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# Synthetic Strategy for Preparing Chiral Double-semicrystalline Polyether Block Copolymers

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# 1) Abbreviations

18C6 - 18-crown-6

- AcOH acetic acid
- Ð dispersity
- DCM dichloromethane
- DSC differential scanning aalorimetry
- ECH epichlorohydrin
- HPLC high performance liquid chromatography
- GPC gel permeation chromatography

MeOH - methanol

 $M_{\rm n}$  – number average molecular weight

 $M_{\rm w}$  – weight average molecular weight

- NMR nuclear magnetic resonance
- PEO poly(ethylene oxide)
- PO propylene oxide
- PPO poly(propylene oxide)
- SAXS small angle x-ray scattering

S,S-(salen)Co<sup>II</sup>-(S,S)-(+)-N,N'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II)

TEA - triethylamine

THF – tetrahydrofuran

- WAXS wide angle x-ray scattering
- XRD x-ray diffraction

#### 2) Materials and Instrumentation

Propylene oxide (PO, TCI, >99%), and (*R*,*R*)- and (*S*,*S*)-(+)-*N*,*N*'-Bis(3,5-di-*tert*-butylsalicylidene)-1,2cyclohexanediaminocobalt(II) ((*R*,*R*)- and (*S*,*S*)-(salen)Co<sup>II</sup>, Sigma Aldrich) were used as received. Anhydrous THF and toluene were obtained from a JC Meyer solvent system. All other reagents were purchased from commercial sources and used as received unless specified. PEO (Sigma Aldrich,  $M_n =$ 10,000 and 20,000) macroinitiator was dried by azeotropic removal of water with toluene. Kinetically resolved propylene oxide monomers were degassed by several freeze-pump-thaw cycles and distilled from CaH<sub>2</sub>. Potassium naphthalenide was prepared from the addition of potassium metal (3 g, 77 mmol) to recrystallized naphthalene (10 g, 78 mmol) in anhydrous THF (250 mL, 0.3 M) under argon. The reaction, equipped with a glass-coated stirbar, was allowed to stir overnight at room temperature before use. All air and moisture sensitive reactions were carried out using standard Schlenk-line techniques.

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy were performed on a Bruker Avance DMX 500 MHz or Varian VNMRS 600 MHz spectrometer at room temperature and referenced to the residual non-deuterated or deuterated solvent shift of CDCl<sub>3</sub> (7.26 ppm and 77.16 ppm respectively). Gel permeation chromatography was carried out on a Waters chromatograph equipped with a Waters Alliance HPLC system pump (2690 separation module) and two Agilent columns (PLGEL 5µm, and MIXED-D 300 × 7.5 mm). Detection was provided by a Waters 2410 differential refractometer and CHCl<sub>3</sub> with 1% TEA was used as the mobile phase. Chromatograms were run at room temperature and calibrated to PEO standards. Optical rotation measurements were conducted on a Rudolph Research Analytical Autopol III polarimeter with a sodium lamp ( $\lambda = 489$  nm) at 23°C and are reported as  $[\alpha]^{T(^{\circ}C)} \lambda(c)$ .

#### 3) Synthetic Procedures



**Representative Procedure for Kinetic Resolution of PO Monomers**. (*R*) and (*S*)-PO were synthesized according to the literature procedure,<sup>1</sup> which was modified slightly to accommodate large scale reactions. (*S*)-PO. In a round bottom flask, glacial acetic acid (36.1 mmol, 2.07 mL) was added to a solution of *S*,*S*-(salen)Co<sup>II</sup> (3.44 mmol, 2.08 g, 0.002 equiv) in toluene (43 mL, 0.08 M) and allowed to stir at room temperature in air for 30 min. During this time the reaction changed from red-orange to brown. The active catalyst was then concentrated in vacuo, leaving a brown solid, which was re-dissolved in PO (1.72 mol, 120.5 mL) and cooled to 0 °C. The round bottom flask was equipped with a reflux condenser and distilled water (946 mmol, 17.0 mL, 0.55 equiv) was added to the reaction dropwise. Special precaution was taken to add the water very slowly to keep the exotherm under control. The reaction was allowed to warm to room temperature and was stirred overnight. The reaction conversion was checked by <sup>1</sup>H NMR and (*S*)-PO was isolated by distillation (45 g, 45%). [ $\alpha$ ]<sup>23</sup><sub>D</sub>-11.7°(neat); lit. [ $\alpha$ ]<sup>23</sup><sub>D</sub>-11.6°(neat).<sup>1</sup>

General Procedure for Synthesis of PPO-b-PEO-b-PPO Triblock Copolymers. All polymerizations were performed in custom thick-walled glass reactors fitted with ACE-threads. The reactors were equipped with glass coated stirbars, connected to a Schlenk line, and fitted with Teflon stoppers and custom burets containing anhydrous THF and PO. Reactors were assembled hot, cooled under vacuum, and charged with telechelic PEO and 18-crown-6 (18C6, 2 equiv per chain end) under argon. Anhydrous toluene was added to the reactor via syringe, stirred at 50 °C for 10-20 minutes, and removed under vacuum to help eliminate water by azeotrope. The reactor was then submitted to several cycles of evacuation followed by argon purge to remove oxygen from the system. THF was added to the reactor via buret until PEO was completely dissolved. Heating to 40 °C was necessary for all solids to go into solution. The potassium alkoxide macroinitiator was formed by titration of PEO with potassium naphthalenide solution (3 M in THF) until the green color persisted, indicating complete deprotonation with the potassium naphthalenide solution being added via cannula through a 6 mm puresep septum. PO monomer was added to the reactor all at once via buret at room temperature, which immediately quenched the green color, turning pink and then pale yellow. Polymerizations were carried out at room temperature for 7-11 days or until no appreciable change in molecular weight was observed by GPC. Reactions were quenched with HCl-treated methanol and solvent was removed under reduced pressure. The crude reaction mixture was then re-dissolved in DCM, extracted with 10% NaHSO<sub>4</sub> aqueous solution, washed with brine, dried with  $MgSO_4$  and concentrated in vacuo. The polymer was purified by a short silica plug using acetone as the eluent to remove a small amount of low molecular weight impurity and switching to 20% MeOH/DCM to elute the desired triblock copolymer.



Figure S1. Experimental setup for preparing PPO-*b*-PEO-*b*-PPO triblock copolymers.

 $M_{\rm w}$  of PPO was determined by <sup>1</sup>H NMR: the relative integration of the PEO –CH<sub>2</sub>s (4H), including the PPO –CH<sub>2</sub> (2H) and –CH (1H), minus 3H, to the PPO –CH<sub>3</sub> peak (set to 3 H). This gave the degree of polymerization of PPO which was multiplied by the molecular weight of PO to determine  $M_{\rm w}$  of PPO.

$$\frac{Mw (PEO)}{Mw (EO)} \times \frac{4}{\left[\int (PEO CH2s + PPO CH + PPO CH2 - 3 H)\right]} \times Mw PO = Mw PPO$$



**Figure S2.** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 500 MHz) of *it-(R)*-PPO-*b*-PEO-*b-it-(R)*-PPO, synthesized by polymerization of kinetically resolved PO from PEO macroinitiator ( $M_n = 20,000$ ).

Dispersities ( $D = M_w/M_n$ ) were determined by gel permeation chromatography calibrated with PEO standards and [mm] (%) was determined by the mm triad content in the <sup>13</sup>C NMR.<sup>3</sup>

*it-(S)-PPO-b-PEO-b-it-(S)-PPO*. *M*<sub>n</sub> = 28,600 g/mol (30 wt% PPO, 70 wt% PEO); Đ = 1.26; [*mm*] = 90%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 3.50 (s, 12 H, PEO –*CH*<sub>2</sub>), 3.42-3.38 (m, 2 H, PPO –*CH*<sub>2</sub>), 3.28-3.27 (m, 1 H, PPO –*CH*), 0.99 (d, *J* = 4.8 Hz, 3 H, PPO –*CH*<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 75.20 (PPO –*C*H, *mm*), 73.12 (PPO –*C*H<sub>2</sub>, *m*), 70.30 (PEO –*C*H<sub>2</sub>), 17.19 (PPO –*C*H<sub>3</sub>).

*at*-**PPO**-*b*-*P*EO-*b*-*at*-**PPO**. *M*<sub>n</sub> = 28,600 g/mol (30 wt% PPO, 70 wt% PEO); Đ = 1.27; [*mm*] = 25%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz) δ 3.63 (s, 12 H, PEO –*CH*<sub>2</sub>), 3.58-3.48 (m, 2 H, PPO –*CH*<sub>2</sub>), 3.41-3.37 (m, 1 H, PPO –*CH*), 1.14-1.12 (m, 3 H, PPO –*CH*<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz) δ 75.42 (PPO –*C*H, *mm*), 75.26 (PPO –*C*H, *mr* + *rm*), 75.23 (PPO –*C*H, *mr* + *rm*), 75.03 (PPO –*C*H, *rr*), 73.27 (PPO –*C*H<sub>2</sub>, *m*), 72.83 (PPO –*C*H<sub>2</sub>, *rrm* or *mrr*), 70.49 (PEO –*C*H<sub>2</sub>), 17.27 (PPO –*C*H<sub>3</sub>).

*it-(R)*-**PPO**-*b*-**PEO**-*b*-*it-(R)*-**PPO**.  $M_n = 28,800 \text{ g/mol} (31 \text{ wt\% PPO}, 69 \text{ wt\% PEO});$  D = 1.36; [mm] = 93%

*it-(S)-PPO-b-PEO-b- it-(S)-PPO.*  $M_n = 14,000 \text{ g/mol} (29 \text{ wt% PPO}, 71 \text{ wt% PEO}); \text{ } = 1.08; [mm] = 90\%$ 

*it-(R)-PPO-b-PEO-b-it-(R)-PPO.*  $M_n = 22,000 \text{ g/mol} (55 \text{ wt\% PPO}, 45 \text{ wt\% PEO}); \text{ } = 1.17; \text{ } [mm] = 90\%$ 



**Figure S3.** Representative GPC traces showing a) PEO macroinititor ( $M_n = 10,000$ ) (—) and *it-(S)*-PPO*b*-PEO-*b-it-(S)*-PPO ( $M_n = 14,000$ ) after polymerization of (*S*)-PO (---) and b) PEO macroinititor ( $M_n = 20,000$ ) (—) and *it-(R)*-PPO-*b*-PEO-*b-it-(R)*-PPO ( $M_n = 28,800$ ) after polymerization of (*R*)-PO (---).



**Figure S4.** MALDI-TOF of PEO macroinititor ( $M_n = 20,000$ ).

**Synthesis of** *it-(R)*-**PPO Homopolymer**. *it-(R)*-PPO was synthesized by trialkylaluminum-activated copolymerization of (*R*)-PO with a small incorporation of epichlorohydrin (ECH, 5 mol%) using trioctylammonium bromide as the initiator, as reported in the literature.<sup>4, 5</sup>

*it-(R)-PPO.*  $M_n$  = 3,300 g/mol; Đ = 1.20; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz)  $\delta$  3.59-3.49 (m, 2 H, -*CH*<sub>2</sub>), 3.43-3.39 (m, 1H, -*CH*), 1.13 (d, *J* = 6.1 Hz, 3 H, -*CH*<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz)  $\delta$  75.70 (-*C*H, *mm*), 73.58 (-*C*H<sub>2</sub>, *m*), 17.60 (-*C*H<sub>3</sub>). *it-(R)-PPO-co-ECH* is referred to as a homopolymer due to the minimal incorporation of ECH. This small incorporation should not affect the overall polymer properties.

## 4) Optical Microscopy

Polarized optical microscopy was employed to observe the spherulitic structures at room temperature after the samples were hot-pressed and annealed for 5 min at 100 °C. The Nikon (Japan) optical microscope was equipped with a Nikon (CoolPix P5000) camera and the wave vector direction of the polarizer was kept perpendicular to the analyzer.

### 5) Wide Angle X-ray Scattering (WAXS)

WAXS experiments were carried out on one of two instruments. The first was a house-made x-ray generator with a rotating Cu target (data presented in Figure 4). The wavelength of the beam was 0.154 nm and a 2D position sensitive detector was placed perpendicular to the beam direction. The sample to detector distance was 245.5 mm, which afforded a scattering wavevector (q) ranging from 4 to 20 nm<sup>-1</sup>. The calibration was based on Si powder with a featured peak position at 28.443°. The second instrument was a Rigaku Smartlab Diffractometer operating at a wavelength of 0.154 nm (data presented in Figure 7).

## 6) Differential Scanning Calorimetry (DSC)

Thermograms were recorded on a TA Instruments Q-2000 DSC using Tzero technique. The rate of heating and cooling was 10 °C/min over a temperature range of -20 to 100 °C. The melting temperatures  $(T_m)$  were reported as the endothermic peak maximums.

### 7) Small Angle X-ray Scattering (SAXS)

SAXS experiments were carried out using the Advanced Light Source synchrotron at beamline 7.3.3 at Lawrence Berkeley National Laboratory. The x-ray wavelength of the beam was 0.154 nm. The thermal

treatment for the sample began with heating to 130 °C past the order-disorder transition. Data collection began upon cooling to 40 °C in increments of 10 or 20 °C, and then heating back to 100 °C, again collecting data upon increasing temperature in increments of 10 or 20 °C. Samples were annealed at temperature for 10 minutes, and observed until the raw 2D scattering patterns appeared to remain static. Using the Nika program implemented in Igor Pro, the 2D scattering patterns were azimuthally integrated into intensity (I) versus q(nm<sup>-1</sup>).<sup>6</sup>



**Figure S5.** Small angle x-ray scattering of a) *at*-PPO-*b*-PEO-*b*-*at*-PPO and b) *it*-(*R*)-PPO-*b*-PEO-*b*-*it*-(*R*)-PPO. Arrows denote expected reflections for the lamellar morphology based on  $q^*$ .



**Figure S6.** Small angle x-ray scattering of a) *at*-PPO-*b*-PEO-*b*-*at*-PPO at 60 °C and b) magnification of the 4<sup>th</sup> ordered peak. c) Small angle x-ray scattering of c) *it*-(*R*)-PPO-*b*-PEO-*b*-*it*-(*R*)-PPO at 60 °C and d) magnification of the 4<sup>th</sup> ordered peak.



**Figure S7.** Comparison of change in domain spacing with temperature of *at*-PPO-*b*-PEO-*b*-*at*-PPO and *it*-(*R*)-PPO-*b*-PEO-*b*-*it*-(*R*)-PPO. The domain spacings at intermediate temperatures 50–99 °C where the self-assembly of PPO-*b*-PEO-*b*-PPO was not disrupted by crystallization are fit to the strongly segregation description of domain spacing for the lamellar mesophase.<sup>7</sup>

#### 8) Hydrogel Formation and Characterization

Thin films (1 mm) of *at*-PPO-*b*-PEO-*b*-*at*-PPO and *it*-(*S*)-PPO-*b*-PEO-*b*-*it*-(*S*)-PPO were hot-pressed at 70 °C and cooled slowly to room temperature. 0.106 g of pressed *it*-(*S*)-PPO-*b*-PEO-*b*-*it*-(*S*)-PPO was placed in 0.520 g of distilled water. 0.150 g of pressed *at*-PPO-*b*-PEO-*b*-*at*-PPO was placed in 0.653 g of distilled water. Both samples were allowed to equilibrate for 48 hours in water resulting in hydrogels at 16.9 and 18.7 polymer wt%, respectively. The samples were characterized by laboratory XRD using a Rigaku Smartlab diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.544$  Å) from a scattering angle of 2.75 to 40°. The one-dimensional data was converted to scattering vector q(nm<sup>-1</sup>).

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