Supporting Information

Highly Crosslinked Polycyclooctyl-Salen Cobalt (III) for the Hydrolytic Kinetic Resolution of Terminal Epoxides

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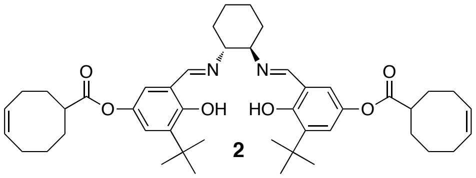
General. Gel-permeation chromatography (GPC) analyses were carried out using a Shimadzu pump coupled to a Shimadzu UV detector with tetrahydrofuran (THF) as the eluant and a flow rate of 1 mL/min on American Polymer Standards column set (100, 1000, 100 000 Å, linear mixed bed). All GPCs were calibrated using poly(styrene) standards and carried out at 25 °C. M_w, M_n, and PDI represent the weight-average molecular weight, number-average molecular weight, and polydispersity index, respectively. NMR spectra were recorded on a Bruker AV-400 (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz) spectrometer. Chemical shifts are reported in ppm and referenced to the corresponding residual nuclei in deuterated solvents. MALDI-TOF data were collected on a Bruker OmniFLEX spectrometer using anthracenediol as a matrix. Chiral gas chromatography data used to determine enantiomeric excesses were obtained on a Shimadzu 10A instrument with a flame ionization detector using a β-Dex 120 column purchased from Supelco using helium as the carrier gas. Preparative size-exclusion chromatography was performed with Toyo-pearl HW-40 resin packed into a 50 mm ID column to a length of 460 mm using 1:1 HPLC grade chloroform and methanol with 0.01 % triethylamine as the mobile phase. Straight phase column chromatography was performed with silica gel 60 Å (230-400 mesh) from Sorbent Technologies. All chlorinated solvents were distilled over CaH_2 and degassed by 3 freeze-pump-thaw cycles. Other reagents were used as received from suppliers. Unless otherwise noted, all reactions were conducted under Schlenk conditions in a nitrogen atmosphere. Grubb's 3rd generation initiator was synthesized according to the literature.[1] Compound **3** was synthesized according to the literature.[2]

Synthesis of crosslinking agent 2



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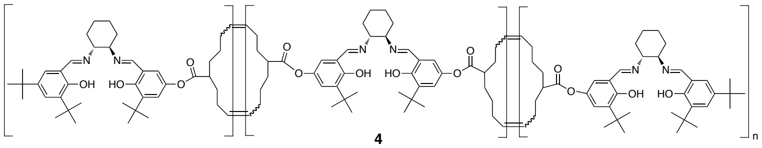
The precursor aldehyde **11** to the crosslinking agent was synthesized according to the literature.[2] 645 mg (1.95 mmol) of **11**, 111 mg (0.977mmol) of (1R,2R)-(-)-1,2-diaminocyclohexane, and 100 mg of 4Å molecular sieves were charged into an oven dried schlenk flask. Through a septa, a solution of 3 mL of anhydrous methanol and 3 mL of dichloromethane was injected. The mixture was stirred at room temperature for 16 hours. Then, the reaction mixture was poured into 50 mL of dichloromethane and washed 3x with 50 mL water and once with 50 mL of brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to afford a dark yellow solid. The solid was purified by silica gel column chromatography using a gradient of 99% hexanes, 1% ethyl acetate, 0.1% triethylamine - 95% hexanes, 5% ethyl acetate, and 0.1% triethylamine. This resulted in the isolation of 645 mg (0.89 mmol; 91% yield) of **2** as a solid yellow foam. Anal. Calcd for $C_{46}H_{62}N_2O_6$: C, 74.76; H, 8.46; N, 3.79. Found: C, 74.85; H, 8.40; N, 3.75. ^1H NMR ($CDCl_3$): $\delta = 1.38$ (s, 18H, CMe_3), 1.46-2.23 (m, 24H, alkyl), 2.42 (m, 2H, alkyl), 2.55 (m, 2H, $CHCO_2$), 3.34 (m, 2H, $NC\mathit{H}CH_2$), 5.71 (m, 4H, CH=C), 6.72 (d, *J* =2.42 Hz, 2H, PhH), 6.92 (dd, *J* = 1.73 Hz, 1.04 Hz, 2H, PhH), 8.22 (s, 2H, PhH), 13.73 (s, 2H, CH=N). ^{13}C NMR ($CDCl_3$): δ = 24.2, 24.4, 25.9, 27.8, 29.1, 29.4, 29.5, 31.4, 31.6, 33.0, 34.8, 43.3, 72.2, 118.1, 121.3, 122.8, 129.5, 130.1, 138.5, 141.8, 157.9, 164.8, 176.5

Synthesis of the copolymers



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Copolymerization procedure. The synthesis of the 5:1 copolymer is described as an example. In an oven dried Schlenk flask was charged 160.5 mg (0.25 mmol) of **3** and 36.9 mg (0.05 mmol) of crosslinking agent **2**. Grubbs' 3rd generation initiator (8.55 mg, 0.01 mmol, 3% catalyst loading) was dissolved in 3 mL of 1,2-dichloroethane and injected through a septum into the Schlenk flask. The mixture was heated at 50°C for 45 minutes, after which time 100 µL of ethyl vinyl ether was added to terminate the polymerization. To crudely purify the resultant copolymers it was passed through a silica column using a gradient of 99% hexanes, 1% ethyl acetate and 0.01 % triethylamine to 75% hexanes and 25% ethyl acetate. Then the column was flushed with 50% hexanes, 40% ethyl acetate, and 10% acetone to remove the high molecular weight copolymer. The copolymers were separated by molecular weight using preparative size-exclusion chromatography. Fractions were collected based on similar GPC retention times as well as MALDI-TOF data. 33 mg of tetramers-decamers and 18 mg of high molecular weight material were recovered.

3:1 low MW copolymer. ^{1}H NMR ($CDCl_3$): δ = 1.24 (s, 9H, CMe_3), 1.38 (s, 14H, CMe_3), 1.40 (s, 10H, CMe_3), 1.38-2.05 (s, 20H, alkyl), 2.53 (m, 1H, $CHCO_2$), 3.31 (s, 2H, NC*H*CH_2), 5.42 (m, 3H, CH=C), 6.74 (s, 1H, PhH), 6.89 (s, 1H, PhH), 6.98 (s, 1H, PhH), 7.31 (s, 1H, PhH), 8.24 (s, 1H, CH=N), 8.31 (s, 1H, CH=N), 13.61 (s, 1H, OH), 13.87 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ = 24.3, 29.1, 29.5, 29.7, 31.4, 31.9, 33.1, 33.2, 34.0, 34.9, 35.0, 72.2, 72.5, 117.8, 118.2, 121.3, 122.7, 126.0, 126.9, 136.3, 138.5, 140.0, 141.6, 157.9, 158.1, 164.7, 165.9, 175.0. (MS) MALDI-TOF *m/z:* 2594, 2690, 2787, 3237, 3333, 3429, 3504, 3504, 3976, 4072, 4168, 4623, 4717, 4816, 4910.

3:1 high MW copolymer. ^{1}H NMR ($CDCl_3$): δ = 1.24 (s, 9H, CMe_3), 1.38 (s, 17H, CMe_3), 1.40 (s, 12H, CMe_3), 1.56-2.24 (m, 25H, alkyl), 2.53 (s, 2H,$CHCO_2$), 3.31 (m, 2H, NC*H*CH_2), 5.41 (m, 3H, CH=C), 6.75 (s, 1H, PhH), 6.89 (s, 1H, PhH), 7.00 (s, 1H, PhH), 7.31 (s, 1H, PhH), 8.23 (s, 1H, CH=N), 8.30 (s, 1H, CH=N), 13.61 (s, 1H, OH), 13.87 (s, 1H, OH). ^{13}C NMR ($CDCl_3$) δ = 24.3, 29.2, 29.5, 29.7, 31.4, 32.5, 33.1, 33.2, 34.0, 34,9, 34.0, 72.1, 72.5, 117.8, 118.2, 121.3, 122.7, 126.0, 126.9, 130.1, 136.4, 138.5, 140.0, 141.6, 157.9, 158.1, 164.7, 165.9, 175.0

5:1 low MW copolymer. ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 9H, CMe_3), 1.38 (s, 12H, CMe_3), 1.40 (s, 15H, CMe_3), 1.56-1.04 (m, 21H, alkyl), 2.53 (m, 1H, $CHCO_2$), 3.31 (m, 2H, NC*H*CH_2), 5.41(m, 3H, CH=C), 6.74 (s, 1H, PhH), 6.88 (s, 1H, PhH), 6.98 (s, 1H, PhH), 7.31 (s, 1H, PhH), 8.23 (s, 1H, CH=N), 8.30 (s, 1H, CH=N), 13.61 (s, 1H, OH), 13.87 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ = 24.2, 29.1, 29.5, 29.7, 32.0, 33.1, 33.2, 34.0, 34.9, 35.0, 72.2, 72.5, 117.8, 118.2, 121.3, 122.7, 126.0, 126.9, 130.1, 136.4, 138.5, 140.0, 141.6, 157.9, 158.1, 164.7, 165.9, 175.0. (MS) MALDI-TOF *m/z:* 2572, 2690, 2788, 2337, 3333, 4329, 3882, 3979, 4072, 4171, 4619, 4715, 4821.

5:1 high MW copolymer. ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 9H, CMe_3), 1.37 (s, 13H, CMe_3), 1.40 (s, 15H, CMe_3), 1.69-2.06 (m, 21H, alkyl), 2.53 (m, 1H, $CHCO_2$), 3.3 (s, 2H, $NC\mathit{H}CH_2$), 5.41(m, 3H, CH=C), 6.74 (s, 1H, PhH), 6.88 (s, 1H, PhH), 6.98 (s, 1H, PhH), 7.30 (s, 1H, PhH), 8.23 (s, 1H, CH=N), 8.30 (s, 1H, CH=N), 13.59 (s, 1H, OH), 13.86 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ = 22.7, 24.2, 24.3, 29.2, 29.5, 29.7, 30.5, 31.4, 31.9, 32.5, 33.1, 33.2, 33.7, 34.0, 34.9, 35.0, 72.1, 72.5, 117.8, 118.2, 121.3, 122.7, 126.0, 126.9, 129.6, 136.4, 138.5, 140.0, 141.6, 157.9, 158.1, 164.7, 165.9, 174.9

8:1 low MW copolymer. ^{1}H NMR ($CDCl_3$): δ = 1.23 (s, 9H, CMe_3) 1.37 (s, 13H, CMe_3) 1.39 (s, 10H, CMe_3), 1.53-2.04 (m, 15H, alkyl), 2.52 (m, 1H, $CHCO_2$), 3.29 (s, 2H, $NC\mathit{H}CH_2$) 5.41 (m, 3H, C=CH), 6.72 (s, 1H, PhH), 6.88 (s, 1H, PhH), 6.98 (m, PhH), 7.30 (m, 1H, PhH), 8.22 (s, 1H, CH=N), 8.30 (s, 1H, CH=N), 13.60 (s, 1H, OH), 13.87 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ = 24.3, 27.4, 29.2, 29.5, 29.7, 30.4, 31.4, 32.5, 33.1, 33.2, 34.0, 34.9, 35.0, 46.2, 72.1, 72.5, 117.8, 118.2, 121.3, 122.7, 126.0, 126.9, 130.1, 136.4, 138.5, 140.0, 141.6, 157.9, 158.1, 164.7, 165.9, 175.0. (MS) MALDI-TOF *m/z:* 2527, 2690, 3237, 3333, 3429, 3664, 3880, 3976, 4072, 4171, 4619.

8:1 high MW copolymer. ^{1}H NMR ($CDCl_3$): δ 1.22 (s, 9H, CMe_3), 1.37 (s, 14H, CMe_3), 1.39 (s, 11H, CMe_3), 1.62-2.04 (m, 15H, alkyl), 2.60 (m, 2H, $CHCO_2$), 3.29 (m, 3H, $NC\mathit{H}CH_2$), 5.41 (m, 3H, C=CH), 6.73 (s, br, 1H, PhH), 6.88 (s, br, 1H, PhH), 6.97 (m, 1H, PhH), 7.30 (m, 1H, PhH), 8.22 (s, 1H, CH=N), 8.29 (s, 1H, CH=N), 13.60 (s, 1H, OH), 13.86 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ = 24.3, 29.2, 29.5, 30.5, 31.4, 32.5, 33.1, 34.0, 34.9, 35.0, 72.1, 72.5, 117.8, 118.2, 121.3, 122.7, 126.0, 126.9, 136.4, 138.5, 140.0, 141.6, 157.9, 158.1, 164.7, 165.9, 175.0

Copolymer metallation

The copolymers were metallated in a glovebox to exclude oxygen during the reaction. 33 mg of the tetramers-decamers were dissolved in 3 mL of methylene chloride. Cobalt (II) acetate tetrahydrate 1.2 eq was dissolved in 2 mL methanol and added dropwise into the copolymer solution. After several seconds, the mixture turned to a deep red color and was stirred for 16 hours. The bulk of the methylene chloride was removed under vacuum. Then, 5 mL of anhydrous methanol was added to precipitate the rest of the metallated ligand. The solution was centrifuged (3000 G) and the methanol was decanted off. Five mL of fresh methanol was added and the tube was shaken to re-disperse the solids and centrifuged and decanted again. The solid residue was dried under high vacuum for 6 hours. Cobalt content was determined by ICP-MS and determined to be 7.28%.

Hydrolytic kinetic resolutions

HKRs were conducted by dissolving 1 mg of catalyst in 1 mL of methylene chloride and 1.5 eq of acetic acid and stirred for 30 minutes. Volatiles were removed by rotary evaporation and excess acetic acid was removed by azeotrope distillation with toluene. The activated catalyst, now brown in color, was placed under high vacuum for 2 hours. The epoxides were added to the catalyst with 170 μL of chlorobenzene as an internal standard. The reaction was initiated by the addition of 0.6 eq. of water. Kinetic studies were undertaken by removal of 3 μL aliquots of the reaction mixture at various time intervals and diluted into 1 mL of diethyl ether. The solution was passed through a silica plug to remove catalyst and concentrated down to 300 μL for GC analysis.

References

1 Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* 2002, **41**, 4035-4037.

2 Zheng, X.; Jones, C. W.; Weck, M. *J. Am. Chem. Soc.* 2007, **129**, 1105-1112.