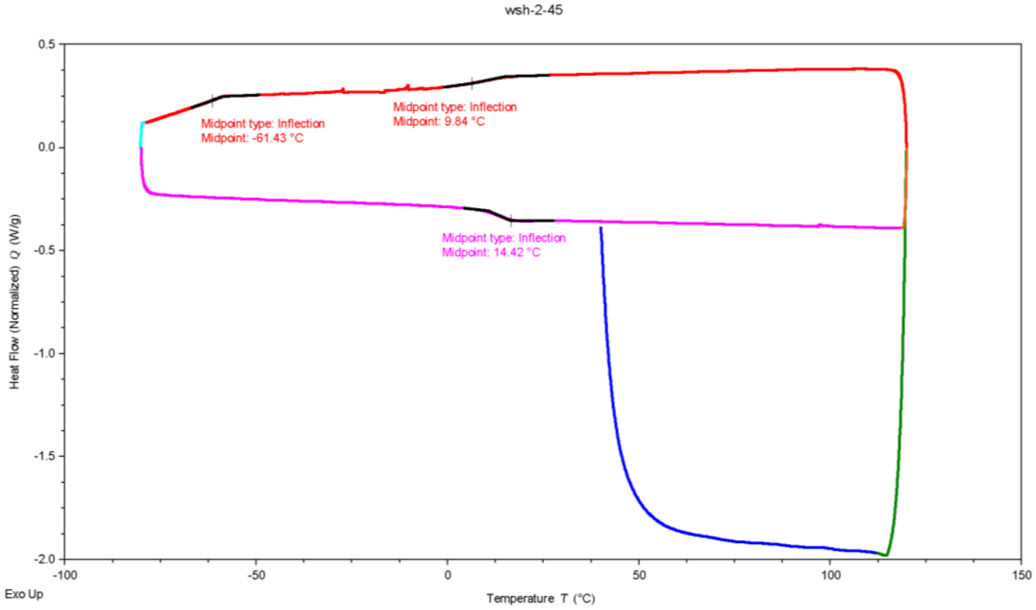


Figure S7. DSC curve of the polymer of AB (Table 2, run 1).

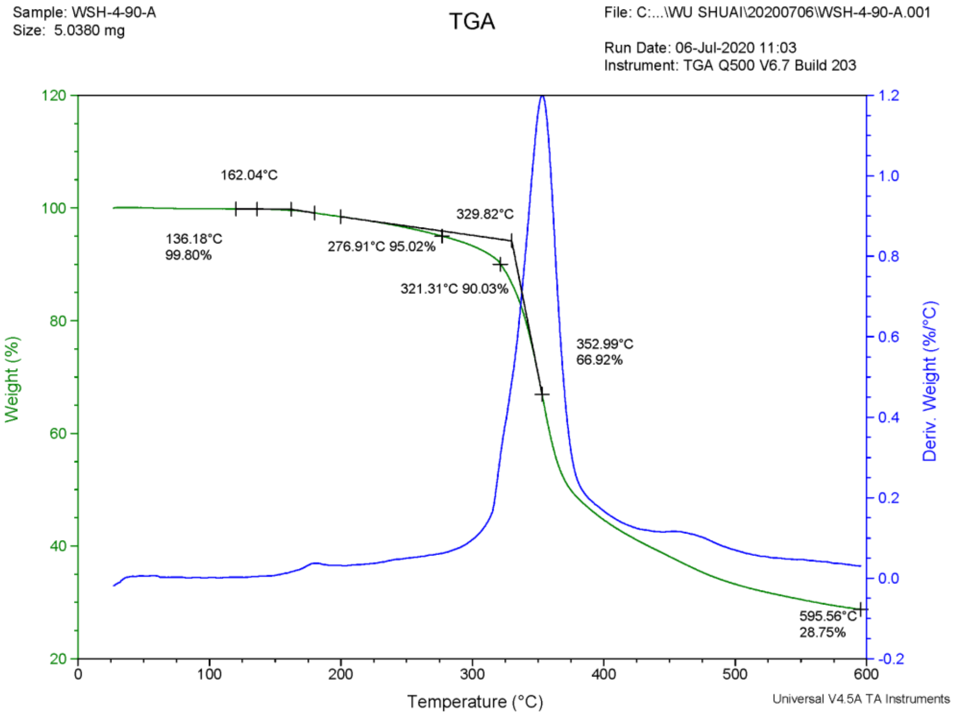


Figure S8. TGA curve of the polymer of A_2 monomer with B_2(I) monomer (Table 1, run 1).

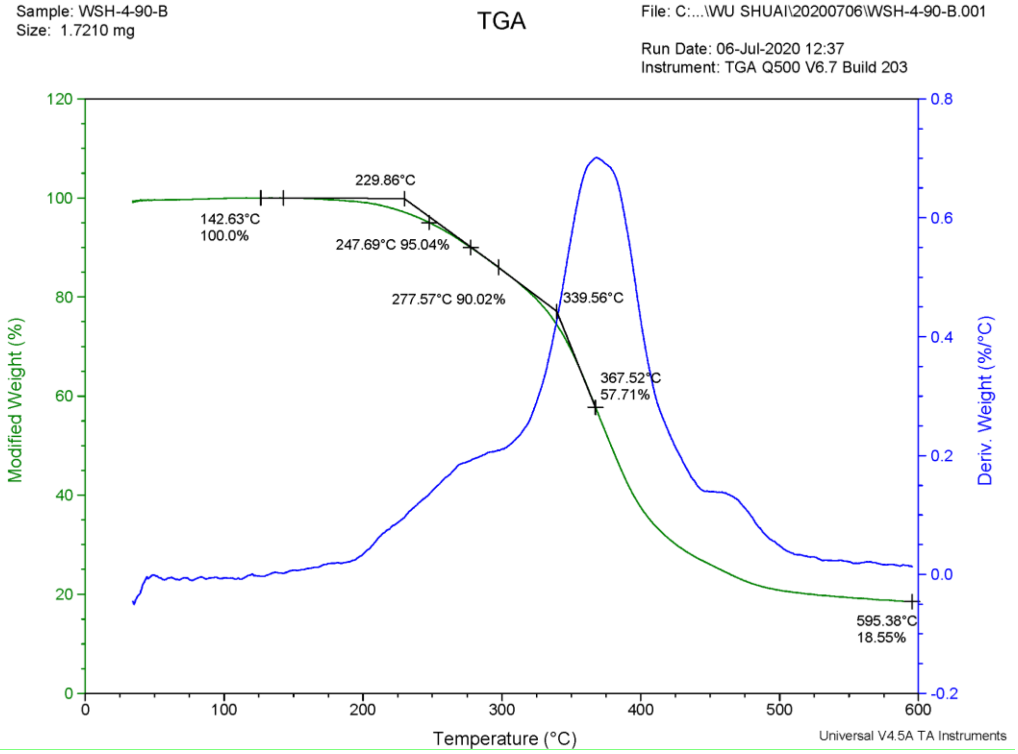


Figure S9. TGA curve of the polymer of A_2 monomer with B_2(II) monomer (Table 1, run 2).

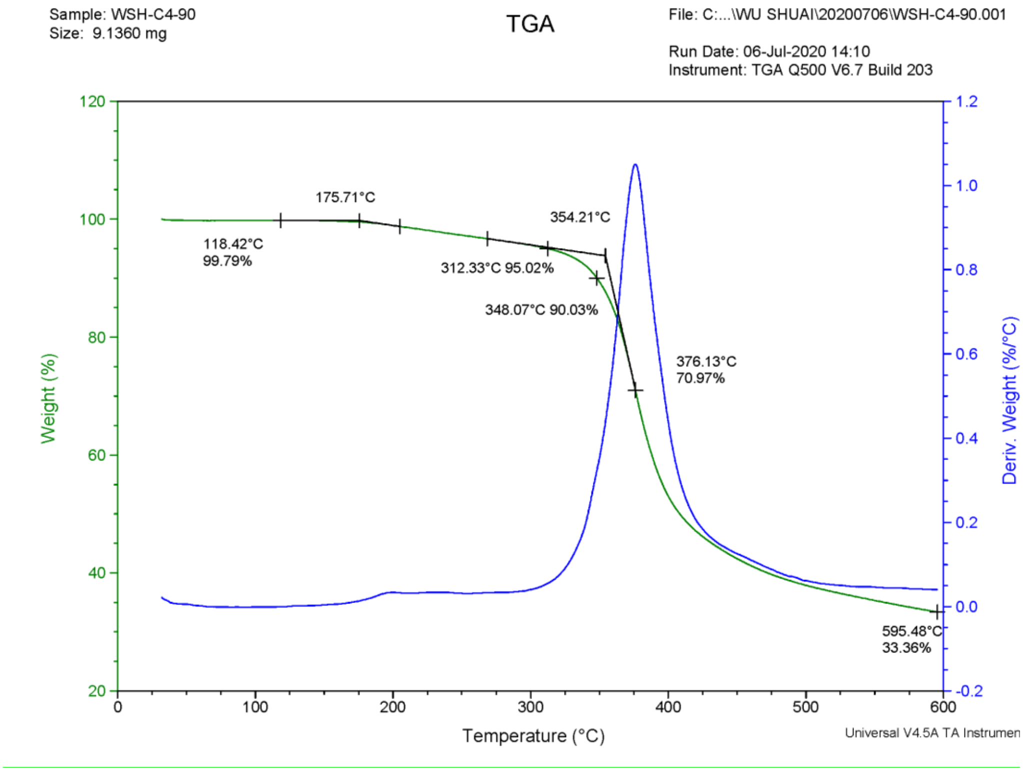


Figure S10. TGA curve of the polymer of A2 monomer with B2(III) monomer (Table 1, run 3).

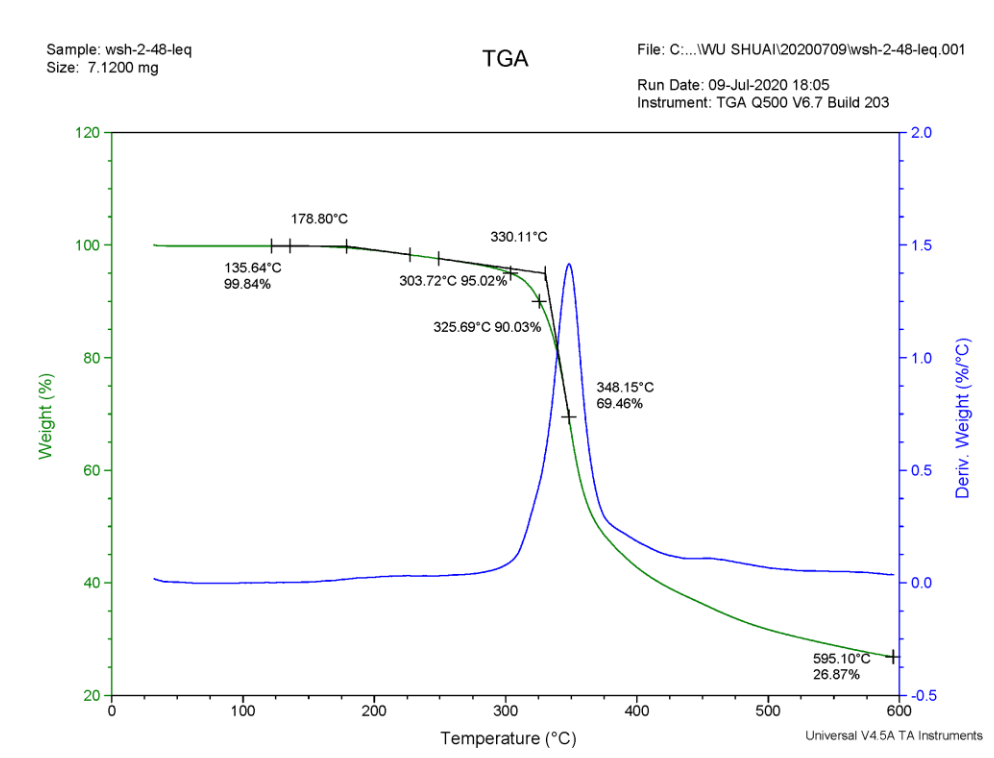


Figure S11. TGA curve of the polymer of AB monomer (Table 2, run 1).

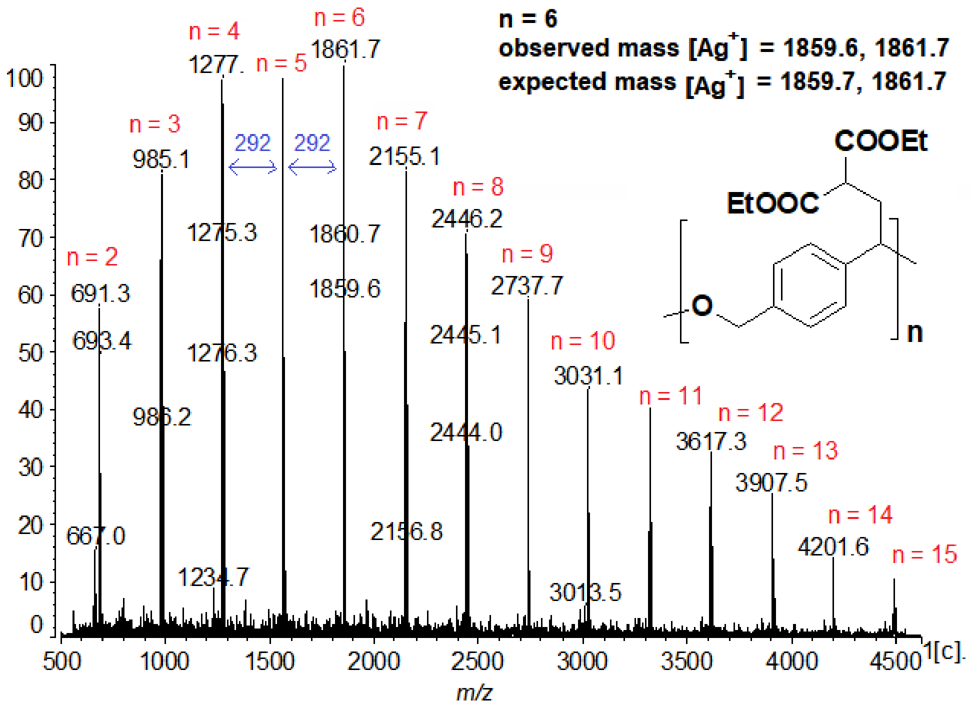


Figure S12. MALDI-TOF MS spectrum of the polymer obtained from the polymerization of AB monomer (run 2, Table 2).

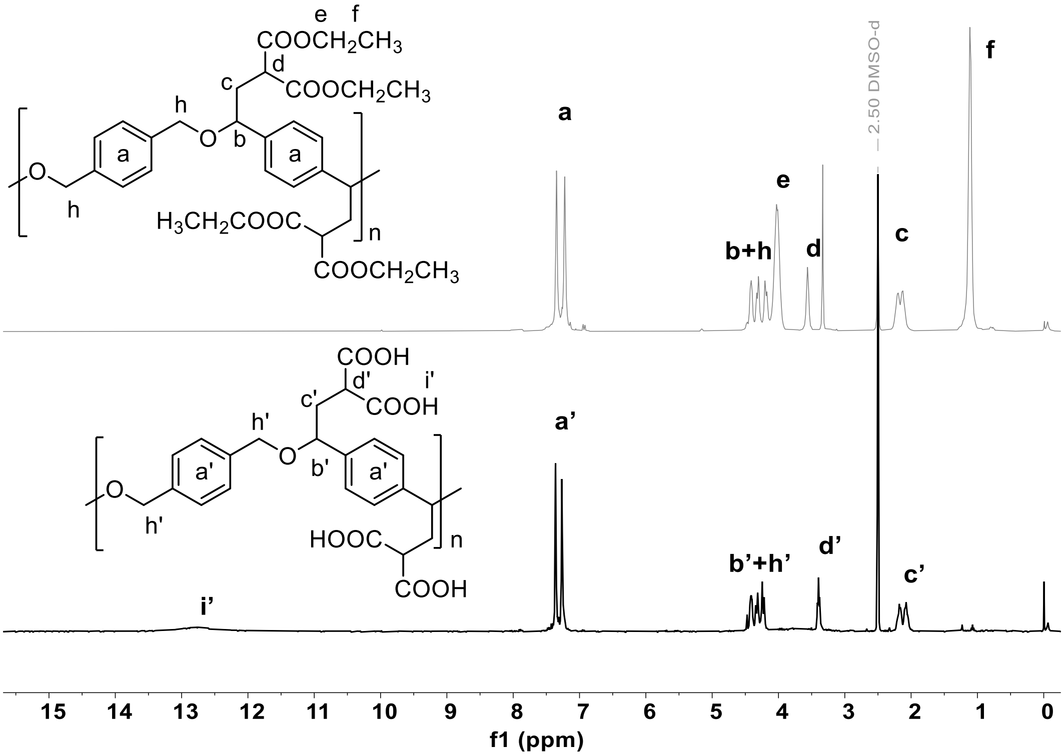


Figure S13. ^{1}H NMR spectrum (DMSO-d^6, 30 °C) of polyethers before and after hydrolysis reaction

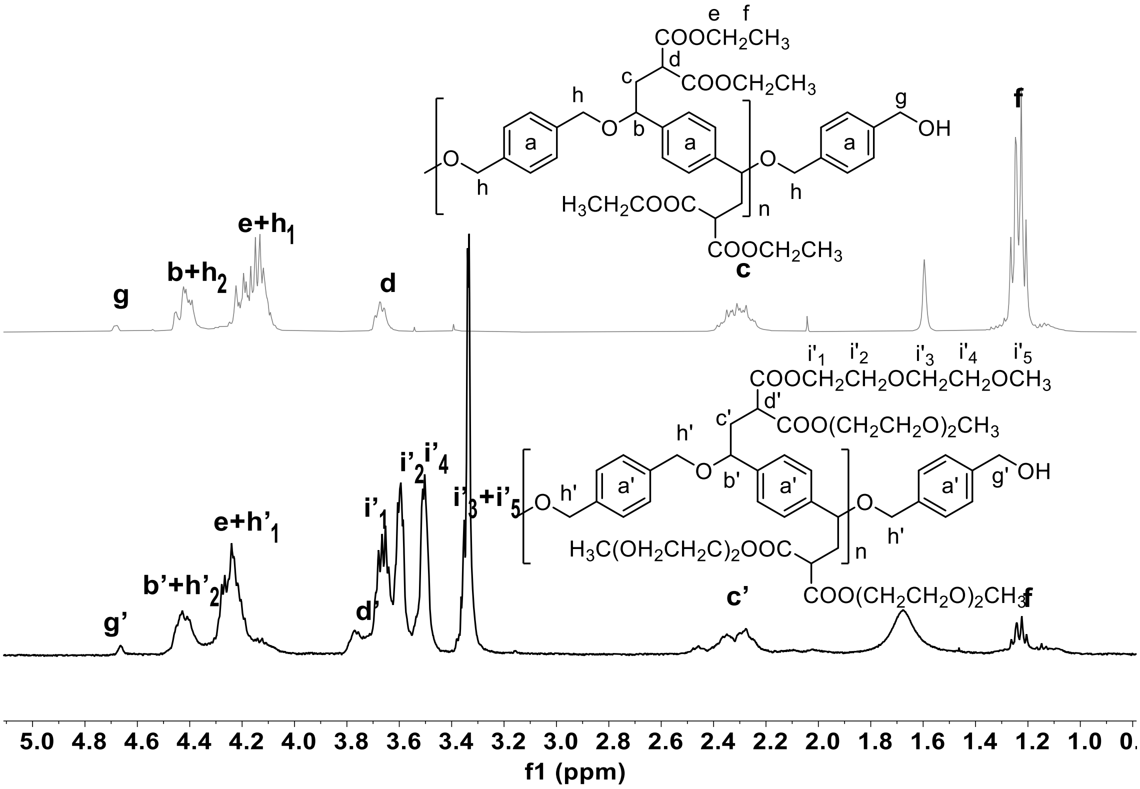
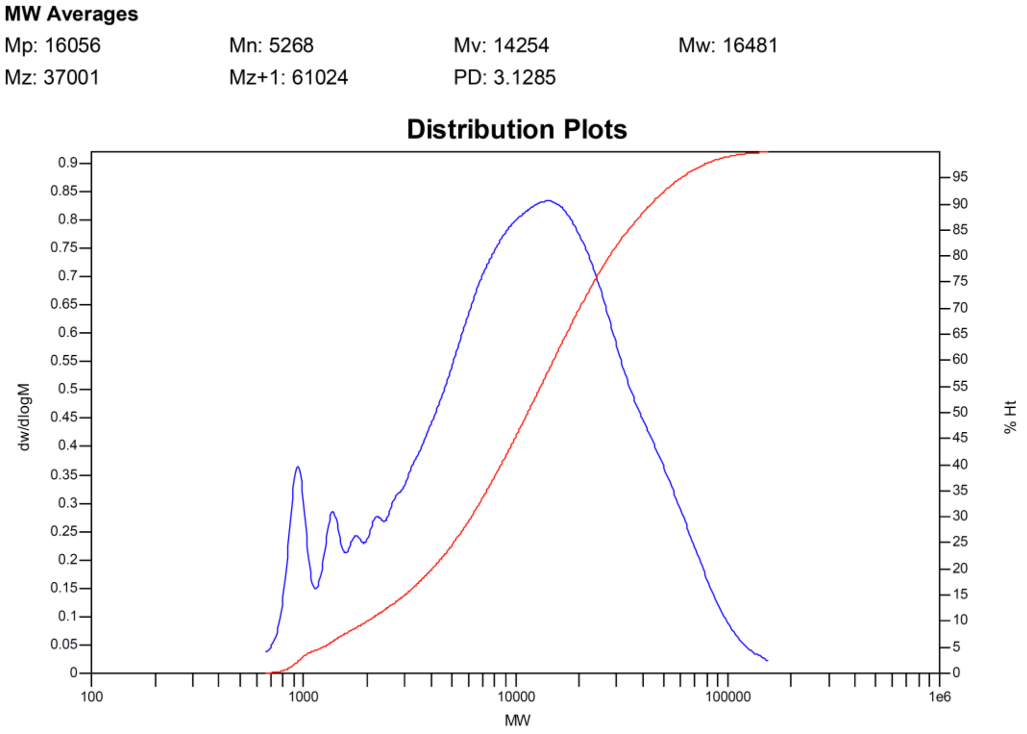


Figure S14. ^{1}H NMR spectra (CCl_3D, 30 °C) of polyethers before and after transesterification reaction



MW Averages

Mp: 16056 Mn: 5268 Mv: 14254 Mw: 16481

Mz: 37001 Mz+1: 61024 PD: 3.1285

Figure S15. GPC curve of the polymer of A_2 monomer with B_2(I) monomer (Table 1, run 1).

MW Averages

Mp: 1481 | Mn: 1194 | Mv: 2154 | Mw: 2339

Mz: 3742 | Mz+1: 5191 | PD: 1.9590

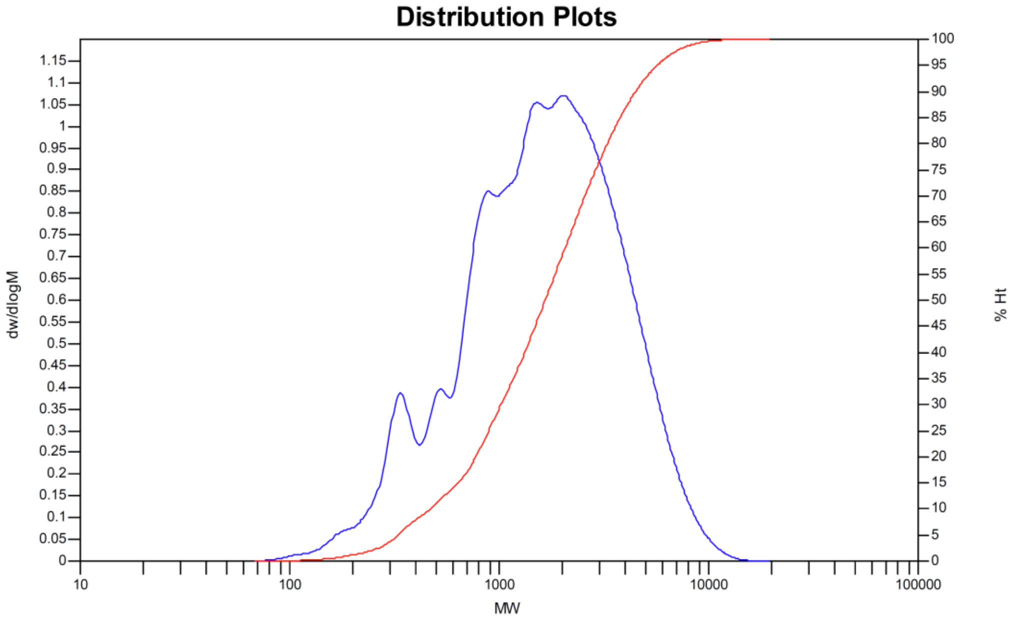


Figure S16. GPC curve of the polymer of A$_2$ monomer with B$_2$(II) monomer (Table 1, run 2).

MW Averages

Mp: 317 | Mn: 2148 | Mv: 10542 | Mw: 12237

Mz: 26359 | Mz+1: 43724 | PD: 5.6969

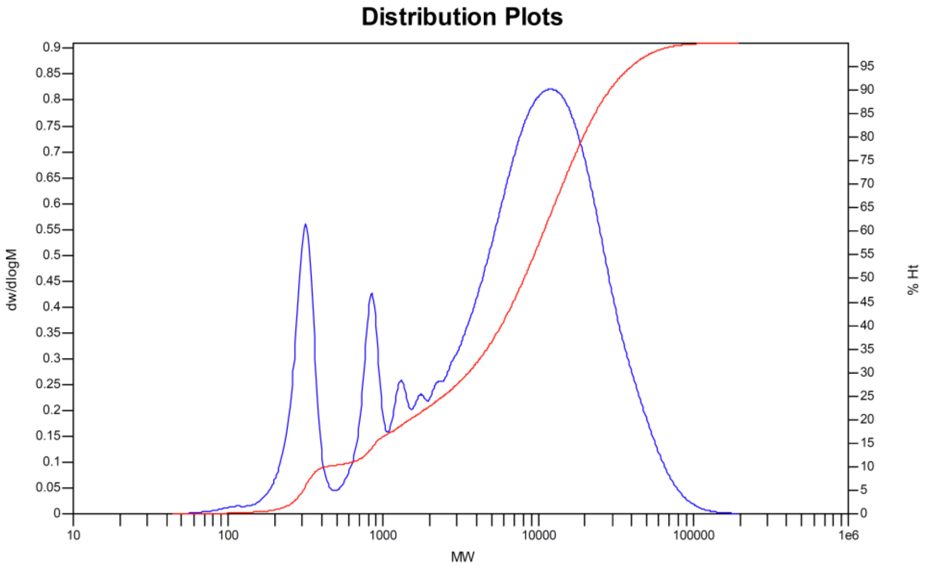


Figure S17. GPC curve of the polymer of A$_2$ monomer with B$_2$(III) monomer (Table 1, run 3).

MW Averages

Mp: 8719	Mn: 4010	Mv: 10068	Mw: 11479
Mz: 25010	Mz+1: 43675	PD: 2.8626	

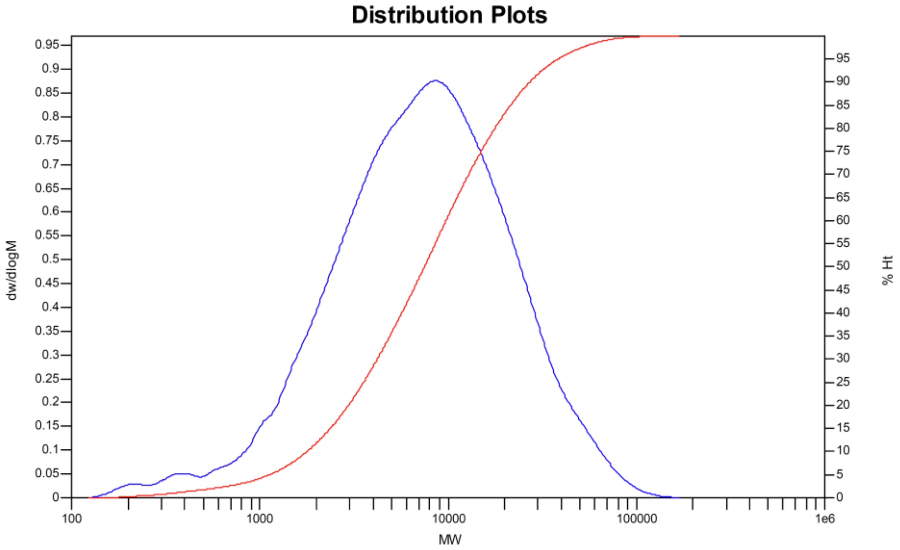


Figure S18. GPC curve of the polymer of AB (Table 2, run 1).

MW Averages

Mp: 3552	Mn: 2080	Mv: 3596	Mw: 3882
Mz: 6148	Mz+1: 8818	PD: 1.8663	

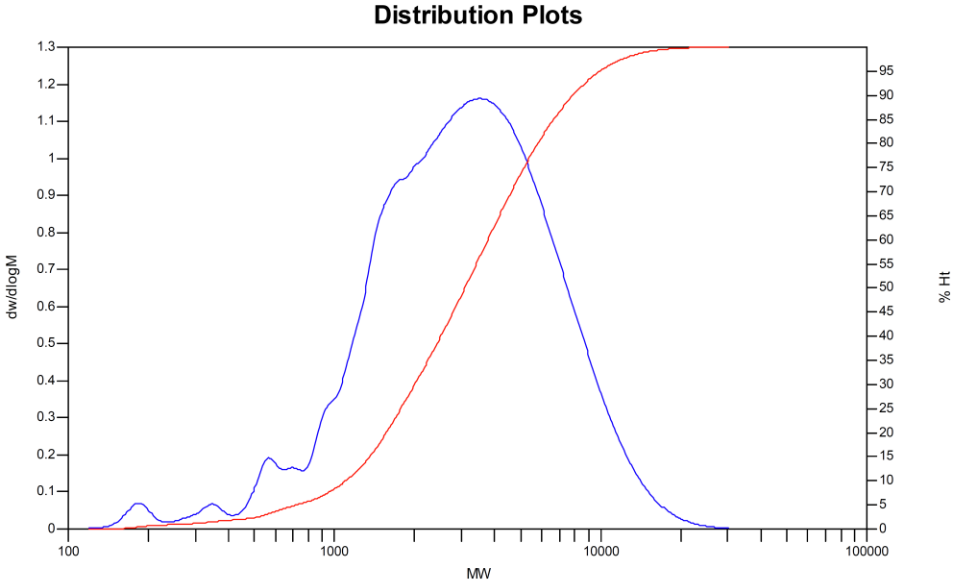


Figure S19. GPC curve of the polymer of AB (Table 2, run 2).

MW Averages

Mp: 16677 Mn: 5740 Mv: 15244 Mw: 17693

Mz: 41167 Mz+1: 71471 PD: 3.0824

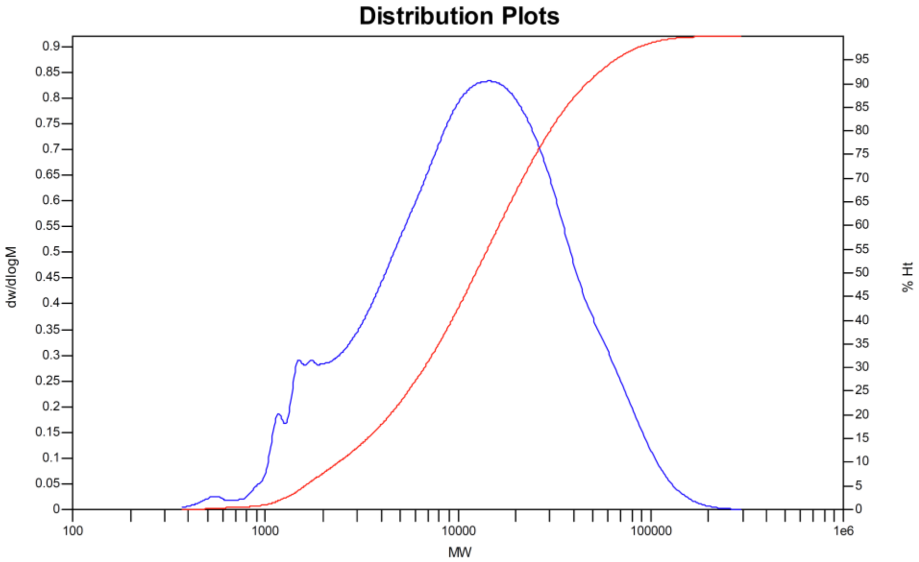


Figure S20. GPC curve of the polymer of AB (Table 2, run 3).

4. Supplementary References

(1) A$_2$ monomer was synthesized according to the literature:

Fang, J.; Hu, B.; Ren, J.; and Wang, Z.-W. Sc(OTf)$_3$-Catalyzed Tandem [3+2] Cycloaddition/Nucleophilic Ring-Opening Reaction of Cyclopropane 1,1-Diesters with Azomethine Ylides. *Asia. J. of Chem.* **2011**, *23(4)*, 1479–1487.

(2) AB monomer was synthesized according to the literature:

Fang, J.; Hu, B.; Ren, J.; and Wang, Z.-W. Sc(OTf)$_3$-Catalyzed Tandem [3+2] Cycloaddition/Nucleophilic Ring-Opening Reaction of Cyclopropane 1,1-Diesters with Azomethine Ylides. *Asia. J. of Chem.* **2011**, *23(4)*, 1479–1487.

Chen, L.; Tilley, J. W.; Guthrie, R. W.; Mennona, F.; Huang, T.-N.; Kaplan, G.; Trilles, R.; Miklowski, D.; Huby, N.; Schwinge, V.; Wolitzky, B.; Karen, R. N-Benzylpyroglutamyl-L-phenylalanine Derivatives as VCAM/VLA-4 Antagonists. *Bioorg. Med. Chem. Lett.* **2000**, *10(8)*, 729–733