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Supporting Information

For

The control mechanism of (BisSalen)Al mediated asymmetric kinetic resolution polymerization of phenethylglycolide

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1 Materials and methods

1.1 Materials

The (*S*)-5,5',6,6',7,7',8,8'-octahydro[1,1'-binaphthalene]-2,2'-diamine (\geq 95%, 99%*ee*) were purchased from Daicel Chiral Technologies (China) Co., Ltd and used as received. Trimethylaluminium (1.0 M solution in heptane) was purchased from J&K Scientific Ltd and used as received. Salicylaldehyde (98%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd and used as received. 2-Amino-4-methylbenzaldehyde (98%) were purchased from Bidepharm and used as received. Benzhydrol (99%) was purchased from Macklin Biochemical Co., Ltd and dried in vacuum overnight. The benzyl alcohol and benzhydrol were dissolved in toluene to obtain the initiator solution with 0.5 M, respectively. All dry solvents were redistilled after collected from solvent purification system and then stored over molecular sieves (4 Å) in a glovebox. Chromatographic *n*-hexane and isopropanol were purchased from Macklin Biochemical Co., Ltd for the analysis of HPLC measurements. All other chemicals were commercially available and used after appropriate purification.

1.2 Methods

Nuclear magnetic resonance measurements were performed at variable temperature on Bruker Avance instrument at 400 MHz (¹H NMR), chloroform-*d* were used as an internal reference.

Shimadzu Prominence LC-20A Series High Performance Liquid Chromatography (HPLC) was applied to measure the enantiomeric excess (*ee*) of unreacted monomer using a UV detector.

2 Synthesis of racemic phenethylglycolide (rac/meso-Pegl)



2.1 2-Hydroxy-4-phenylbutanoic acid

To a solution of racemic 2-amino-4-phenylbutanoic acid (10 g, 55.9 mmol) in a mixture of water (200 mL) and H₂SO₄ (22 mL) at 0 °C, was added under stirring, a solution of sodium nitrite (15.4 g, 223.5 mmol) in water (100 mL) dropwise over a period of 30 min. The reaction mixture was stirred at -5 to 0 °C. for another 5 h, followed by stirring at room temperature for 16 h. The reaction mixture was extracted by ethyl acetate (300 mL × 3). Organic layer was washed with brine, dried over anhydrous Na₂SO₄, and concentrated. The white crystals of (i) were obtained by crystallization from ethyl acetate/hexane (9.2 g, 91%). ¹H NMR (400 MHz, Deuterium Oxide) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.18 (m, 3H), 4.18 (d, *J* = 7.9, 1H), 2.68 (t, *J* = 7.9 Hz, 2H), 2.10 – 1.88 (m, 2H).

2.2 3,6-Diphenethyl-1,4-dioxane-2,5-dione (rac/meso-Pegl)

Racemic 2-hydroxy-4-phenylbutanoic acid (5 g, 28 mmol) and *p*-toluenesulfonic (0.5 g, 3 mmol) acid was dissolved in 250 mL toluene, and the mixture was heated under reflux for 8 h. The reaction mixture was washed by the saturated sodium bicarbonate solution and then the toluene was removed using evaporator. The residue was purified by column chromatography to afford a diastereomeric mixture of *rac*-Pegl (58.0%)and *meso*-Pegl (42.0%).¹H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.27 (m, 2H), 7.22 (t, J = 6.4 Hz, 3H), 4.90 – 4.83 (m, 1H), 3.00 – 2.74 (m, 2H), 2.49 – 2.19 (m, 2H).



Figure S1. HPLC chromatogram of rac/meso-Pegl

3 Procedures of SS-1 mediated ROP of rac/meso-Pegl

3.1 Analysis of Polymerization Process



In a typical polymerization reaction, a flame-dried 5 mL Schlenk tube with a Teflon cap was first introduced into an Argon-filled glovebox. *Rac*-Pegl (162 mg, 1.0 mmol, 50 equiv.) were dissolved in toluene (1.0 mL) in the Schlenk tube. The initiator of benzhydrol solution (20 μ L, 10 μ mol, 1 equiv.) and *SS*-1 (10 mg, 10 μ mol, 1 equiv.) were added and stirred for 3 minutes. The sealed tube was taken out of glovebox, and then immersed in the external temperature bath of 80 °C. Polymerization was quenched by air at a certain time and monomer conversion was monitored by ¹H NMR spectrum and HPLC.

| | | | Н | PLC analys | sis | Unre | eacted mone | omer | Po | olymerizatio | n |
|-------|--------|----------|-------|------------|-------|-------|-------------|-------|-------|--------------|------|
| Entry | Time/h | Conv.ª/% | L% | meso/% | D/% | L% | meso/% | D/% | L% | meso/% | D/% |
| 1 | 0 | 0 | 29.00 | 42.00 | 29.00 | 29.00 | 42.00 | 29.00 | 0 | 0 | 0 |
| 2 | 3 | 12.0 | 26.58 | 41.16 | 32.27 | 23.39 | 36.22 | 28.40 | 5.61 | 5.78 | 0.60 |
| 3 | 7 | 23.1 | 25.04 | 38.19 | 36.77 | 19.26 | 29.37 | 28.28 | 9.74 | 12.63 | 0.72 |
| 4 | 19 | 46.8 | 17.87 | 28.95 | 53.18 | 9.51 | 15.40 | 28.29 | 19.49 | 26.60 | 0.71 |
| 5 | 31 | 58.8 | 10.48 | 21.03 | 68.49 | 4.32 | 8.67 | 28.22 | 24.68 | 33.33 | 0.78 |
| 6 | 43 | 62.1 | 9.14 | 16.55 | 74.31 | 3.46 | 6.27 | 28.17 | 25.54 | 35.73 | 0.83 |

| Table S | 51. SS-' | I mediated | ROP of | of <i>rac/mesc</i> | -Pegl. |
|---------|----------|------------|--------|--------------------|--------|
|---------|----------|------------|--------|--------------------|--------|

Conditions: $[rac/meso-Pegl]_0/[Cat.]_0/[Ph_2CHOH]_0 = 50/1/1$, $[rac/meso-Pegl]_0 = 0.5$ M in 1 mL toluene, T = 80 °C. aConversions of monomers measured by 1H NMR spectra of the reaction solution. bEnantiomeric excess of the unreacted monomer measured by chiral HPLC.

Since the reactions in Table S1 only went up to 62.1%, we conducted a second

reaction and extended the reaction time as much as possible until L-Pegl and meso-Pegl were fully reacted.

In a typical polymerization reaction, a flame-dried 5 mL Schlenk tube with a Teflon cap was first introduced into an Argon-filled glovebox. *Rac*-Pegl (324 mg, 1.0 mmol, 100 equiv.) were dissolved in toluene (1.0 mL) in the Schlenk tube. The initiator of benzhydrol solution (20 μ L, 10 μ mol, 1 equiv.) and *SS*-1 (10 mg, 10 μ mol, 1 equiv.) were added and stirred for 3 minutes. The sealed tube was taken out of glovebox, and then immersed in the external temperature bath of 80 °C. Polymerization was quenched by air at a certain time and monomer conversion was monitored by ¹H NMR spectrum and HPLC.

| | | | Н | PLC analys | sis | Unre | acted mon | omer | Po | olymerizatio | n |
|-------|--------|----------|-------|------------|-------|-------|-----------|-------|-------|--------------|------|
| Entry | Time/h | Conv.ª/% | L% | meso/% | D/% | L% | meso/% | D/% | L% | meso/% | D/% |
| 1 | 4 | 8 | 29.43 | 39.08 | 31.49 | 27.07 | 35.95 | 28.97 | 1.93 | 6.05 | 0.03 |
| 2 | 28 | 62.3 | 9.09 | 15.08 | 75.83 | 3.43 | 5.69 | 28.59 | 25.57 | 36.31 | 0.41 |
| 3 | 30 | 65.5 | 6.93 | 11.25 | 81.92 | 2.39 | 3.88 | 28.26 | 26.61 | 38.12 | 0.74 |
| 4 | 34 | 66.7 | 5.66 | 9.76 | 84.58 | 1.88 | 3.25 | 28.17 | 27.12 | 38.75 | 0.83 |
| 5 | 38 | 67.6 | 4.30 | 7.69 | 88.01 | 1.39 | 2.49 | 28.52 | 27.61 | 39.51 | 0.48 |
| 6 | 42 | 69.0 | 2.95 | 5.85 | 91.19 | 0.92 | 1.81 | 28.27 | 28.08 | 40.19 | 0.73 |
| 7 | 48 | 69.4 | 2.64 | 5.23 | 92.14 | 0.81 | 1.60 | 28.19 | 28.19 | 40.40 | 0.81 |
| 8 | 54 | 69.8 | 1.95 | 4.73 | 93.32 | 0.59 | 1.43 | 28.18 | 28.41 | 40.57 | 0.82 |
| 9 | 59 | 70.1 | 1.80 | 4.35 | 93.85 | 0.54 | 1.30 | 28.06 | 28.46 | 40.70 | 0.94 |
| 10 | 65 | 71.8 | 0.26 | 0.31 | 99.43 | 0.07 | 0.09 | 28.04 | 28.93 | 41.91 | 0.96 |

Table S2. Analysis of the Polymerization Progess.

Conditions: $[rac/meso -Pegl]_{o}/[Cat.]_{o}/[Ph_{2}CHOH]_{0} = 100/1/1$, $[rac/meso-Pegl]_{0} = 1$ M in 1 mL toluene, T = 80 °C. aConversions of monomers measured by 1H NMR spectra of the reaction solution. bEnantiomeric excess of the unreacted monomer measured by chiral HPLC.

3.2 Analysis of HPLC

For determining of the enantiomer ratio of the unreacted monomer during the polymerization, the recovered materials of the NMR samples were measured by chiral HPLC. The unreacted monomer was collected as the hexane/isopropanol = 90/10

soluble part. The unreacted monomer was determined using a UV (210 nm) detector (Column, Chiralpak AD; flow rate, 0.5 mL min⁻¹; eluent, hexane/isopropanol = 90/10; temperature, 40°C.) and the enantiomeric excess (*ee*) of the unreacted monomer was determined from the ratio of the peak areas (R.Time of L-Pegl: 20-23 min, R.Time of *meso*-Pegl: 23-25 min, R.Time of D-Pegl: 25-28 min).



Figure S2. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S1, Entry 2).





Figure S3. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S1, Entry 3).

Figure S4. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S1, Entry 4).



| 峰号 | 保留时间 | 面积 | 高度 | 面积% |
|----|--------|---------|--------|---------|
| 1 | 21.549 | 687269 | 30543 | 10.482 |
| 2 | 23.733 | 1379060 | 57178 | 21.032 |
| 3 | 26.625 | 4490631 | 159895 | 68.486 |
| 总计 | | 6556960 | 247616 | 100.000 |





Figure S6. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S1,Entry 5).



| DA Ch | 2 210nm | |
|-------|---------|----------|
| 峰号 | 保留时间 | 面积 |
| 1 | 30.206 | 57427799 |
| - | | |

Р

| 2 210nm | | | |
|---------|---|--|---|
| 保留时间 | 面积 | 高度 | 面积% |
| 30.206 | 57427799 | 1673996 | 29.427 |
| 33. 596 | 76266512 | 1860629 | 39.081 |
| 37.101 | 61457233 | 1550163 | 31.492 |
| | 195151544 | 5084788 | 100.000 |
| | 2 210nm 保留时间 30.206 33.596 37.101 | 2 210nm 田和 保留时间 面积 30.206 57427799 33.596 76266512 37.101 61457233 195151544 | 2 210nm 信度 保留时间 面积 高度 30.206 57427799 1673996 33.596 76266512 1860629 37.101 61457233 1550163 195151544 5084788 |



Figure S7. HPLC chromatogram of the unreacted *rac/meso*-Pegl (Table S2, Entry 1).

Figure S8. HPLC chromatogram of the unreacted *rac/meso*-Pegl (Table S2, Entry 2).



Figure S9. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S2, Entry 3).



Figure S10. HPLC chromatogram of the unreacted *rac/meso*-Pegl (Table S2, Entry



Figure S11. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S2, Entry







Figure S13. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S2, Entry



Figure S14. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S2, Entry



Figure S15. HPLC chromatogram of the unreacted *rac/meso*-Pegl (Table S2, Entry



Figure S16. HPLC chromatogram of the unreacted rac/meso-Pegl (Table S2, Entry

4 Microstructure analysis of Poly(Pegl)



Figure S17. ¹³C NMR spectra of Poly(PegI) at methylene carbon.

the [rrr] signals at 31.08 ppm were identified by heterotactic Poly(Pegl), (ii) the [mmm] signals at 30.94 ppm was identified by isotactic Poly(Pegl), (iii) the [mmm] signals at 30.94 ppm of Poly(Pegl) obtained by *SS*-1.



4.1 Microstructure analysis of Poly(Pegl)

Figure S18. ¹³C NMR spectra of Poly(PegI) at methylene carbon.

5¹H and ¹³C NMR spectra







Figure S19. ¹H NMR spectrum of (S)-L1.





Figure S20. ¹H NMR spectrum of SS-1.



Figure S22. ¹H NMR spectrum of 2-hydroxy-4-phenylbutanoic acid (i).



Figure S23. ¹H NMR spectrum of 2-hydroxy-4-phenylbutanoic acid (ii).