Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Ring-Opening Copolymerization of Epoxides and Anhydrides Using Manganese(III) Asymmetrical Schiff base Complexes as Catalysts

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1. Experimental

1.1. Reagents and methods

Tetrahydrofuran (HPLC grade) was purchased from Fisher Scientific and purified over solvent columns. Other solvents were used as received from Sigma Aldrich and stored over 3 Å activated molecular sieves. Cyclohexene oxide (CHO) or styrene oxide (SO), purchased from Sigma Aldrich, was dried over CaH_2, distilled and stored under dried N_2 prior to use. Maleic anhydride (MA) purchased from Alfa Aesar, was dried overnight under vacuum, sublimed twice under fried N_2 prior to use. Phthalic anhydride (PA) was recrystallized from $CHCl_3$ before use. 4-(Dimethylamino)pyridine (DMAP), triphenylphosphine (Ph_3P) and bis(triphenylphosphine)iminium chloride (PPN^+Cl^-) were purchased from Fluka and used as received.

All manipulations of air and water sensitive compounds were carried out under dry N_2 using the standard vacuum line and Schlenk techniques. Elemental analyses were performed on a Perkin-Elmer 240 °C elemental analyzer. Infrared spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region 4000-400 cm^{-1} using KBr pellets. ^1H NMR spectra were recorded on a JEOL EX 400 spectrometer in $CDCl_3$ or DMSO-d_6 at room temperature. Gel permeation chromatography (GPC) analyses of the molecular weights (M_n and M_w) and molecular weight distribution (PDI = M_w/M_n) of the polymers were performed on a Waters 150C instrument in THF using polystyrene as standard. MALDI-TOF-MS analysis was performed on a Voyager DE-STR from Applied Biosystems equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. Mass spectra of 1000 shots were accumulated. The polymer samples were dissolved in HPLC THF at a concentration of 1

mg/mL. The citionization agent used was KCF_3COO (Alfa Aesar, > 99%) dissolved in THF HPLC grade at a concentration of 5 mg/mL. The matrix used was DCTB (Alfa Aesar, DCTB = *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) and was dissolved in THF HPLC grade at a concentration of 40 mg/mL. Solution of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded from the crude products. In-house developed software was used to characterize the polymers in detail and allowed to elucidate the individual chain structures, the copolymer's chemical composition and topology.

1.2. Complex synthesis

1.2.1. Synthesis of the half-unit Schiff-base precursor ***HL⁰***

*(**HL⁰** = (Z)-4-((2-aminophenylimino)(phenyl)methyl)-3-methyl-1H-pyrazol-5(4H)-one)*

To a solution of 1-phenyl-3-methyl-4-benzoyl-2-pyrazolin-5-one (5.6 g, 20 mmol) in absolute EtOH (35 mL), a solution of 1, 2-diaminobenzene (2.2 g, 20 mmol) in absolute EtOH (5 mL) was added slowly, and the resulted mixture was refluxed for 6 h. After cooling to room temperature, the insoluble precipitate was filtered off, and recrystallized with absolute EtOH to give an orange microcrystalline product. Yield: 5.2 g, 71%. Calc. for $C_{23}H_{20}N_4O$: C, 74.98; H, 5.47; N, 15.21%; Found: C, 74.89; H, 5.53; N, 15.18%; IR (KBr, cm^{-1}): 3405 (w), 3334 (s), 3224 (s), 3060 (w), 2922 (w), 1631 (vs), 1588 (vs), 1567 (s), 1527 (w), 1498 (s), 1471 (m), 1395 (s), 1315 (w), 1284 (w), 1207 (m), 1143 (w), 1074 (w), 1052 (w), 1007 (w), 962 (w), 921 (w), 836 (w), 777 (w), 752 (m), 695 (m), 654 (w), 624 (w), 585 (w), 507 (w), 467 (w) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, ppm): 12.11 (s, 1H, -OH), 8.02 (d, 2H, -Ph), 7.50 (t, 2H, -Ph), 7.41 (m, 5H, -Ph), 7.15 (t, 1H, -Ph), 6.84 (t, 1H, -Ph), 6.66 (d, 2H,

-Ph), 6.28 (t, 1H, -Ph), 5.44 (s, 2H, -NH_2), 1.42 (s, 3H, -CH_3). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 166.0, 165.9, 147.9, 144.8, 139.6, 131.9, 130.6, 129.3, 129.2, 129.1, 128.8, 128.7, 128.6, 128.5, 128.3, 124.3, 122.5, 118.5, 118.4, 116.2, 115.9, 100.9, 16.0.

1.2.2 Synthesis of series of asymmetrical bis-Schiff-base ligand ***H_2L^n*** *(n = 1-4)*

For **H_2L^1**: To a solution of **HL^0** (0.737 g, 2 mmol) in absolute $CHCl_3$ (10 mL), a solution of salicylaldehyde (210 μL, 2 mmol) in absolute EtOH (5 mL) was added slowly, and the resultant mixture was refluxed for 5 h. After cooling to room temperature, the insoluble precipitate was filtered off, and washed with cold absolute EtOH (10 mL) three times to give the bright yellow microcrystalline product of **H_2L^1**. Yield: 0.71 g, 75%. Calc. for $C_{30}H_{24}N_4O_2$: C, 76.25; H, 5.12; N, 11.86%; found: C, 76.21; H, 5.09; N, 11.79%; FT-IR (KBr, cm^{-1}): 3404 (b), 3057 (w), 2924 (w), 1616 (vs), 1591 (s), 1539 (m), 1491 (s), 1466 (m), 1385 (s), 1366 (m), 1281 (w), 1213 (w), 1180 (w), 1148 (w), 1119 (w), 1069 (w), 1051 (w), 1024 (w), 1005 (w), 976 (w), 907 (w), 864 (w), 820 (w), 779 (w), 752 (m), 694 (w), 654 (w), 588 (w), 548 (w), 511 (w), 442 (w). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.95 (s, 1H, -OH), 12.07 (s, 1H, -OH), 8.95 (s, 1H, -CH=N), 8.02 (d, 2H, -Ph), 7.94 (d, 1H, -Ph), 7.45 (m, 9H, -Ph), 7.24 (t, 1H, -Ph), 7.17 (t, 1H, -Ph), 7.00 (m, 3H, -Ph), 6.82 (d, 1H, -Ph), 1.45 (s, 3H, -CH_3). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 164.7, 163.6, 161.3, 157.2, 149.5, 146.4, 146.1, 137.7, 133.5, 132.9, 132.5, 131.4, 130.6, 129.8, 129.6, 129.2, 128.9, 128.6, 128.5, 128.4, 123.5, 122.6, 122.3, 121.6, 120.5, 120.3, 118.5, 116.1, 107.8, 16.0.

For **H_2L^2:** The bright yellow asymmetrical bis-Schiff-base ligand **H_2L^2** solid product was prepared in the same way as **H_2L^1** except that 5-bromo-salicylaldehyde (0.40 g, 2 mmol) was used instead of salicylaldehyde (210 μL, 2 mmol). Yield: 0.87 g , 79%. Calc. for

$C_{30}H_{23}BrN_4O_2$: C, 65.34; H, 4.20; N, 10.16%; found: C, 65.31, H, 4.31, N, 10.13%; FT-IR (KBr, cm^{-1}): 3404 (b), 3060 (w), 2928 (w), 1614 (vs), 1587 (s), 1572 (m), 1531 (m), 1500 (m), 1466 (m), 1387 (s), 1368 (m), 1296 (w), 1277 (w), 1238 (w), 1211 (w), 1171 (w), 1146 (w), 1099 (w), 1070 (w), 1049 (w), 1028 (w), 1001 (w), 910 (w), 862 (w), 827 (w), 802 (w), 777 (m), 754 (s), 704 (w), 691 (w), 652 (w), 625 (w), 586 (w), 554 (w), 507 (w), 476 (w), 444 (w). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 13.18 (s, 1H, -OH), 11.58 (s, 1H, -OH), 8.95 (s, 1H, -CH=N), 8.35 (s, 1H, -Ph), 8.09 (d, 2H, -Ph), 7.52 (m, 6H, -Ph), 7.41 (m, 3H, -Ph), 7.18 (m, 2H, -Ph), 6.98 (t, 2H, -Ph), 6.57 (d, 1H, -Ph), 1.44 (s, 3H, $-CH_3$). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 164.9, 163.8, 159.0, 156.1, 149.3, 146.9, 146.7, 136.9, 135.4, 134.1, 132.4, 131.3, 129.8, 129.4, 129.2, 128.9, 128.6, 128.5, 128.3, 126.4, 123.5, 122.6, 122.3, 121.7, 120.5, 120.2, 118.3, 115.7, 107.7, 16.3.

For **H_2L^3:** The orange asymmetrical bis-Schiff-base ligand **H_2L^3** solid product was prepared in the same way as **H_2L^1** except that *o*-vanillin (0.304 g, 2 mmol) was used instead of salicylaldehyde (210 μL, 2 mmol). Yield: 0.68 g, 68%. Calc. for $C_{31}H_{26}N_4O_3$: C, 74.09; H, 5.21; N, 11.15%; found: C, 74.01; H, 5.29; N, 11.09%; FT-IR (KBr, cm^{-1}): 3399 (b), 3061 (w), 2918 (w), 1612 (vs), 1574 (s), 1539 (m), 1487 (s), 1456 (m), 1377 (s), 1365 (m), 1302 (w), 1277 (w), 1257 (s), 1209 (w), 1188 (w), 1141 (w), 1118 (w), 1101 (w), 1072 (w), 1051 (w), 1008 (w), 972 (w), 912 (w), 868 (w), 833 (w), 777 (w), 758 (m), 732 (w), 698 (w), 654 (w), 615 (w), 590 (w), 555 (w), 511 (w), 484 (w), 422 (w). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.89 (s, 1H, -OH), 12.10 (s, 1H, -OH), 8.95 (s, 1H, -CH=N), 8.02 (d, 2H, -Ph), 7.46 (m, 9H, -Ph), 7.25 (t, 1H, -Ph), 7.17 (t, 2H, -Ph), 7.05 (t, 1H, -Ph), 6.94 (t, 1H, -Ph), 6.86 (d, 1H, -Ph), 3.80 (s, 3H, -OMe), 1.46 (s, 3H, $-CH_3$). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 165.6, 163.8,

163.3, 148.4, 148.0, 143.8, 139.3, 132.0, 131.5, 131.0, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.3, 127.3, 126.3, 124.5, 123.8, 120.6, 119.5, 119.3, 118.7, 118.6, 118.5, 116.2, 101.3, 56.3, 16.1.

For **H_2L^4:** The bright yellow asymmetrical bis-Schiff-base ligand **H_2L^3** solid product was prepared in the same way as **H_2L^1** except that 5-bromo-2-hydroxy-3-methoxy-benzaldehyde (0.46 g, 2 mmol) was used instead of salicylaldehyde (210 μL, 2 mmol). Yield: 0.83 g, 71%. Calc. for $C_{31}H_{25}BrN_4O_3$: C, 64.03; H, 4.33; N, 9.64%; found: C, 64.01; H, 4.40; N, 9.59%; FT-IR (KBr, cm^{-1}): 3426 (b), 3078 (w), 2925 (w), 1614 (vs), 1590 (s), 1570 (m), 1530 (m), 1501 (s), 1464 (m), 1381 (s), 1367 (m), 1329 (w), 1271 (w), 1252 (m), 1194 (w), 1144 (w), 1119 (w), 1067 (w), 1049 (w), 1024 (w), 1005 (w), 974 (w), 905 (w), 866 (w), 837 (w), 779 (s), 754 (m), 708 (w), 691 (w), 652 (w), 584 (w), 565 (w), 507 (w), 447 (w), 417 (w). ^{1}H NMR (400 MHz, DMSO-d_6, ppm): 13.07 (s, 1H, -OH), 11.44 (s, 1H, -OH), 8.95 (s, 1H, -CH=N), 8.07 (m, 2H, -Ph), 7.88 (d, 1H, -Ph), 7.53 (m, 4H, -Ph), 7.40 (m, 4H, -Ph), 7.28 (d, 1H, -Ph), 7.19 (m, 2H, -Ph), 7.00 (t, 1H, -Ph), 6.68 (d, 1H, -Ph), 3.87 (s, 3H, -OMe), 1.46 (s, 3H, $-CH_3$). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 164.6, 163.8, 163.5, 159.0, 149.4, 148.1, 146.9, 146.7, 132.9, 132.0, 131.1, 131.0, 129.4, 129.2, 129.1, 128.9, 128.6, 128.3, 127.3, 126.4, 124.5, 121.7, 121.3, 120.6, 120.2, 120.2, 118.6, 118.5, 101.3, 56.3, 16.2.

*1.2.3. Synthesis of series of Mn(III) complexes [Mn(L^n)(Cl)] (n =1-4, **1-4**)*

For [Mn(L^1)(Cl)] (**1**): solid **H_2L^1** (0.142 g, 0.3 mmol) and anhydrous $Mn(OAc)_2$ (74 mg, 0.3 mmol) were added to a flame dried Schlenk flask charged with a Teflon-coated stir bar. Under an atmosphere of dry N_2, absolute CH_2Cl_2 (6 mL) and EtOH (6 mL) were injected and the resultant mixture was stirred at ambient temperature for 8 h. The stopper of the flask was

removed, solid anhydrous LiCl (76.3 mg, 1.8 mmol) was added to the solution and the resultant reddish brown solution was stirred at room temperature for 24 h while exposed to dry air. The final solution was filtered and the clear filtrate was left to stand at room temperature for several days to give the dark brown polycrystalline solid product of **1**. Yield: 118 mg , 70%. Calc. for $C_{30}H_{22}MnClN_4O_2$: C, 64.18; H, 3.92; N, 9.98%; found: C, 64.11; H, 4.03; N, 9.92%; FT-IR (KBr, cm^{-1}): 3024 (w), 2926 (w), 1627 (s), 1557 (s), 1530 (s), 1466 (vs), 1441 (s), 1377 (s), 1306 (m), 1250 (w), 1211 (m), 1148 (m), 1126 (w), 1089 (w), 1055 (m), 1028 (w), 1011 (w), 974 (w), 926 (w), 868 (w), 827 (w), 787 (m), 754 (s), 718(m), 692 (w), 662 (w), 619 (w), 596 (w), 551 (w), 492 (w), 451 (w). ESI-MS (in THF) *m/z*: 561.92 (100%), $[M-H]^+$; 525.47 (19%), $[M-Cl]^+$.

For [Mn(L^2)(Cl)] (**2**): Dark brown polycrystalline product of complex **2** was prepared in the same way as complex **1** except that $\mathbf{H_2L^2}$ (0.165 g, 0.3 mmol) and mixed $CHCl_3$-MeOH solvents were used instead of $\mathbf{H_2L^1}$ (0.142 g, 0.3 mmol) and mixed CH_2Cl_2-EtOH solvents. Yield: 110 mg, 57%. Calc. for $C_{30}H_{21}BrClMnN_4O_2$: C, 56.27; H, 3.28; N, 8.75%; found: C, 56.23; H, 3.33; N, 8.69%. FT-IR (KBr, cm^{-1}): 3047 (w), 2934 (w), 1631 (m), 1555 (vs), 1522 (m), 1464 (s), 1414 (m), 1377 (s), 1356 (m), 1308 (w), 1286 (w), 1250 (w), 1219 (w),1204 (w), 1167 (w), 1134 (w), 1059 (w), 1015 (w), 978 (w), 856 (w), 818 (w), 806 (w), 789 (w), 750 (s), 718 (w), 698 (w), 654 (w), 617 (w), 602 (w), 579 (w), 546 (w), 498 (w), 473 (w), 453 (w), 417 (w). ESI-MS (in THF) *m/z*: 640.82 (100%), $[M-H]^+$; 604.36 (21%), $[M-Cl]^+$.

For [Mn(L^3)(Cl)] (**3**): Dark brown polycrystalline product of complex **3** was prepared in the same way as complex **1** except that $\mathbf{H_2L^3}$ (0.151 g, 0.3 mmol) was used instead of $\mathbf{H_2L^1}$ (0.142 g, 0.3 mmol). Yield: 106 mg, 60%. Calc. for $C_{31}H_{24}ClMnN_4O_3$: C, 62.95; H, 4.06; N,

9.48%; found: C, 62.89; H, 4.16; N, 9.40%; FT-IR (KBr, cm^{-1}): 3061 (w),3042 (w), 2920 (s), 2851 (m), 1628 (s), 1555 (s), 1526 (s), 1499 (w), 1464 (vs), 1381 (m), 1308 (w), 1288 (w), 1250 (m), 1213 (m), 1178 (w), 1157 (w), 1084 (w), 1059 (w), 1011 (w), 980 (w), 937 (w),905 (w), 880 (w), 864 (w), 787 (w), 752 (w), 737 (m), 714 (w), 689 (w), 660 (w), 596 (w), 563 (w), 546 (w), 513 (w), 488 (w), 469 (w), 417 (w). ESI-MS (in THF) *m/z*: 591.95 (100%), $[M-H]^+$; 555.49 (23%), $[M-Cl]^+$.

For $[Mn(L^4)(Cl)]$ (**4**): Dark brown polycrystalline product of complex **4** was prepared in the same way as complex **1** except that $\mathbf{H_2L^4}$ (0.174 g, 0.3 mmol) was used instead of $\mathbf{H_2L^1}$ (0.142 g, 0.3 mmol). Yield: 133 mg, 66%. Calc. for $C_{31}H_{23}BrClMnN_4O_3$: C, 55.54; H, 3.43; N, 8.36%; found: C, 55.50, H, 3.52, N, 8.34%; FT-IR (KBr, cm^{-1}): 3057 (w), 2928 (w), 1629 (s), 1557 (s), 1524 (s), 1493 (w), 1464 (vs), 1381 (s), 1354 (m), 1313 (m), 1288 (w), 1213 (m), 1178 (w), 1155 (w), 1121 (w), 1070 (w), 1059 (w), 1013 (w), 980 (w), 914 (w), 883 (w), 851 (w), 799 (w), 760 (m), 738 (m), 719 (w), 692 (w), 664 (w), 602 (w), 581 (w), 543 (w), 519 (w), 449 (w), 415 (w). ESI-MS (in THF) *m/z*: 670.84 (100%), $[M-H]^+$; 634.39 (15%), $[M-Cl]^+$.

1.3. Structure determination

Single crystal of complex $[Mn(L^1)Cl(EtOH)]$ ([**1**(EtOH)]) of suitable dimensions was mounted onto thin glass fibers. All the intensity data were collected on a Bruker SMART CCD diffractometer (Mo-Kα radiation and λ = 0.71073 Å) in Φ and ω scan modes. Structures were solved by Direct methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against F^2 using SHELXTL-97. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS. All hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and refinement parameters for the

complex are presented in Table 1S. Relevant atomic distances and bond angles are collected in Table 2S.

1.4. Copolymerization procedures of epoxide and anhydride

1.4.1. Representative copolymerization procedure in bulk

In the standard Schlenk vacuum line system, CHO (2.5 mmol), MA (2.5 mmol), catalyst **4** (0.01 mmol) and co-catalyst DMAP (0.01 mmol) were placed in a vial equipped with a small stir bar. The vial was sealed with a Teflon lined cap, and placed in an aluminum heat block preheated to the desired temperature of 110 °C. After the allotted reaction time of 150 min, the vial was removed from the heat block and a small aliquot was removed from crude ^{1}H NMR analysis to determine monomer conversion. The viscous reaction mixture was then dissolved in a minimum amount of CH_2Cl_2, and precipitated with an excess of anhydrous diethyl ether. The polymer was collected and dried in vacuum to give a white solid product.

1.4.2. Representative copolymerization procedure in solution

In the standard Schlenk vacuum line system, CHO (2.5 mmol), MA (2.5 mmol), catalyst **4** (0.01 mmol) and co-catalyst DMAP (0.01 mmol) were placed in a vial equipped with a small stir bar. Then absolute toluene (1 mL) was injected into the vial. The vial was sealed with a Teflon lined cap, and placed in an aluminum heat block preheated to the desired temperature of 110 °C. After the allotted reaction time of 300 min, the vial was removed from the heat block and a small aliquot was removed from crude ^{1}H NMR analysis to determine monomer conversion. The viscous reaction mixture was then dissolved in a minimum amount of CH_2Cl_2, and precipitated with an excess of anhydrous diethyl ether. The polymer was collected and dried in vacuum to give a white solid product.

1.5. Characterization of representative copolymers from epoxide and anhydride

Copolymer (CHO-MA): IR (KBr, cm^{-1}): 3316 (w), 2941 (m), 2866 (m), 2649 (w), 2342 (w), 1788 (s), 1733 (vs), 1649 (w), 1573 (w), 1535 (w), 1454 (m), 1403 (m), 1323 (m), 1300 (w), 1252 (s), 1211 (s), 1169 (s), 1094 (m), 1050 (w), 1025 (m), 956 (w), 915 (w), 848 (w), 812 (w), 725 (w), 624 (w), 583 (w), 518 (w), 477 (w). ^{1}H NMR (400 MHz, $CDCl_3$): 6.35-6.21 (m, 2H, -CH=CH-), 4.92 (s, 2H, -CH-), 2.11-1.39 (m, 8H, $-CH_2-$).

Copolymer (CHO-PA): IR (KBr, cm^{-1}): 3547 (w), 2941 (m), 2865 (m), 2661 (w), 2405 (w), 1728 (vs), 1648 (w), 1597 (w), 1579 (w), 1530 (w), 1490 (w), 1449 (m), 1350 (m), 1324 (s), 1277 (s), 1122 (s), 1069 (s), 1025 (w), 992 (m), 961 (m), 919 (w), 880 (w), 847 (w), 772 (w), 742 (m), 706 (m), 652 (w), 604 (w), 558 (w), 438 (w). ^{1}H NMR (400 MHz, $CDCl_3$): 7.82-7.41 (m, 4H, -Ph-), 5.14 (s, 2H, -CH-), 2.10-1.40 (m, 8H, $-CH_2-$).

Copolymer (SO-MA): IR (KBr, cm^{-1}): 3316 (w), 2956 (m), 2874 (w), 2649 (w), 1962 (w), 1732 (vs), 1649 (m), 1574 (w), 1535 (w), 1496 (w), 1453 (m), 1401 (m), 1350 (w), 1207 (s), 1162 (s), 1078 (w), 1026 (w), 1001 (w), 915 (w), 818 (w), 760 (m), 699 (m), 637 (w), 525 (w). ^{1}H NMR (400 MHz, DMSO-δ_6): 7.32 (s, 5H, -Ph-), 6.44 (d, 2H, -CH=CH-), 6.03-5.94 (m, 1H, -CH-), 4.40-4.10 (m, 2H, $-CH_2-$).

Copolymer (SO-PA): IR (KBr, cm^{-1}): 3305 (w), 2951 (w), 2877 (w), 2372 (w), 1729 (vs), 1647 (w), 1598 (w), 1578 (w), 1495 (w), 1452 (w), 1387 (w), 1355 (w), 1280 (s), 1120 (s), 1068 (s), 1041 (w), 1027 (w), 972 (w), 896 (w), 787 (w), 743 (m), 699 (m), 648 (w), 573 (w), 529 (w). ^{1}H NMR (400 MHz, $CDCl_3$): 7.66-7.28 (m, 9H, -Ph-), 6.30-6.17 (m, 1H, -CH-), 4.58-4.30 (m, 2H, $-CH_2-$).

Table 1S Crystal data and structure refinement for complex [**1**(EtOH)]

Compound	[**1**(EtOH)]
Empirical formula	$C_{32}H_{28}ClMnN_4O_3$
Formula weight	606.97
Crystal system	Monoclinic
Space group	*C2/c*
a/Å	34.592(10)
b/Å	6.880(2)
c/Å	24.471(7)
α (˚)	90
β (˚)	102.024(6)
γ (˚)	90
V/Å^3	5696(3)
Z	8
ρ/g·cm^{-3}	1.416
Crystal size/mm	0.33×0.25×0.21
T/K	296(2)
F(000)	2512
μ/mm^{-1}	0.598
Data/restraints/parameters	5512/0/371
Quality-of-fit indicator	0.957
No. Unique reflections	5512
No. Observed reflections [$I>2\sigma(I)$]	14608
R_1	0.0773
$_wR_2$	0.1777

Table 2S Interatomic distances (Å) and bond angles (˚) with esds for [**1**(EtOH)]

[**1**(EtOH)]			
Mn(1)-N(1)	2.017(5)	Mn(1)-N(2)	1.984(5)
Mn(1)-O(1)	1.948(4)	Mn(1)-O(2)	1.875(4)
Mn(1)-O(3)	2.271(5)	Mn(1)-Cl(1)	2.535(2)
N(1)-Mn(1)-N(2)	80.70(19)	N(1)-Mn(1)-O(1)	92.29(18)
N(1)-Mn(1)-O(2)	170.14(19)	N(1)-Mn(1)-O(3)	86.49(18)
N(1)-Mn(1)-Cl(1)	90.93(15)		

^{1}H NMR (400 MHz, DMSO-d_6, ppm): 12.89 (s, 1H, -OH), 12.10 (s, 1H, -OH), 8.95 (s, 1H, -

CH=N), 8.02 (d, 2H, -Ph), 7.46 (m, 9H, -Ph), 7.25 (t, 1H, -Ph), 7.17 (t, 2H, -Ph), 7.05 (t, 1H, -Ph), 6.94 (t, 1H, -Ph), 6.86 (d, 1H, -Ph), 3.80 (s, 3H, -OMe), 1.46 (s, 3H, $-CH_3$).

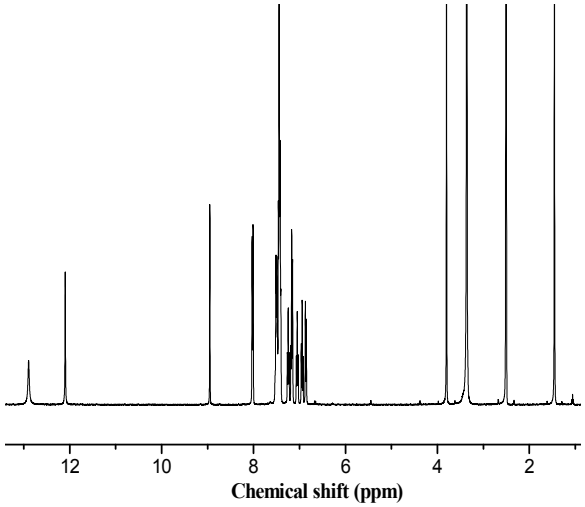

Figure S1: Representative ^{1}H NMR spectrum of ligand $\mathbf{H_2L^3}$.

^{13}C NMR (400 MHz, DMSO-d_6, ppm): 165.6, 163.8, 163.3, 148.4, 148.0, 143.8, 139.3, 132.0, 131.5, 131.0, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.3, 127.3, 126.3, 124.5, 123.8, 120.6, 119.5, 119.3, 118.7, 118.6, 118.5, 116.2, 101.3, 56.3, 16.1.

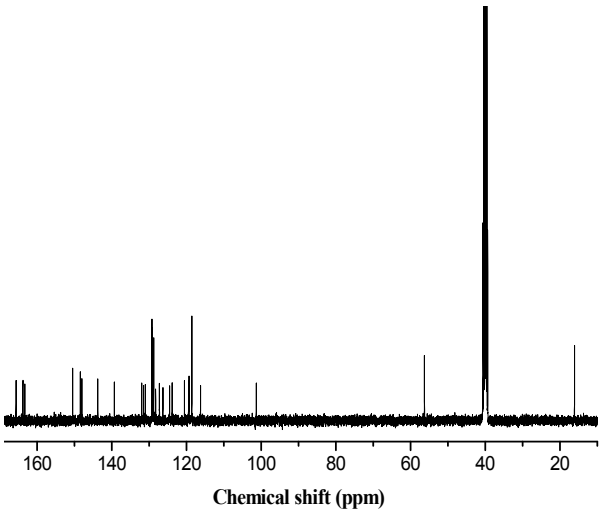

Figure S2: Representative ^{13}C NMR spectrum of ligand $\mathbf{H_2L^3}$.

Copolymerization cyclohexene oxide with maleic anhydride

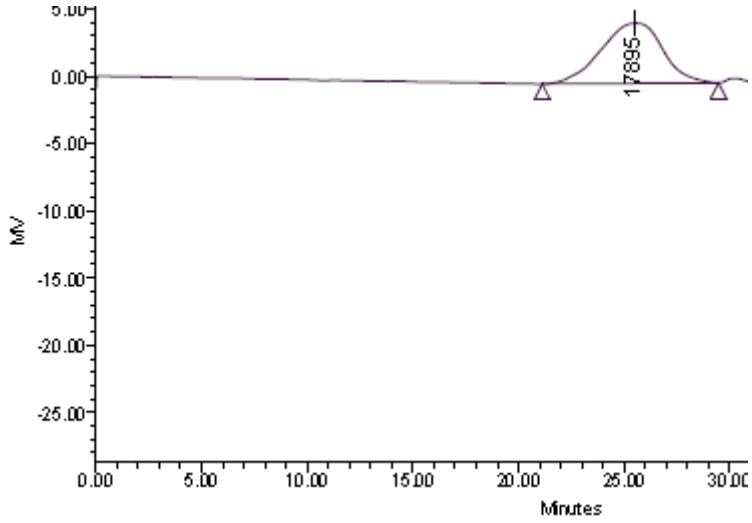

Figure S3: Representative GPC graph of alternating copolymers from CHO and MA catalyzed by **4**/DMAP catalyst in bulk.

Copolymerization styrene oxide with maleic anhydride

^{1}H NMR (400 MHz, DMSO-d_6): 7.32 (s, 5H, -Ph-), 6.44 (d, 2H, -CH=CH-), 6.03-5.94 (m, 1H, -CH-), 4.40-4.10 (m, 2H, -CH_2-).

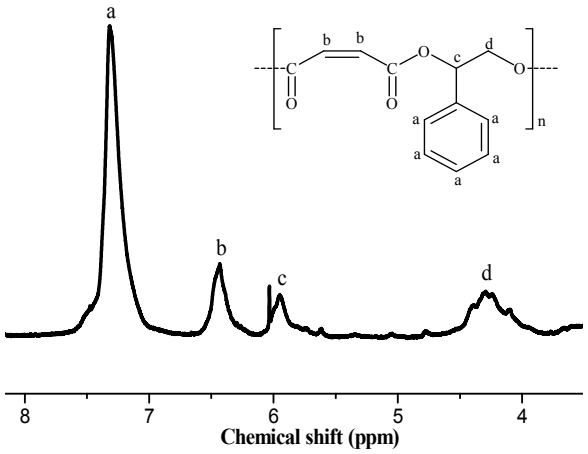

Figure S4: Representative ^{1}H NMR spectrum of alternating copolymers from SO and MA in the presence of **4**/DMAP as catalyst.

Copolymerization styrene oxide with phthalic anhydride

^{1}H NMR (400 MHz, $CDCl_3$): 7.66-7.28 (m, 9H, -Ph-), 6.30-6.17 (m, 1H, -CH-), 4.58-4.30 (m, 2H, -CH_2-).

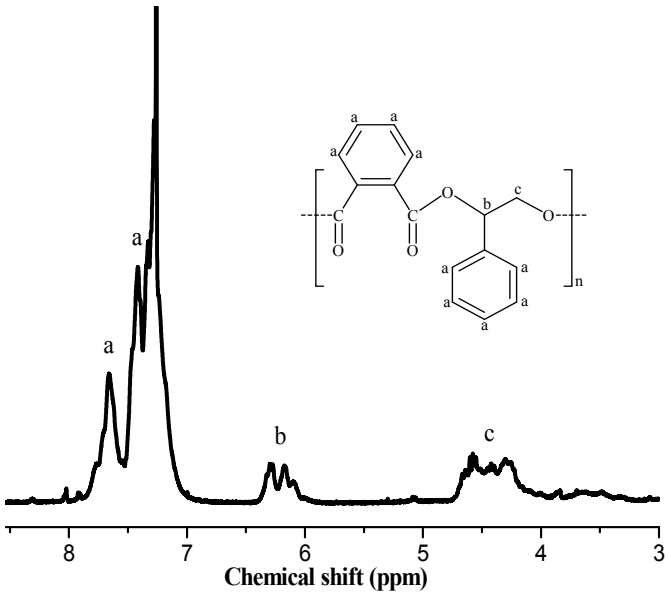

Figure S5: Representative ^{1}H NMR spectrum of alternating copolymers from SO and PA in the presence of **4**/DMAP as catalyst.

Copolymerization cyclohexene oxide with phthalic anhydride

^{1}H NMR (400 MHz, $CDCl_3$): 7.82-7.41 (m, 4H, -Ph-), 5.14 (s, 2H, -CH-), 2.10-1.40 (m, 8H, -CH_2-).

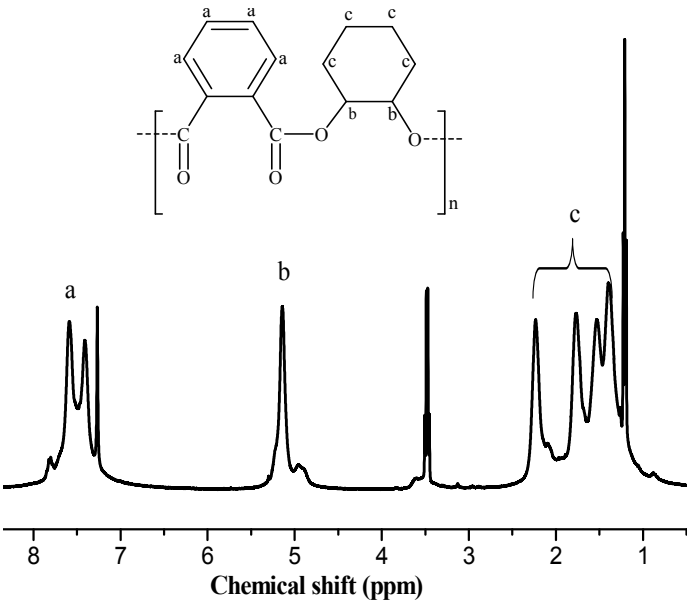

Figure S6: Representative ^{1}H NMR spectrum of alternating copolymers from CHO and PA in the presence of **4**/DMAP as catalyst.

Copolymerization cyclohexene oxide with maleic anhydride

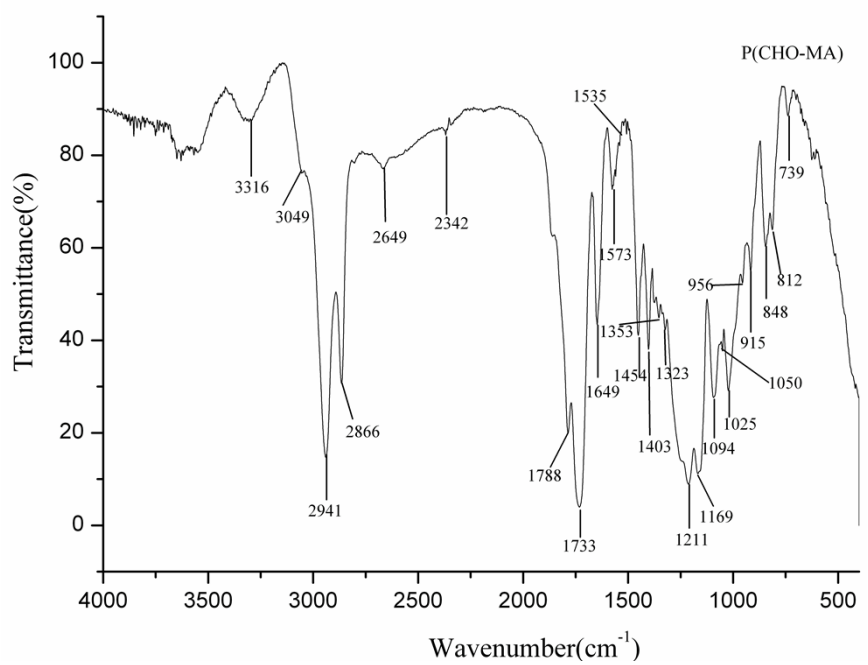

Figure S7: Representative FTIR spectrum of alternating copolymers from CHO and MA in the presence of **4**/DMAP as catalyst.