# Supporting Information

# Diversity-Oriented Synthesis of Chemically Recyclable Poly(sulfonamide ester)s through Organocatalytic Aziridine-Based Multicomponent Polymerization

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## **1. Experimental Section**

#### **1.1 Materials**

1,4-Benzenedimethanol (98%), 1,5-pentanediol (98%), 2,2-dimethyl-1,3-propanediol (99%), 2,5-furandimethanol (98%), poly(ethylene glycol) (average  $M_n$  200, 400, & 600), 1,12-dodecanediol (98%), 2,3-butanediol (98%), 2,5-dimethyl-2,5-hexanediol (99%), succinic anhydride (98%), phthalic anhydride (99%), *cis*-5-norbornene-endo-2,3-dicarboxylic anhydride (99%), 4,4'-oxydiphthalic anhydride (97%), 4,4'- (hexafluoroisopropylidene)diphthalic anhydride (97%), 4-methylbenzyl alcohol (98%), 6-heptyn-1-ol (98%), 1-octadecanol (98%), 1H,1H,11H-eicosafluoro-1-undecanol (98%), poly(ethylene glycol) methyl ether (average  $M_n \sim 2,000$ ), sodium hydroxide (NaOH), hydrochloric acid, methanesulfonyl chloride (>99%), pyridine (99%), potassium carbonate were purchased commercially and used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone before use. *N*,*N*-dimethylformamide (DMF), and acetonitrile were dried over CaH<sub>2</sub> and distilled before use. Bis(aziridine)s **1a**, and **1b** were prepared according to reported procedures.<sup>1,2</sup>

### **1.2 Characterizations**

Nuclear magnetic resonance (<sup>1</sup>H NMR and <sup>13</sup>C NMR) spectra were recorded with a Bruker AVANCE III 400 spectrometer. Size exclusion chromatography (SEC) measurements were carried out in DMF with 0.01 M LiBr at 60 °C with the Agilent 1260 Infinity II instrument, equipped with two PLgel 10  $\mu$ m MIXED-B columns and a differential refractive index (DRI) detector. The system was calibrated with poly(methyl methacrylate) (PMMA) standards at a flow rate of 1.0 mL/min. FT-IR spectra were obtained on a Thermo-Fisher Nicolet 6700 spectrometer. Thermal stabilities were evaluated by performing the thermogravimetric analysis (TGA) on an STA 449 F5 Jupiter instrument under dry nitrogen at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed using a Mettler Toledo DSC3 calorimeter. Two scanning cycles of heating-cooling were performed in the temperature range from 25 to 150 °C with heating rates of 10 °C/min under nitrogen.  $T_g$  was determined from the second heating run.

## 2. Supporting Schemes, Figures, and Tables



Fig. S1 SEC traces of samples synthesized in Table 1.



Fig. S2 FT-IR spectrum of poly(sulfonamide ester) P1.



Scheme S1 A proposed mechanism for organocatalytic multicomponent polymerization of bis(aziridine), diol, and anhydride.



Scheme S2 Multicomponent polymerization of bis(aziridine) 1b, 1,4benzenedimethanol 2a, and succinic anhydride 3a.



Fig. S3 <sup>1</sup>H (CDCl<sub>3</sub>, 400 MHz, 25 °C) NMR spectra of P5-P7.



Fig. S4 FT-IR spectrum of poly(sulfonamide ester) P12.

**Table S1.** Multicomponent polymerization of bis(aziridine) 1a, 4,4'-oxydiphthalicanhydride 4a, and 4-methylbenzyl alcohol 5a.



entry <sup>a</sup>	catalyst	solvent	time (h)	M <sub>n,SEC</sub> <sup>b</sup> (Da)	$M_{ m w,SEC}^b$ (g/mol)	$PDI^{b}$
1	MTBD	DMF	16	5880	13760	2.34
2	DBU	DMF	16	8930	16790	1.88
3	PMDETA	DMF	16	7510	14490	1.93
4	<i>t</i> -BuP <sub>2</sub>	DMF	16	6740	12130	1.80

<sup>a</sup>Reaction conditions: 1a (0.2 mmol, 1.0 equiv., 0.5 M), 4a (1.0 equiv.), 5a (2.2 equiv.).
<sup>b</sup>Determined by SEC in DMF at 60 °C (PMMA standards calibration).



Fig. S5 SEC traces of samples in Table S1.



Fig. S6 <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C) spectrum of hydrolyzed polymer P2.



Scheme S3 Depolymerization of poly(sulfonamide ester) P12.



Fig. S7 <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 25 °C) spectrum of hydrolyzed polymer P12.

## 3. Polymer Characterization Data



### **P1**

**FT-IR** (neat): 3276, 2942, 2863, 1728, 1582, 1487, 1329, 1241, 1149, 1089 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.80 (d, *J* = 8.0 Hz, 4H), 7.24 (s, 4H), 7.01 (d, *J* = 8.0 Hz, 4H), 5.36 (br, 2H), 5.02 (s, 4H), 4.60-4.42 (m, 2H), 3.22-3.02 (m, 2H), 2.68-2.20 (m, 8H), 2.01-1.77 (m, 4H), 1.68-1.48 (m, 4H), 1.34-0.97 (m, 8H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 172.3, 172.1, 159.1, 136.9, 135.8, 128.3, 128.2, 119.1, 74.4, 66.1, 56.4, 32.6, 30.7, 29.2, 29.0, 24.0, 23.4.



### **P2**

**FT-IR** (neat): 3282, 2939, 2858, 1732, 1581, 1488, 1330, 1240, 1152, 1092 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.90 (d, *J* = 8.0 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 4H), 5.62-5.31 (m, 2H), 4.71-4.55 (m, 2H), 4.19-3.92 (m, 4H), 3.26-3.10 (m, 2H), 2.73-2.24 (m, 8H), 2.06-1.77 (m, 6H), 1.77-1.53 (m, 8H), 1.51-1.06 (m, 8H);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 172.5, 172.4, 159.2, 137.0, 129.5, 119.2, 74.4, 64.6, 56.7, 32.8, 30.9, 29.2, 29.1, 28.1, 24.1, 23.6, 22.3.



**P3** 

**FT-IR** (neat): 3276, 2937, 2861, 1724, 1580, 1484, 1320, 1245, 1148, 1089 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.90 (d, *J* = 8.0 Hz, 4H), 7.12 (d, *J* = 8.0 Hz, 4H), 5.67-5.43 (m, 2H), 4.72-4.53 (m, 2H), 3.97-3.84 (m, 4H), 3.26-3.12 (m, 2H), 2.70-2.32 (m, 8H), 2.04-1.59 (m, 14H), 1.40-1.13 (m, 8H);

<sup>13</sup>C NMR (100 MHz, CDCl3): δ 172.4, 172.3, 159.2, 129.4, 119.2, 74.5, 69.4, 56.6, 34.7, 32.6, 31.0, 29.2, 29.1, 24.2, 23.6, 21.8.



**FT-IR** (neat): 3278, 2935, 2861, 1731, 1582, 1487, 1331, 1241, 1149, 1091 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.82 (d, *J* = 8.0 Hz, 4H), 7.03 (d, *J* = 8.0 Hz, 4H), 6.28 (s, 2H), 5.67-5.27 (m, 2H), 5.00 (s, 4H), 4.65-4.41 (m, 2H), 3.25-2.96 (m, 2H), 2.63-2.17 (m, 10H), 2.10-1.78 (m, 4H), 1.73-1.46 (m, 4H), 1.37-0.95 (m, 8H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 172.3, 171.9, 159.1, 149.9, 136.9, 129.4, 119.1, 111.7, 74.4, 58.2, 56.4, 32.6, 30.7, 29.1, 28.9, 24.0, 23.4.



## **P5**

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.80 (d, J = 8.0 Hz, 4H), 7.07 (d, J = 8.0 Hz, 4H), 5.66-5.26 (m, 4H), 4.75-4.50 (m, 2H), 4.34-4.16 (m, 4H), 3.82-3.52 (m, 8H), 3.36-3.09 (m, 2H), 2.72-2.24 (m, 8H), 2.17-1.87 (m, 4H), 1.79-1.52 (m, 4H), 1.45-1.05 (m, 8H).

### **P6**

**FT-IR** (neat): 3272, 2929, 2868, 1727, 1582, 1488, 1325, 1243, 1154, 1089 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.80(d, *J* = 8.0 Hz, 4H), 7.05(d, *J* = 8.0 Hz, 4H), 5.41-5.03(m, 4H), 4.76-4.51(m, 2H), 4.34-4.16(m, 4H), 3.78-3.47(m, 28H), 3.37-3.15(m, 2H), 2.76-2.26(m, 8H), 2.14-1.89(m, 4H), 1.83-1.54(m, 4H), 1.44-1.01(m, 8H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 172.54, 172.36, 159.60, 137.06, 129.92, 128.83, 119.25, 119.19, 119.10, 77.35, 77.03, 76.71, 74.48, 70.56-68.97, 63.99, 63.87, 56.74, 34.73-32.76, 30.95, 29.06, 24.12-22.62.

## **P7**

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.81(d, *J* = 8.0 Hz, 4H), 7.05(d, *J* = 8.0 Hz, 4H), 5.30-4.91(m, 4H), 4.79-4.49(m, 2H), 4.36-4.12(m, 4H), 3.89-3.40(m, 44H), 3.34-3.11(m,2H), 2.78-2.21(m,8H), 2.17-1.85(m, 4H), 1.77-1.52(m, 4H), 1.45-1.08(m, 8H).



**FT-IR** (neat): 3272, 2927, 2856, 1728, 1581, 1488, 1328, 1241, 1152, 1090 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.00-7.80 (m, 4H), 7.22-7.02 (m, 4H), 5.47-5.13 (m, 2H), 4.72-4.52 (m, 2H), 4.15-3.98 (m, 4H), 3.31-3.10 (m, 2H), 2.70-2.30 (m, 8H), 2.08-1.89 (m, 4H), 1.77-1.55 (m, 8H), 1.41-1.13 (m, 24H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 173., 172.5, 159.2, 137.0, 129.4, 119.1, 77.3, 77.0, 76.7, 74.4, 65.1, 56.7, 33.0, 30.9, 29.5, 29.3, 29.2, 29.1, 28.5, 25.8, 24.9, 24.1, 23.6.



**P9** 

**FT-IR** (neat): 3267, 2936, 2863, 1724, 1581, 1488, 1327, 1241, 1152, 1090 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.99-7.76 (m, 4H) , 7.21-7.02 (mm, 4H), 5.78-5.26 (m, 4H), 5.03-4.77 (m, 2H), 4.74-4.77 (m, 2H), 3.30-3.08 (m, 2H), 2.70-2.28 (m, 8H), 2.06-1.90 (m, 4H), 1.79-1.41 (m, 8H), 1.38-1.01 (m, 14H);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 172.7, 172.0, 159.2, 136.9, 129.5, 119.2, 74.8, 71.4, 63.0, 56.7, 42.3, 31.7, 29.3, 24.4, 23.8, 20.0.



### P10

**FT-IR** (neat): 3273, 2939, 2857, 1718, 1581, 1485, 1326, 1247, 1154, 1067 cm<sup>-1</sup>;

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.82-7.56 (m, 4H), 7.52-7.31 (m, 4H), 7.23-7.13 (m, 4H), 6.79-6.47 (m, 4H), 5.70-5.49 (m, 2H), 4.89-4.52 (m, 2H), 4.28-3.96 (m, 4H), 3.29-3.12 (m, 2H), 2.25-1.87 (m, 4H), 1.83-1.47(m, 8H), 1.41-1.07(m, 6H), 1.06-0.88 (m, 4H);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 167.9, 167.0, 158.7, 136.8, 131.5, 129.3, 128.8, 118.72, 118.69, 75.5, 75.4, 70.6, 56.6, 34.7, 33.0, 32.6, 30.9, 24.1, 23.6, 21.9.

**FT-IR** (neat): 3278, 2943, 2865, 1732, 1581, 1483, 1331, 1247, 1154, 1090 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.91-7.73 (m, 4H), 7.13-6.93 (m, 4H), 6.35-5.96 (m, 4H), 5.84-5.56 (m, 2H), 4.61-4.31 (2H, m), 3.94-3.61 (m, 4H), 3.35-2.77 (m, 10H), 2.04-1.74 (m, 4H), 1.69-1.33 (m, 10H), 1.29-0.99 (m, 8H), 0.97-0.79 (m, 4H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 173.6-172.9, 172.0-171.5, 159.1, 137.6, 136.2-133.6, 129.5-129.3, 119.0, 74.8-73.7, 70.2-68.9, 57.0, 56.5-56.3, 48.9-47.7, 47.3, 46.8-46.0, 34.5-33.9, 32.8-32.1, 31.1-30.7, 24.5-23.9, 23.6, 22.0-21.5.



## P12

**FT-IR** (neat): 3282, 2936, 2862, 1720, 1580, 1488, 1323, 1266, 1154, 1114 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.95-7.44 (m, 6H), 7.42-6.62 (m, 16H), 5.64-4.98 (m, 6H), 4.94-4.46 (m, 2H), 3.43-3.08 (m, 2H), 2.31 (br, 6H), 2.19-1.91 (m, 4H), 1.83-1.49 (m, 4H), 1.43-1.03 (m, 8H);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 167.2-165.7, 159.1-157.9, 138.4-138.2, 136.9-135.9, 134.7-134.0, 132.2-131.3, 129.4-128.4, 120.9, 119.3-118.3, 75.9-75.4, 67.9-67.4, 56.5, 33.7-32.3, 30.9-30.2, 24.4-23.5, 21.2.



### P13

**FT-IR** (neat): 3286, 2936, 2863, 1717, 1584, 1488, 1265, 1155, 1118 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 7.97-7.49 (m, 6H), 7.38-6.71 (m, 8H), 5.85-5.24 (m, 2H), 4.89-4.67 (m, 2H), 4.47-4.10 (m, 4H), 3.43-3.16 (m, 2H), 3.15-2.66 (m, 2H), 2.34-1.85 (m, 10H), 1.83-0.96 (m, 22H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.8-166.3, 159.1, 137.0, 131.8, 129.2, 119.0, 84.2, 75.6, 68.6, 66.1-65.8, 57.1-56.4, 33.3-32.6, 31.0-30.6, 28.0, 27.9, 25.01, 24.95, 24.2-23.6, 18.2.



P14

**FT-IR** (neat): 3279, 2916, 2851, 1715, 1579, 1491, 1463, 1266, 1158, 1114 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.04-7.49 (m, 6H), 7.37- 6.71 (m, 8H), 5.99-5.31 (m, 2H), 4.92-4.64 (m, 2H), 4.45-4.10 (m, 4H), 3.50-3.14 (m, 2H), 2.26-1.88 (m, 4H), 1.84-1.55 (m, 8H), 1.53-0.99 (m, 68H), 0.87 (t, *J* = 8.0 Hz, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.02, 166.28, 158.96, 137.17-131.71, 129.23, 118.98, 77.35, 77.03, 76.71, 75.50, 66.86, 66.44, 63.11, 57.15, 56.89, 48.02, 47.08, 38.87, 37.75, 32.80-28.45, 25.98-22.69, 20.93.



### P15

**FT-IR** (neat): 3284, 2942, 2866, 1729, 1582, 1487, 1263, 1215, 1148, 1116 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.04-7.52 (m, 6H), 7.48-6.67 (m, 8H), 6.05 (t, *J* = 52 Hz, 2H), 5.75-5.18 (m, 2H), 5.05-4.53 (m, 6H), 3.45-3.13 (m, 2H), 2.32-1.49 (m, 8H), 1.49-0.90 (m, 8H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.1-164.1, 159.0, 137.2-136.3, 132.1, 129.2, 119.0, 113.5-104.5, 76.2, 60.4, 56.6, 32.9-31.9, 30.8-30.3, 29.7, 24.1-23.3.



**FT-IR** (neat): 2916, 2883, 1717, 1582, 1463, 1342, 1277, 1234, 1148, 1098 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS): δ 8.40-7.51 (m, 6H), 7.36-6.66 (m, 8H), 6.09-5.52 (m, 2H), 4.86-4.32 (m, 6H), 4.07-3.50 (m, 268H), 3.44-3.25 (m, 2H), 3.38 (s, 6H), 2.24-1.93 (m, 4H), 1.80-1.57 (m, 4H), 1.51-1.12 (m, 8H);

<sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 169.0, 165.6, 158.3, 136.7, 134.6, 131.1, 129.5, 129.0, 118.8, 72.2, 71.5, 70.2, 70.1, 68.3, 64.7, 58.7, 56.2, 33.5-29.2, 29.5-22.2.



P17

**FT-IR** (neat): 3284, 2946, 2866, 1728, 1584, 1486, 1257, 1212, 1139, 1073 cm<sup>-1</sup>; <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.29-7.39 (m, 10H), 7.21-6.69 (m, 4H), 6.05 (t, J = 52 Hz, 2H), 5.73-5.21 (m, 2H), 5.04-4.51 (m, 6H), 3.48-2.96 (m, 2H), 2.39-1.47 (m, 8H), 1.47-0.90 (m, 8H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.0, 164.5, 159.0, 136.9, 129.3, 119.0, 113.5, 110.6, 107.5, 105.0, 60.8, 56.5, 33.0-29.7, 24.6-23.4.



4. SEC (DMF, 60 °C) Traces of Poly(sulfonamide ester)s P1-P17







## 5. TG Curves of Poly(sulfonamide ester)s P1-P17







## 6. DSC Curves of Poly(sulfonamide ester)s P1-P17







## 7. NMR Spectra of Poly(sulfonamide ester)s P1-P17, and Bis(hydroxy

# sulfonamide) 6















































## 8. Full SEC Traces of Poly(sulfonamide ester)s P1-P117

## **P1**

















**Chromatogram Plot** 



**Distribution Plot** 







**Distribution Plot** 



## Chromatogram Plot

**P8** 



**Distribution Plot** 





**Chromatogram Plot** 



1e4 Fitted MW (g/mol)

**Chromatogram Plot** 



**Chromatogram Plot** 



**Distribution Plot** 









**Chromatogram Plot** 





**Chromatogram Plot** 

0.2

0.1

1e3



1e4 Fitted MW (g/mol) 10

5

1e5

**Chromatogram Plot** 



**Distribution Plot** 





**Chromatogram Plot** 



**Chromatogram Plot** 



**Distribution Plot** 



## 9. References

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