Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

Contents

General Information

All reactions were conducted in glassware with magnetic stirring. Epibromohydrin and 2,2-dimethoxy-propane were purchased from Aldrich and used directly without further purification. (*S,S*)-(*N,N'*-bis(3-*tert*-butylsalicylidene-5-(thiophen-2-yl)-cyclohexane-1,2-diamine and (*S,S*)-(*N,N'*-bis(3-*tert*-butylsalicylidene-5-(*N*-Boc pyrrol-2-yl)-cyclohexane-1,2- diamine were prepared by previously reported procedures.[1] THF was distillated from sodium/benzophenone and DCM was distillated from CaH_2 before use. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on either a Bruker AM 360, AM 300 or AM 250 instrument with samples dissolved in $CDCl_3$ and data are reported in ppm with the solvent signal as reference (7.24 ppm for ^{1}H NMR and 77 ppm for ^{13}C NMR). IR spectra were recorded as KBr disks using a Perkin-Elmer spectrometer. UV-vis spectra were obtained using a Bio-TEK UNIKON XL spectrometer. Optical rotations were measured on a Perkin-Elmer 241 digital polarimeter with a sodium (489 nm) lamp. Mass spectra were recorded on a Finnigan MAT 95 S spectrometer. Chiral gas chromatography (GC) analyses were performed on Fisons instrument GC 8000 instruments equipped with FID detectors and a chiraldex β-PM chiral capillary column (50 m x 0.25mm) using hydrogen as carrier gas. Elemental analysis was performed by the national analytical centre of scientific research in solaize. Energy Dispersive Spectroscopy (EDS) was performed on a Field Emission Gun Scanning Electron Microscope (FEG-SEM) Zeiss Supra 55 VP. The EDS is a SAMx IDFix analysis package using a new Silicon Drift Detector (SDD) working at 5 kV. EPR spectra were recorded with a Bruker ELEXSYS 500 spectrometer. For low temperature studies, an Oxford Instrument continuous-flow liquid helium or nitrogen cryostat and a temperature control system were used.

Experimental section

Preparation of complex 3.[2] To a solution of (*S,S*)-(*N,N'*-bis(3-*tert*-butylsalicylidene-5-(thiophen-2-yl)-cyclohexane-1,2-diamine **1** (0.599 g, 1 mmol) in degassed DCM (3.5 mL), a solution of $Co(OAc)_2.4H_2O$ (300 mg, 1.2 mmol) in degassed MeOH (3.6 mL) was slowly added with continuous stirring under argon. The resulting mixture was stirred for 90 min at room temperature and then 30 min at 0 °C. After filtration under reduced pressure, the residue was washed with cold MeOH (20 mL) and then recristallized in a mixture of DCM and MeOH (1:1) to afford complex **3** (666 mg, >99 %) as a dark red powder. IR (KBr, υ (cm^{-1})) 2949, 2863, 1630, 1598, 1533, 1405, 1320, 688. LRMS (ESI): 656.31 (48) $[M+H]^+$, 655.29 (100), 295.14 (30). HRMS (ESI): Calcd for $C_{36}H_{40}CoO_2N_2S_2$ 655.1863, found 655.1867. Anal. Calcd. for

[1] A. Voituriez, M. Mellah, E. Schulz, *Synth. Met.* **2006**, *156*, 166-175; X. Hong, M. Mellah, F. Bordier, R. Guillot, E. Schulz, *ChemCatChem*. **2012**, DOI: 10.1002/cctc.201200085.
[2] S. E. Schaus, B. D. Brandes, J. F. Larrow, M. Tokunaga, K. B. Hansen, A. E. Gould, M. E. Furrow, E. N. Jacobsen, *J. Am. Chem. Soc.* **2002**, *124*, 1307.

$C_{36}H_{40}CoO_2N_2S_2$: C, 65.93; H, 6.15; N, 4.27; found: C, 65.95; H, 6.32; N, 4.20. $[\alpha]_D^{20}$ + 1387 (c 0.003, $CHCl_3$). UV-Vis: λ_{max} $CHCl_3$ 273, 327, 391.

Preparation of complex 4.[3] To a solution of **3** (500 mg, 0.76 mmol) in THF (100 mL) in an O_2 atmosphere, acetic acid (1 mL, 17.5 mmol) was added with continuous stirring. The solution was stirred vigorously for 1.5 h in O_2 at room temperature before the solvents were removed under reduced pressure. 4 x 50 mL of toluene were finally added and then removed under reduced pressure to afford **4** (507 mg, 0.71 mmol 93%) as a brown powder, which was used without further purification. ^{1}H NMR (250 MHz, DMSO) δ 7.93 (s, 1H), 7.92 (s, 1H), 7.70 (t, *J* = 2.2 Hz, 2H), 7.49 (d, *J* = 2.2 Hz, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.36 (d, *J* = 4.8 Hz, 1H), 7.33 (d, *J* = 4.8 Hz, 1H), 7.26 (d, *J* = 3.3 Hz, 1H), 7.22 (d, *J* = 3.3 Hz, 1H), 7.05-7.12 (m, 2H), 3.4-3.5 (m, 2H), 2.90-3.10 (m, 4H), 1.9-2.1 (m, 4H), 1.8 (s, 3H), 1.71 (s, 9H), 1.66 (s, 9H). IR (KBr, υ (cm^{-1})) 2947, 2863, 1631, 1607, 1406, 690. LRMS (ESI): 657.29 (22), 656.29 (48), 655.29 (100) $[M\text{-}OAc]^+$. HRMS (ESI): Calcd for [M-OAc] $C_{36}H_{40}CoO_2N_2S_2$ 655.1863, found 655.1905. Anal. Calcd. for $C_{38}H_{45}CoO_5N_2S_2.1/2H_2O$: C, 63.08; H, 6.12; N, 3.87; found: C, 63.04; H, 6.12; N, 3.82. $[\alpha]_D^{20}$ + 940 (c 0.003, $CHCl_3$). UV-Vis: λ_{max} $CHCl_3$ 274, 326, 414.

Preparation of complex 5. To the solution of (*S*,*S*)-(*N*,*N*'-bis(3-*tert*-butylsalicylidene-5-(N-Boc pyrrol-2-yl)-cyclohexane-1,2- diamine **2** (340 mg, 0.445 mmol) in degassed DCM (1.6 mL), a solution of $Co(OAc)_2.4H_2O$ (167 mg, 0.668 mmol) in degassed MeOH (2.3 mL) was added with continuous stirring. The resulting mixture was stirred for 90 min at room temperature and then 30 min at 0 °C. After filtration under reduced pressure, the residue was repeatedly washed with cold MeOH (20 mL) and then dissolved in THF (60 mL). Acetic acid (72 µL, 1.2 mmol) was added with continuous stirring and the solution was stirred vigorously for 16 h under O_2 atmosphere at room temperature before the solvents were removed under reduced pressure. Finally 3*30 mL of toluene were added and then removed under reduced pressure to afford complex **5** (360 mg, 90 %) as a brown powder, which was used without further purification. IR (KBr, υ (cm^{-1})) 2945, 2864, 1736, 1626, 1533, 1439, 1363, 1324, 1305, 1252, 1143, 1085, 724. HRMS (ESI): Calcd for [M-OAc] $C_{46}H_{58}CoO_6N_4$ 821.3688, found 821.3671. $[\alpha]_D^{20}$ - 1648 (c 0.01, $CHCl_3$). UV-Vis: λ_{max} $CHCl_3$ 270, 369, 421.

Preparation of complex 6. To a solution of complex **3** (202 mg, 0.308 mmol) in acetonitrile (4.5 mL) in air at room temperature, a solution of ferrocenium.BF_4 (84 mg, 0.308 mmol) in acetonitrile (4.5 mL) was added in portions during 10 min. The solution was then stirred for 18 h before most of the solvents were removed under reduced pressure. The obtained oil was extracted with hot hexane (20 mL * 5) to remove ferrocene and then concentrated under reduced pressure to give complex **6** (> 99 %) as a dark green

[3] Prepared according to a slightly modified procedure as reference 2.

powder, which was used without further purification. ^{1}H NMR (300 MHz, DMSO) δ 8.03 (s, 2H), 7.89 (d, *J* = 1.8 Hz, 2H), 7.65 (d, *J* = 1.8 Hz, 2H), 7.41 (d, *J* = 5,1 Hz, 2H), 7.31 (d, *J* = 3.3 Hz, 2H), 7.11 (dd, *J* = 5.1, 3.3 Hz, 2H), 3.63-3.66 (m, 2H), 3.07-3.12 (m, 4H), 2.0 – 2.1 (m, 4H), 1.78 (s, 18H). ^{19}F NMR (235 MHz, DMSO): δ -148.11, -148.17. IR (KBr, υ (cm^{-1})) 2945, 2862, 1633, 1600, 1426, 1320, 1167, 1083, 817, 702. LRMS (ESI): 655.35 (100) $[M\text{-}BF_4]^+$ $[\alpha]^{20}$ + 1063 (c 0.003, $CHCl_3$). UV-Vis: λ_{max} $CHCl_3$ 276, 323, 410.

Preparation of racemic 3-bromopropane-1,2-diol. A mixture of epibromohydrin (22.4 g, 163.5 mmol), *p*-toluenesulfonic acid (60 mg, 0.35 mmol) and H_2O (14 mL) was heated to reflux during 7 h, then Na_2CO_3 (74 mg, 0.70 mmol) was added to the mixture with caution. A distillation under reduced pressure (112 °C, 6.7 mbar) afforded the desired product (17.98 g, 71 %) as colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ 3.87-3.96 (m, 1H), 3.76 (dd, *J* = 3.8, 11.3 Hz, 1H), 3.66 (dd, *J* = 5.1, 11.3 Hz, 1H), 3.48 (dd, 1H, *J* = 5.3, 10.5 Hz), 3.44 (dd, *J* = 6.3, 10.5 Hz, 1H), 2.79 (s, 2H). ^{13}C NMR (90 MHz, $CDCl_3$) δ 71.7 (CH_2), 64.5 (CH), 35.1 (CH_2).

Preparation of racemic 4-(bromomethyl)-2,2-dimethyl-1,3-dioxolane. To a solution of 3-bromopropane-1,2-diol (330 mg, 2.1 mmol) in DCM (13 mL), Amberlyst 15 (26 mg) and 2,2-dimethoxypropane (510 µL, 4.2 mmol) were added with continuous stirring. The mixture was stirred at room temperature for 18 h and then filtrated on celite before removal of the solvents under reduced pressure. The resulting residue was purified by chromatography on silica gel (pentane/diethylether 95/5) to afford the product (420 mg, >99 %) as a colourless oil. ^{1}H NMR (360 MHz, $CDCl_3$) δ 4.26-4.33 (m, 1H), 4.09 (dd, *J* = 6.5, 9.0 Hz, 1H), 3.83 (dd, *J* = 5.0, 9.0 Hz, 1H), 3.39 (dd, 1H, *J* = 4.7, 10.0 Hz), 3.26 (dd, *J* = 8.0, 10.0 Hz, 1H), 1.41 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 110.4 (C_q), 75.4 (CH_2), 68.4 (CH), 32.9 (CH_2), 27.1 (CH_3), 25.5 (CH_3). IR (NaCl, υ (cm^{-1})) 2988, 2937, 2883, 1381, 1372, 1256, 1214, 1061, 843.

Representative dynamic HKR of epibromohydrin under homogeneous conditions. THF (145 µL) and water (33 µL, 1.81 mmol) were added to a solution of complex **4** (0.024 mmol) in epibromohydrin (104 µL, 1.21 mmol) dropwise at 0 °C with continuous stirring. The resulting solution was stirred at 4 °C for 48 h before the addition of DCM (5.4 mL), Amberlyst 15 (16 mg) and 2,2-dimethoxypropane (317 µL, 2.4 mmol). The mixture was stirred at room temperature for another 18 h and then filtrated on celite before removal of the solvents under reduced pressure. The obtained residue was finally purified by chromatography on silica gel (pentane/diethylether = 95/5) to afford the product as a clear liquid. The ee of the resulted acetal was determined by chiral GC analysis (column chiraldex β-PM, 110 °C, isothermal, t_{maj}= 5.97 min, t_{min}= 6.12 min, $[\alpha]_D^{20}$ –29.0 (c 2.45, C_6H_6) for 84 % ee, lit $[\alpha]_D^{20}$ +34.6 (c 5.80, C_6H_6) for

(*R*)-3-bromo-1,2-propanediol acetonide.[4] The absolute stereochemistry of the main product was consequently assigned as *(S)*.

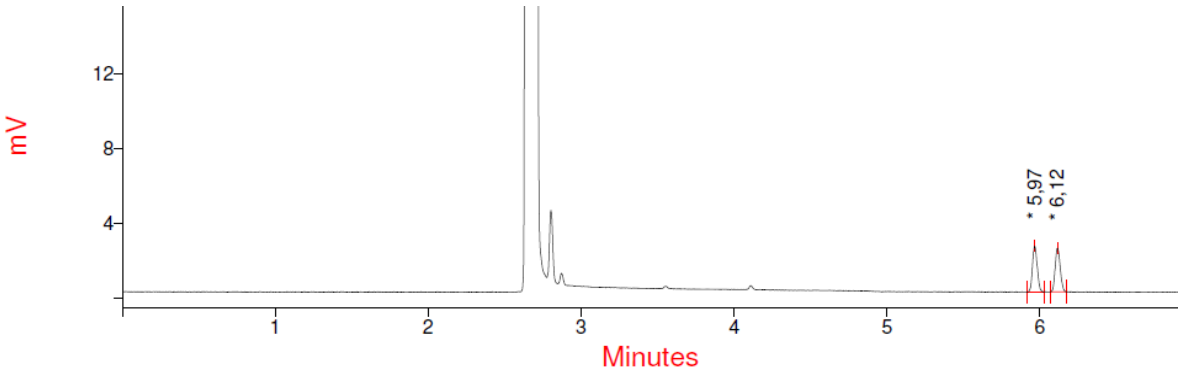
Representative dynamic HKR of epibromohydrin under heterogeneous conditions in a batch reactor. THF (145 µL) and water (33 µL, 1.81 mmol) were added to a suspension of polymerized complexes (2 mol % in Co) in epibromohydrin (104 µL, 1.21 mmol) dropwise at 0 °C with continuous stirring. The resulting suspension was stirred at R.T. for 48 h, diluted with THF (5 mL) and the products solution removed by filtration. The catalyst residue was rinsed five times with THF (5 mL), and the combined solutions were concentrated at reduced pressure before the addition of DCM (5.4 mL), Amberlyst 15 (16 mg) and 2,2-dimethoxypropane (317 µL, 2.42 mmol). The resulting mixture was stirred at RT for another 18 h, then filtrated on celite and the solvents removed under reduced pressure. The residue was purified by chromatography on silica gel (pentane/diethylether = 95/5) for the determination of the yield of the reaction and the enantiomeric excess of the product. In the schlenk tube, the remaining catalyst was dried under vacuum and reused directly for the next run.

Representative dynamic HKR of epibromohydrin under heterogeneous conditions in a fixed-bed reactor. In a HPLC system, the polymer **4a** (150 mg, 0.18 mmol in Co) and C18 modified silica (150 mg) were mixed and confined in a short HPLC pre-column. THF (8 mL) containing epibromohydrin (780 µL, 9.08 mmol) and chlorobenzene (375 µL) was introduced to the system and maintained as a constant flow of 1.0 $mL.min^{-1}$. Water (250 µL, 13.6 mmol) was then injected to the system to start the reaction and the conversion of the substrate was monitored by GC analysis by taking an aliquot of 2 µL at specific times. At the end of the reaction, the catalyst residue was rinsed with a flow of dry THF during 30 minutes and the combined solutions were concentrated at reduced pressure before the addition of DCM (40 mL), Amberlyst 15 (120 mg) and 2,2-dimethoxypropane (2.4 µL, 18.2 mmol). The resulting mixture was stirred at RT for another 18 h, and then filtrated on celite. The solvents were removed under reduced pressure and the residue was purified by chromatography on silica gel (pentane/diethylether = 95/5) for the determination of the yield of the reaction and the enantiomeric excess of the product. The catalyst anchored in the fixed-bed reactor could be reused in other runs without further treatment.

[4] Y. Kawakami, T. Asai, K. Umeyama, Y. Yamashita, *J. Org. Chem.* **1982**, 47, 3581.

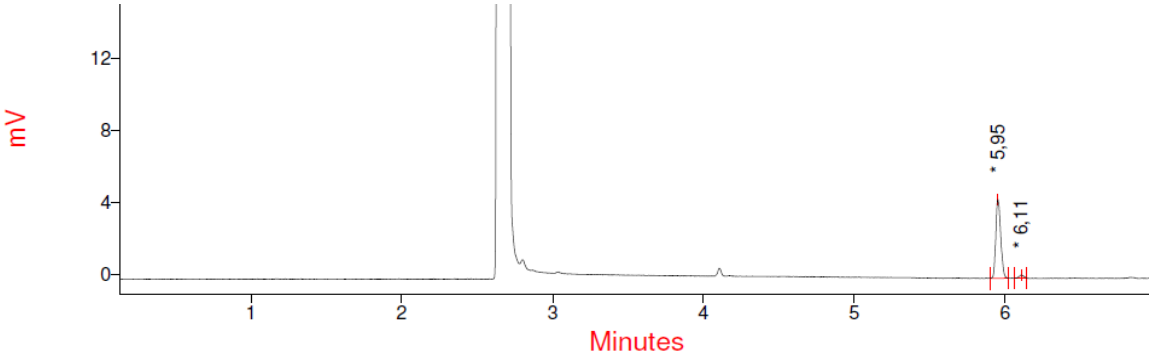
Determination of enantiomeric purity of various terminal epoxides

GC Chromatogram of a racemic sample



Retention time (min.)	Area (%)
5,97	49.99
6,12	50.01

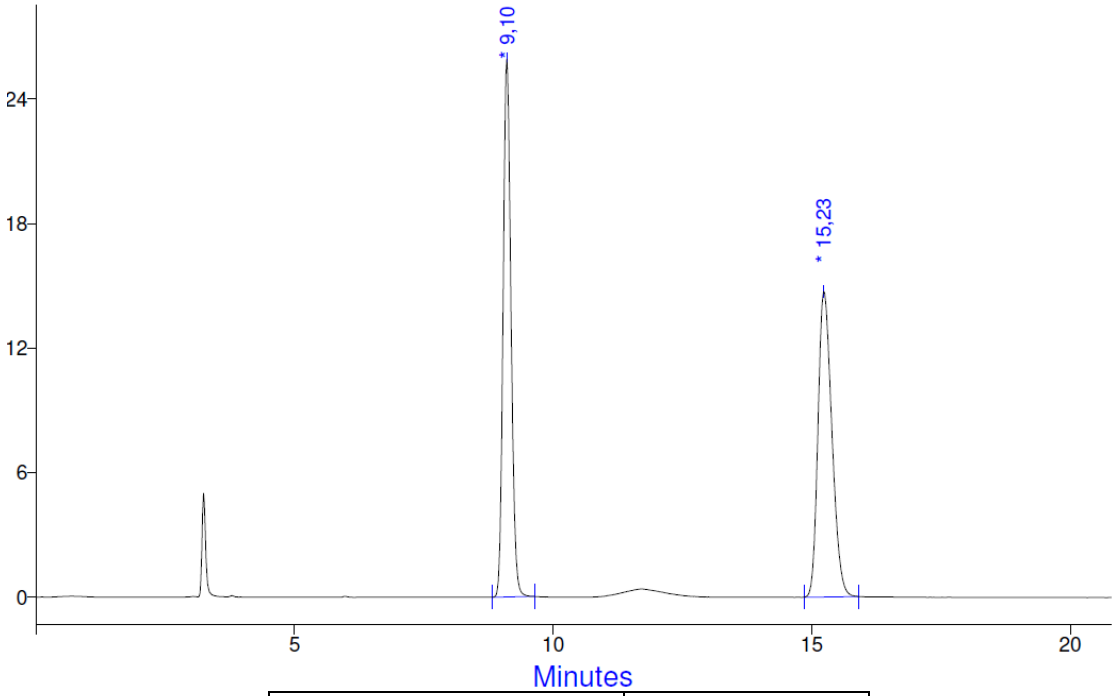
GC Chromatogram of an enantioenriched sample



Retention time (min.)	Area (%)
5,95	96.53
6,11	3.47

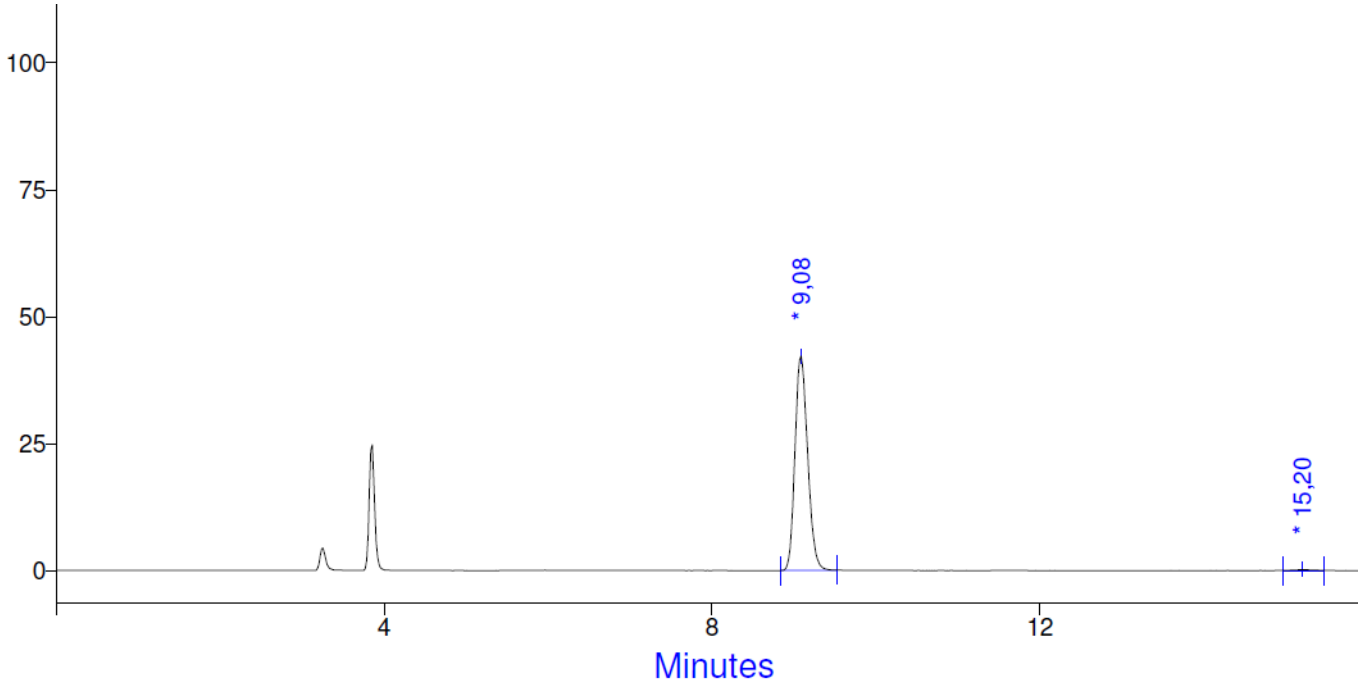
2-phenoxy-methyl-oxirane. Salen Co^{III} complexes (0.024 mmol) and the additives (0.024 mmol) were dissolved in a mixture of 2-phenoxy-methyl-oxirane (655 µl, 4.84 mmol) and chlorobenzene (55 mg, 0.48 mmol), to which water (48 µL, 2.66 mmol) was added dropwise at 0 °C with continuous stirring. The resulting solution was stirred at 0 °C for 16 h before addition of THF (5 mL) and a subsequent filtration on silica gel. The conversion of epoxide was determined by achiral GC analysis (column VF-1ms) with chlorobenzene as internal standard. The ee of the epoxide was determined by chiral HPLC analysis (column chiralcel OD-H, Hexane/iPrOH = 95/5, 1.0 mL/min, 25 °C, t_{maj}= 9.08 min, t_{min}= 15.20 min).

HPLC Chromatogram of a racemic sample



Retention time (min.)	Area (%)
9,10	49.94
15,23	50.06

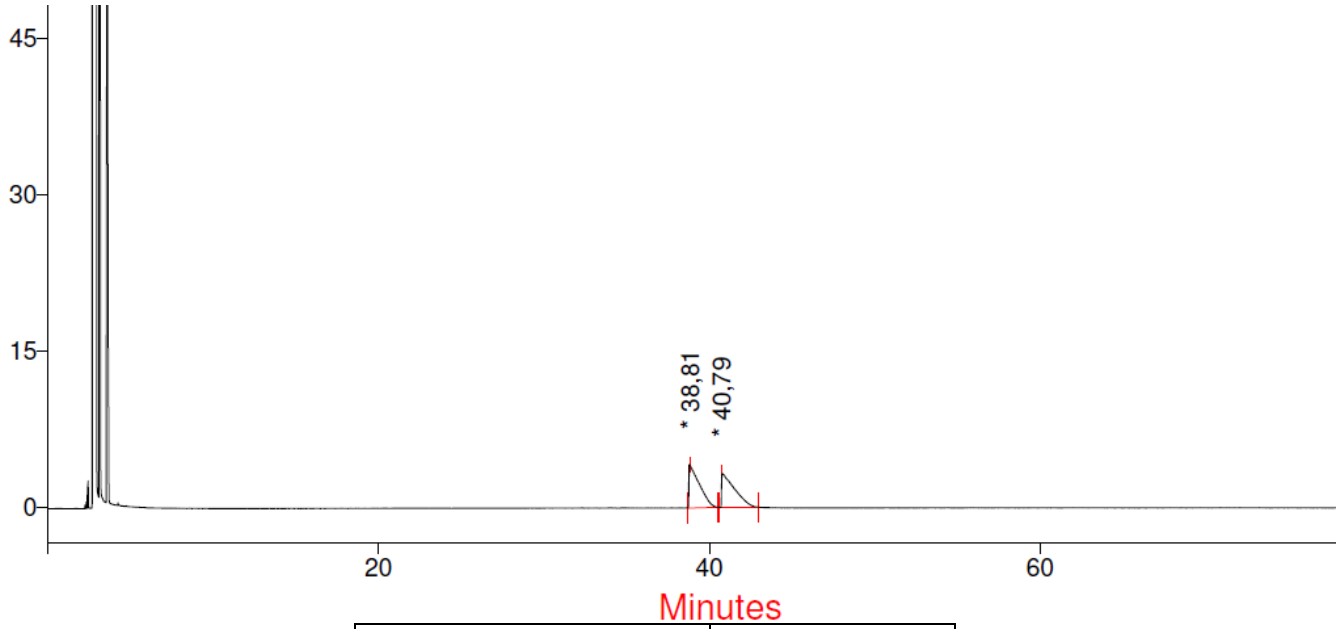
HPLC Chromatogram of a enantioenriched sample



Retention time (min.)	Area (%)
9,08	99.72
15,20	0.28

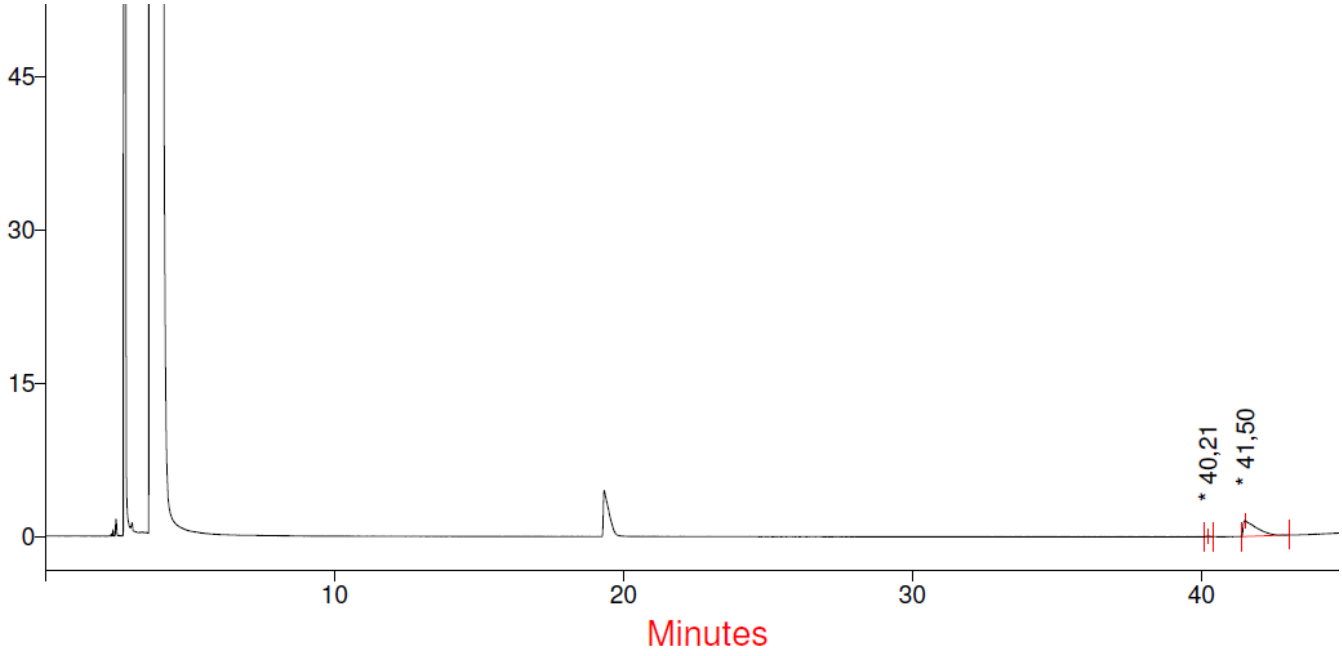
2-Allyloxymethyl-oxirane. Water (48 µL, 2.66 mmol) was added to a solution of the salen Co^{III} complexes (0.024 mmol) and the additives (0.024 mmol) in 2-allyloxymethyl-oxirane (574 µl, 4.84 mmol) and chlorobenzene (55 mg, 0.48 mmol) dropwise at 0 °C with continuous stirring. The resulting solution was stirred at 0 °C for 16 h before addition of THF (5 mL) and subsequent filtration on silica gel. The yield of resoluted epoxide was determined by achiral GC analysis (column VF-1ms) with chlorobenzene as internal standard. The ee of resoluted epoxide was determined by chiral GC analysis (column chiraldex B-PM, 35 °C isothermal, t_{maj}= 41.50 min, t_{min}= 40.21 min).

GC Chromatogram of a racemic sample



Retention time (min.)	Area (%)
38,81	50.43
40,79	49.57

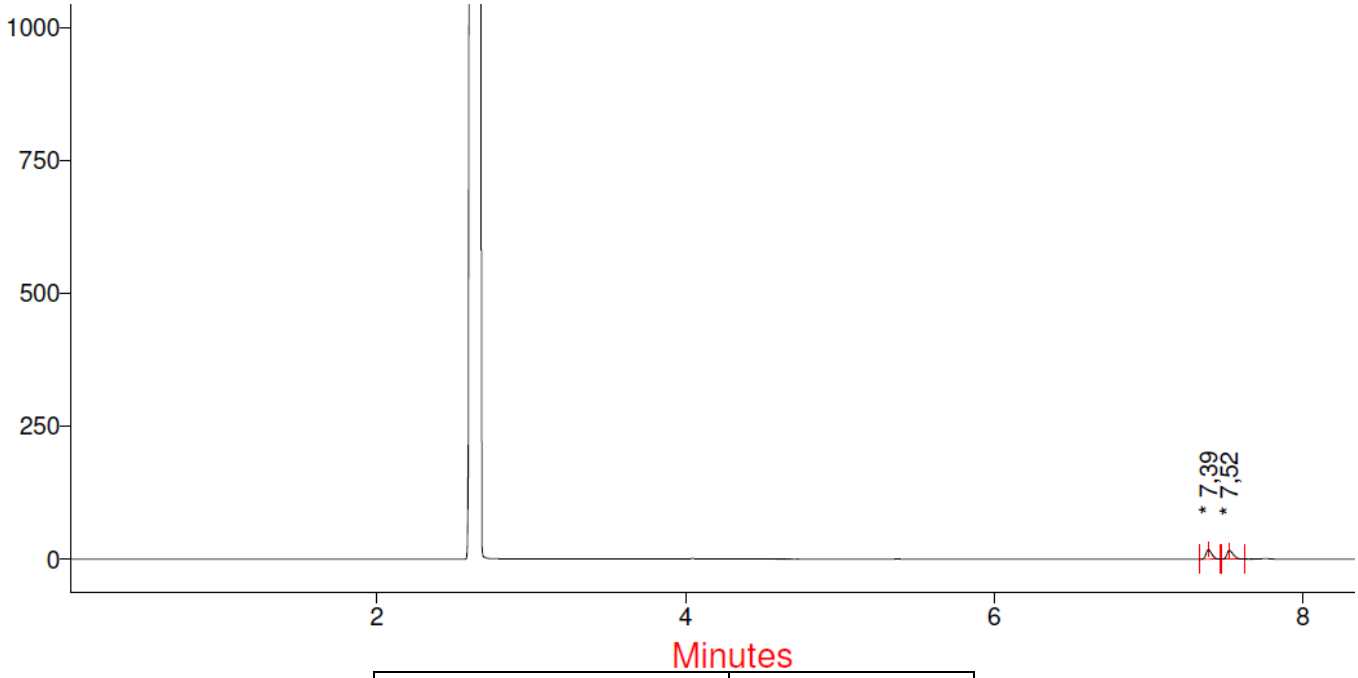
GC Chromatogram of an enantioenriched sample



Retention time (min.)	Area (%)
40,21	0.59
41,50	99.41

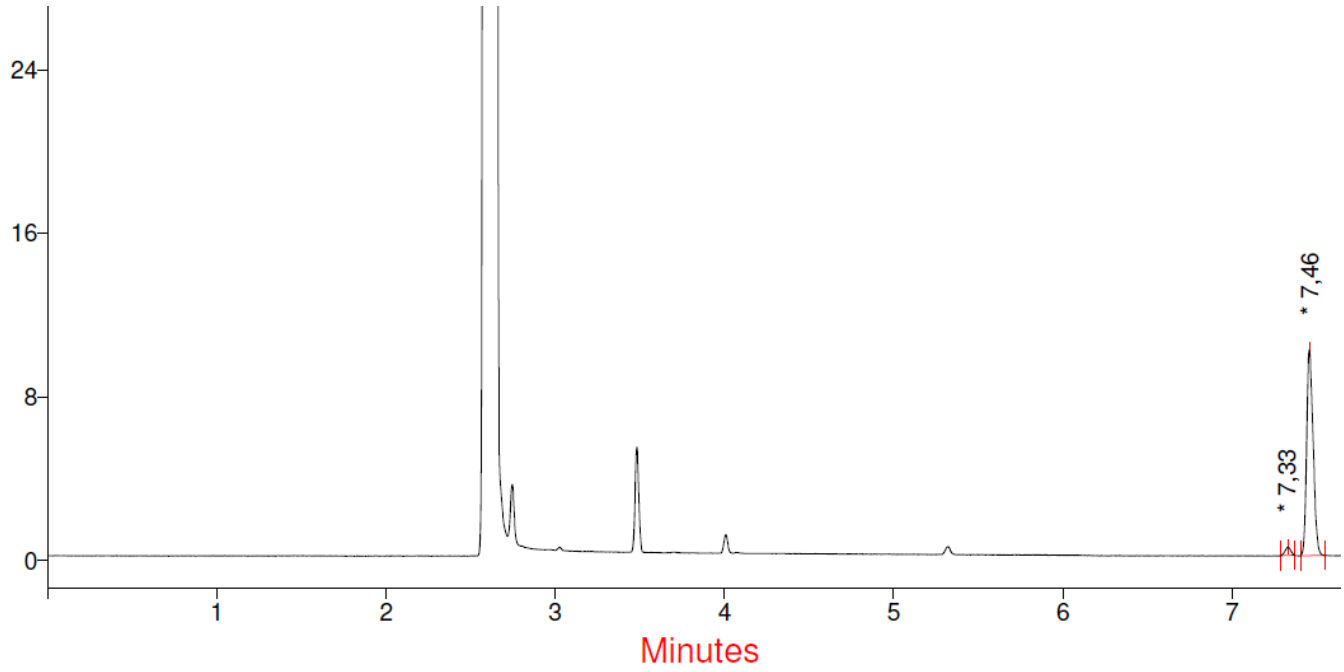
2-phenyl oxirane. THF (35 µL) and water (35 µL, 1.92 mmol) were added to a solution of the salen Co^{III} complexes (0.024 mmol) and the additives (0.024 mmol) in 2-phenyl oxirane (400 µl, 3.5 mmol) and chlorobenzene (55 mg, 0.48 mmol) dropwise at 0 °C with continuous stirring. The resulting solution was stirred at 0 °C for 72 h before addition of THF (5 mL) and subsequent filtration on silica gel. The yield of resoluted epoxide was determined by achiral GC analysis (column VF-1ms) with chlorobenzene as internal standard. The ee of resoluted epoxide was determined by chiral GC analysis (column chiraldex B-PM, 110 °C 10 min, 10 °C/min until 170 °C, t_{maj}= 7.46 min, t_{min}= 7.33 min).

GC Chromatogram of a racemic sample



Retention time (min.)	Area (%)
7,39	49.91
7,52	50.09

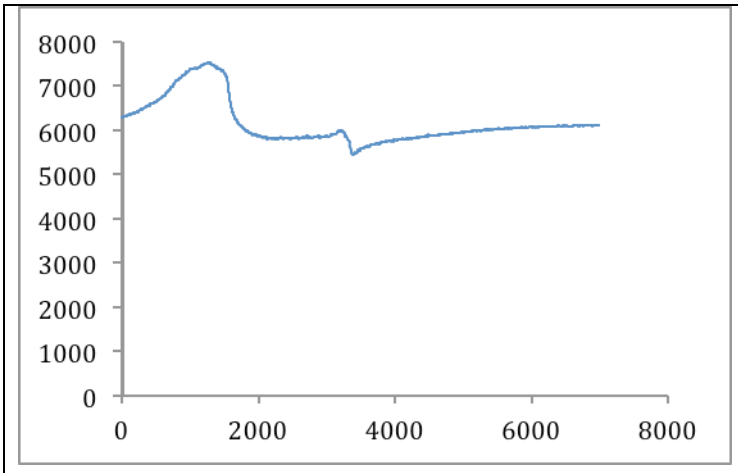
GC Chromatogram of a enantioenriched sample



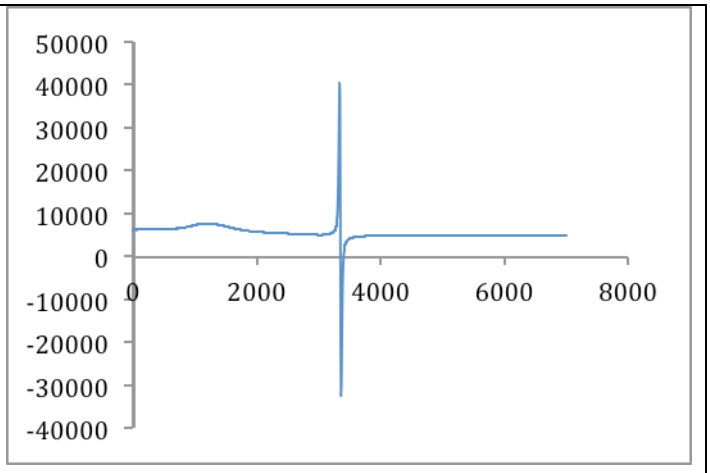
Retention time (min.)	Area (%)
7,33	2.08
7,46	97.92

Representative procedure for the chemical oxidative polymerizations. For polymerizations under argon atmosphere, a solution of monomer complex (0.25 mmol) in chloroform (2.5 mL) was added to a schlenk tube charged with a suspension of $FeCl_3$ (407 mg, 2.5 mmol) in chloroform (2.5 mL) or a solution of NOBF4 (293 mg, 2.5 mmol) in chloroform under argon. The resulted suspension was stirred at room temperature under argon for 3 h, and then added to MeOH (200 mL) dropwise under vigorous stirring. The precipitate was filtrated under reduced pressure, rinsed successively with MeOH, water, MeOH and THF to afford the targeted polymerized species as black powders. The same procedure was performed without argon protection for the polymerization under air atmosphere.

EPR analysis of *Poly*-3a and *Poly*-Co(III)



a) EPR spectrum of *Poly*-**3a**



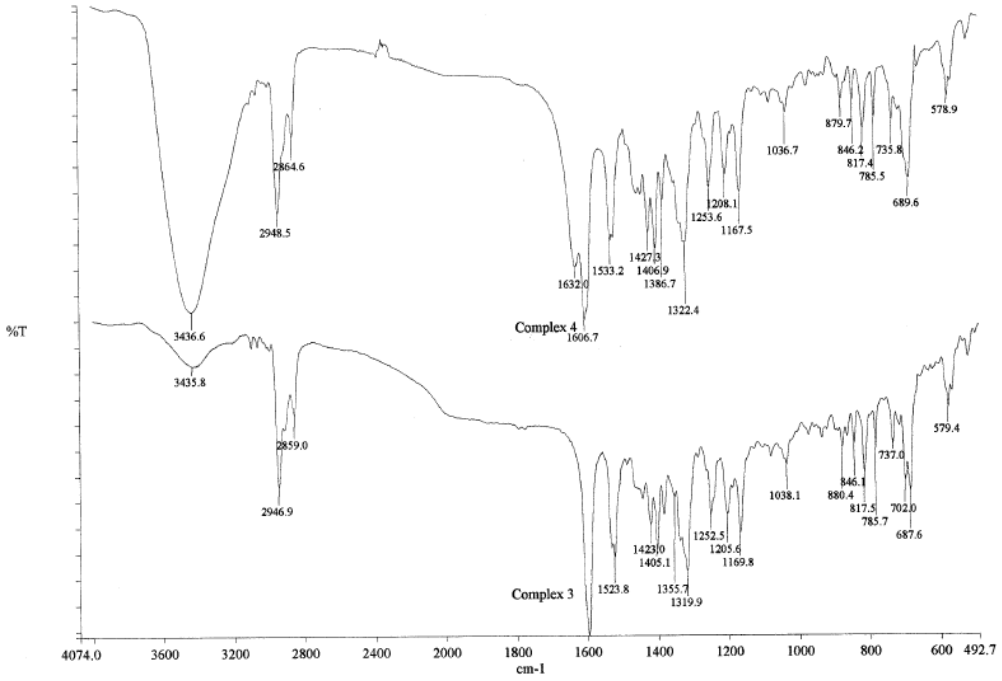
b) EDS spectrum of *Poly*-Co(III)

*X-band EPR powder spectra of Poly-**3a** (a) and Poly-Co(III) (b) at 10 K : Microwave frequency: 9.39 GHz; microwave power: 0.5mW; modulation amplitude: 0.5 mT; modulation frequency: 100 kHz; gain: 46 dB.*

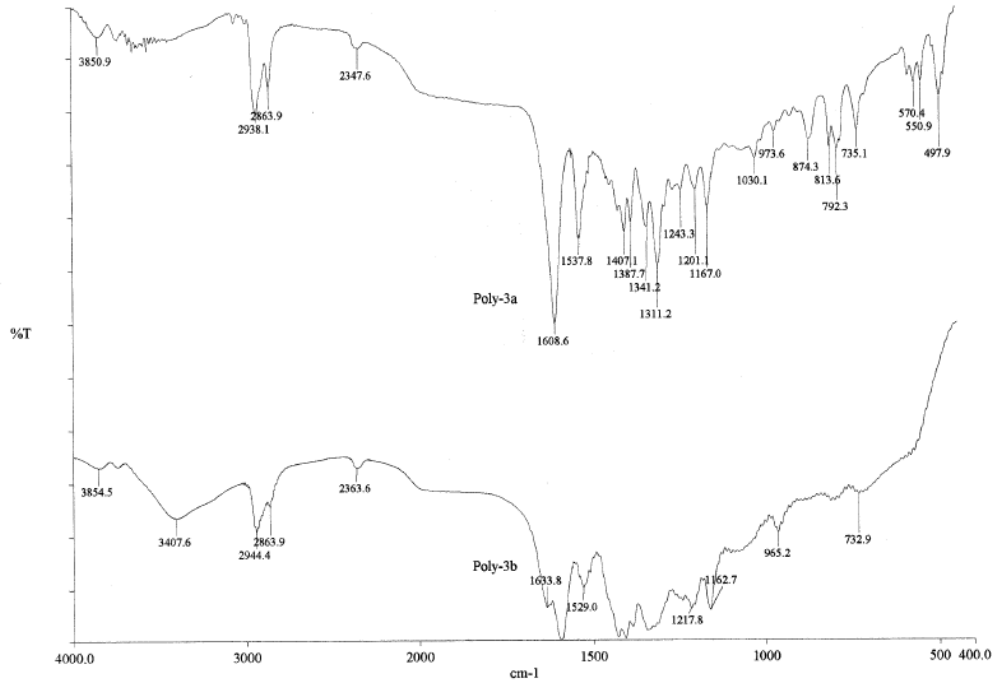
Both EPR spectra of *Poly*-**3a** and *Poly*-Co(III) showed a broad band at 1500G, which could result from the interaction of the signals of low-spin Co(II) metal centers in the polymers. EPR spectra of *Poly*-Co(III) showed a strong signal (g = 2.002) at 3500G, which is characteristic for the signal of a phenoxyl radical. Together with the signal at 1500G, this indicated the existence of Co(II) phenoxyl radicals in *Poly*-Co(III). However, no obvious signal at 3500G was observed for the spectrum of *Poly*-**3a**, the metal centers in *Poly*-**3a** was thus identified as Co(II).

IR analyses of the monomer and polymer complexes

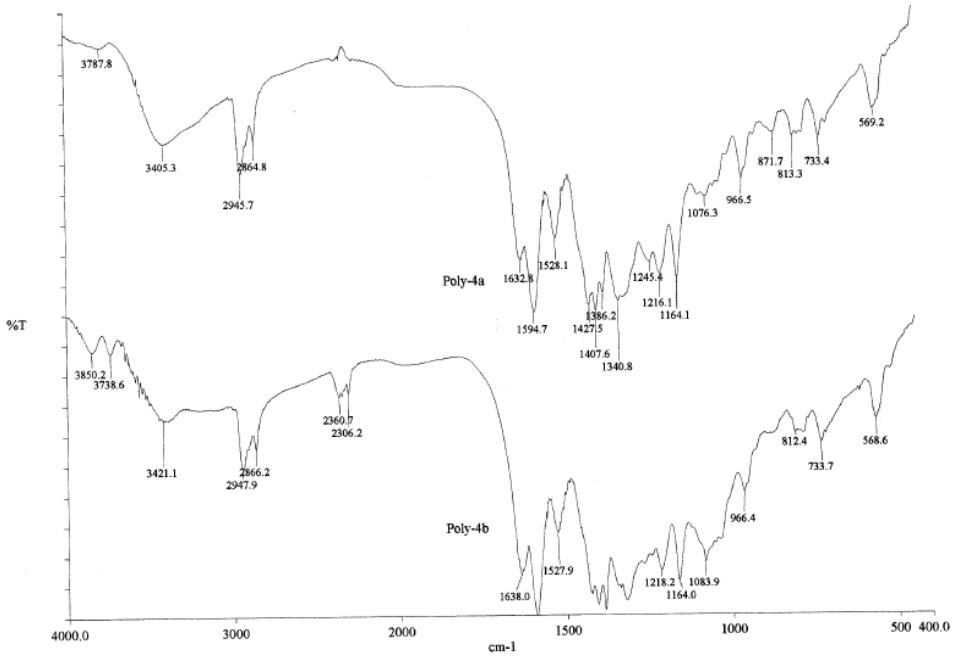
IR spectra of complexes **3** and **4**



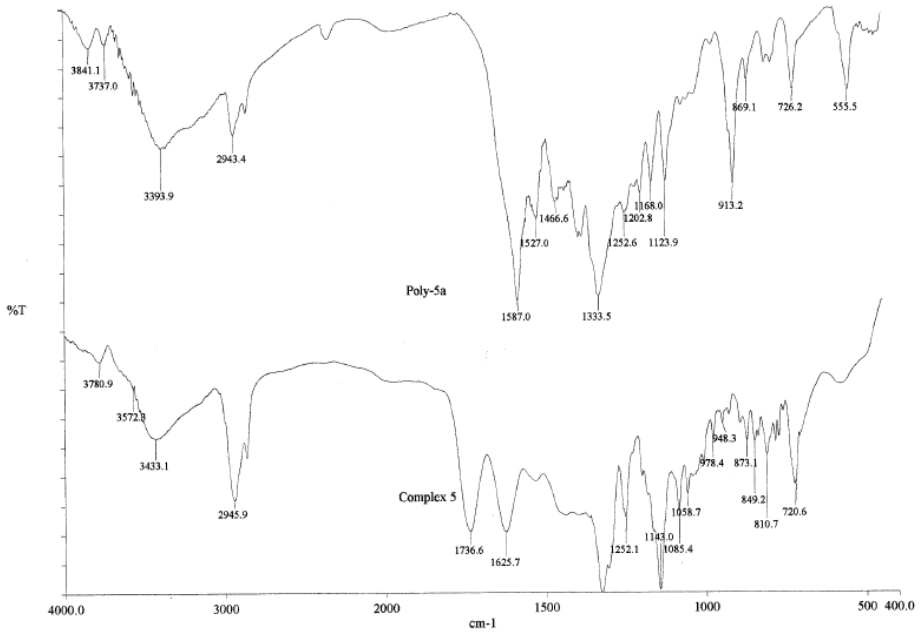
IR spectra of *Poly*-**3a** and *Poly*-**3b**



IR spectra of *Poly*-**4a** and *Poly*-**4b**



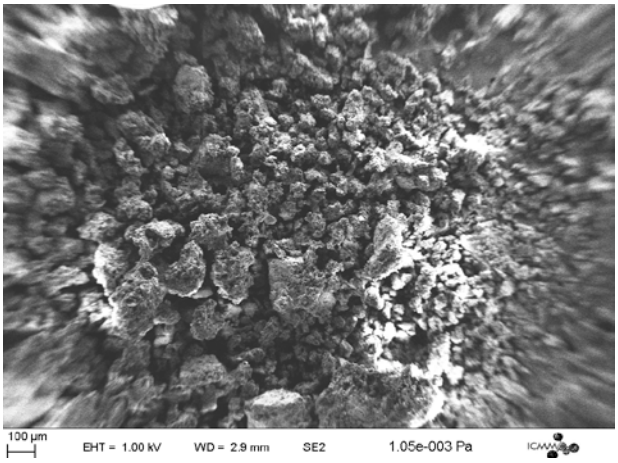
IR spectra of *Poly*-**5a** and complex **5**

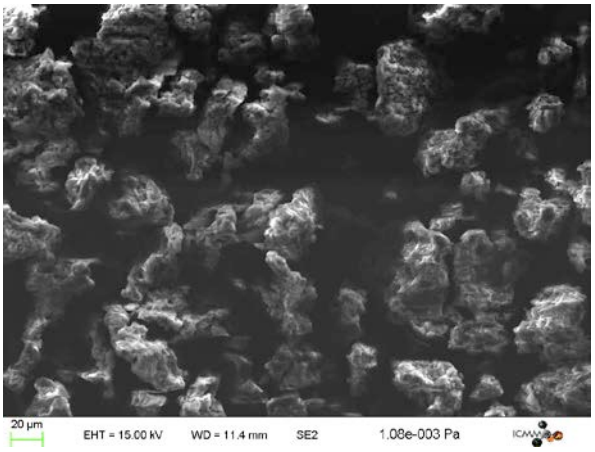


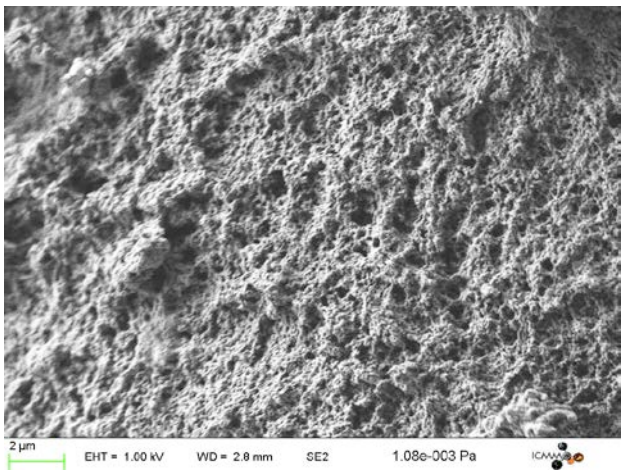
EDS (MEB) analyses of the polymers

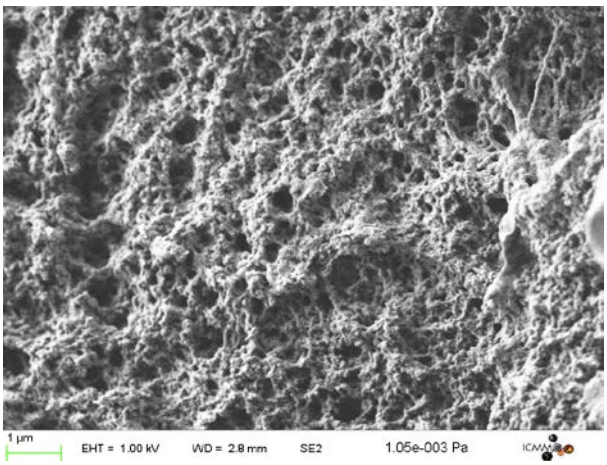
Energy Dispersive Spectroscopy (EDS) was performed on a Field Emission Gun Scanning Electron Microscope (FEG-SEM) Zeiss Supra 55 VP. The EDS is a SAMx IDFix analysis package using a new Silicon Drift detector (SDD) working at 5 kV.

SEM images of *Poly*-**4a** with different magnifications



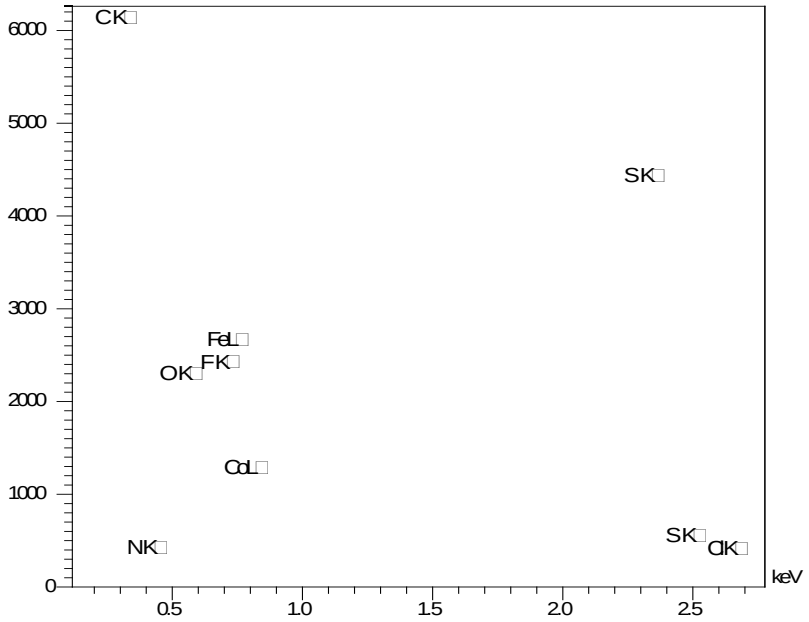




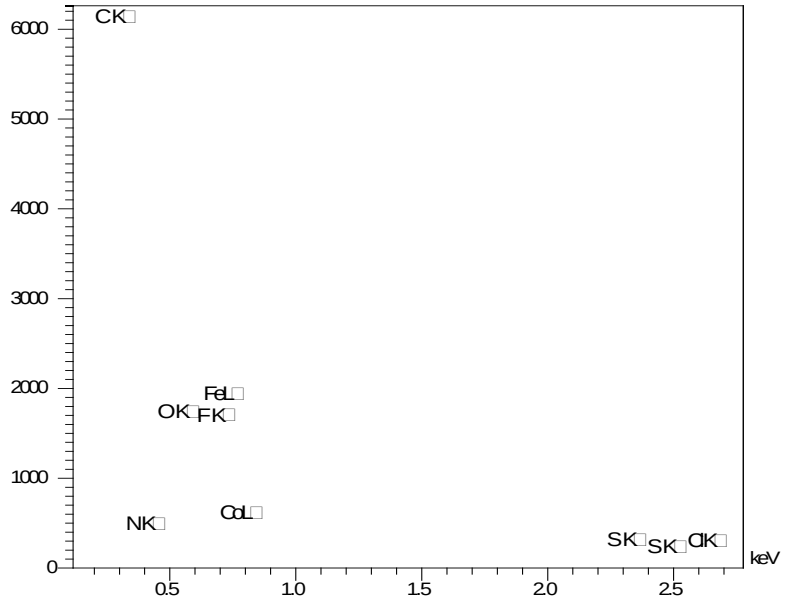


The EDS technique allows the easy determination of the chemical species that are present in a sample. The samples were deposited on a stub and an acquisition was performed during about 1 minute and at 5 kV in order to optimize the analysis and the detection of low energy X-ray signals and in particular the fluor signal. The boron signal is situated in close proximity to the carbon signal and is thus not significant.

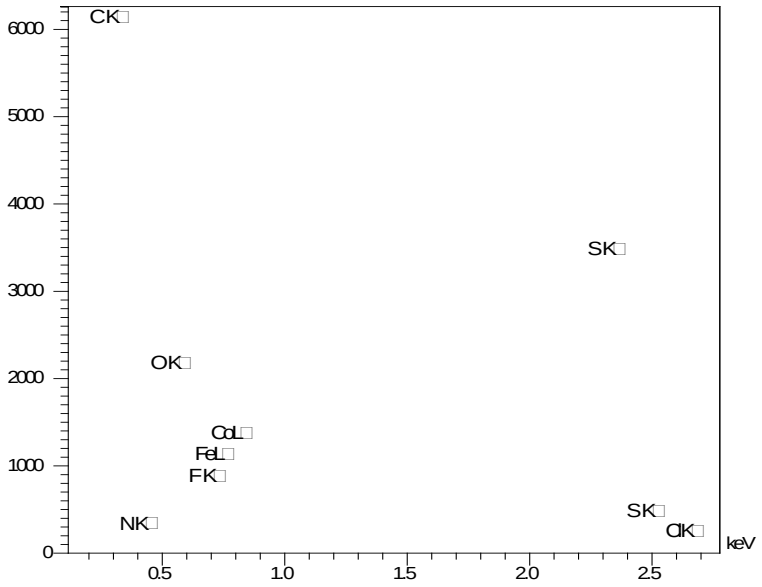
EDS spectrum of *Poly*-**4b**



EDS spectrum of *Poly*-**5b**



EDS spectrum of *Poly*-**4**/**6**



Elemental analyses of *Poly*-**4b** and *Poly*-**4**/**6**.

	Co content (%)	F content (%)	B content (%)	Percentage Co(III)-BF_4
Poly-**4b**	6.03	6.71	0.89	81 %
Poly-**4**/**6**	6.38	4.27	0.58	49 %

Kinetic studies of *Poly*-4/6 upon multi-substrate recycling studies

Epibromohydrin (104 µL, 1.21 mmol) was added to a suspension of polymer **4**/**6** (20 mg, 2 mol %) in THF (145 µL) containing water (33 µL, 1.81 mmol) and chlorobenzene (50 µL) at 20 °C with continuous stirring (1100 rpm). An aliquot of 2 µL was taken from the resulting suspension for GC analysis (column VF-1ms) at specified time. Conversions of epibromohydrin were calculated with chlorobenzene as internal standard. Remaining substrate and product are then removed by filtration and the recovered catalyst in the schlenk tube was repeatedly rinsed with dry THF and dried under vacuum before the reuses.