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Enhanced Cooperativity through Design: Pendant Co^{III}–Salen Polymer Brush Catalysts for the Hydrolytic Kinetic Resolution of Epichlorohydrin (Salen = *N,N'*-Bis(salicylidene)ethylenediamine Dianion)

Christopher S. Gill,[a] **Krishnan Venkatasubbaiah,**[a] **Nam T. S. Phan,**[a]
Marcus Weck,[b, c] **and Christopher W. Jones***[a, b]

Abstract: The Co^{III}–salen-catalyzed (salen = *N,N'*-bis(salicylidene)ethylenediamine dianion) hydrolytic kinetic resolution (HKR) of racemic epoxides has emerged as a highly attractive and efficient method of synthesizing chiral C_3 building blocks for intermediates in larger, more complex molecules. HKR reaction rates have displayed a second order dependency on the concentration of active sites, and thus researchers have proposed a bimetallic transition state for the HKR mechanism. Here we report the utilization of pendant Co^{III}–salen catalysts on silica supported polymer brushes as a catalyst for the HKR of epichlorohydrin. The novel polymer brush architecture provided a unique framework for promoting site–site interactions as required in the proposed bimetallic transition state of the HKR mechanism. Furthermore, the polymer brushes mimic the environment of soluble polymer-based catalysts, whereas the silica support permitted facile recovery and reuse of the catalyst. The polymer brush catalyst displayed increased activities over the soluble Jacobsen Co–salen catalyst and was observed to retain its high enantioselectivities (>99%) after each of five reactions despite decreasing activities. Analysis indicated decomposition of the salen ligand as an underlying cause of catalyst deactivation.

Keywords: asymmetric synthesis · cobalt–salen · heterogeneous catalysis · kinetic resolution · polymer brush

Introduction

The Co^{III}–salen-catalyzed (salen = *N,N'*-bis(salicylidene)-ethylenediamine dianion) hydrolytic kinetic resolution (HKR) of racemic epoxides has emerged as a highly attractive and efficient method of synthesizing chiral C_3 building blocks for intermediates in larger, more complex molecules, especially useful in the pharmaceutical industry.[1] The HKR reaction has been shown to involve a bimetallic mechanism as evident from a second-order dependency of activity upon the concentration of Co^{III} sites. This second-order dependency arose from a proposed dual-activation pathway of the reaction.[2] The two cobalt centers are proposed to bind hydroxide and epoxide individually. The cobalt-activated hydroxide is suggested to perform a nucleophilic attack on the α carbon of the epoxide. Hydrolysis of the intermediate species then purportedly regenerates the two active sites as the catalytic cycle repeats. Accordingly, activities of the original homogeneous Co^{III}–salen catalyst suffered, owing to unfavorable statistical interactions between the catalytic active sites in solution, resulting in very slow rates at low catalyst concentrations. Researchers have noted significant increases in activity when utilizing multiple Co–salen oligomeric,[3] dendritic,[4] and polymeric catalysts.[5,6] These multisited, soluble catalysts gave significant increases in activity versus the homogeneous Co–salen but remained difficult to recycle through distillation, dialysis membranes, or polymer precipitation. To this end, many researchers studied heterogenization of the expensive Co^{III}–salen catalysts to aid in their re-

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[a] C. S. Gill, Dr. K. Venkatasubbaiah, Dr. N. T. S. Phan, Prof. Dr. C. W. Jones
School of Chemical & Biomolecular Engineering
Georgia Institute of Technology
311 Ferst Dr., Atlanta, Georgia 30332 (USA)
Fax: (+1) 404-894-2866
E-mail: christopher.jones@chbe.gatech.edu

[b] Prof. Dr. M. Weck, Prof. Dr. C. W. Jones
School of Chemistry and Biochemistry
Georgia Institute of Technology
901 Atlantic Dr., Atlanta, Georgia 30332 (USA)

[c] Prof. Dr. M. Weck
Molecular Design Institute and Department of Chemistry
New York University, New York, New York 10003 (USA)

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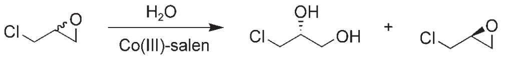
covery and reuse.[7] A variety of methods have been introduced including ship-in-a-bottle synthesis,[8] grafting to silicas,[9] membrane reactors,[10] ionic liquids,[11] and fluorous systems.[12] Despite the ability to recover and recycle the catalysts, retention of the high activities remained difficult.

Grafting polymer brushes to solid surfaces has received increasing attention in recent years in several areas including microelectronics and biotechnology.[13] However, the use of grafted polymer brushes as heterogeneous catalyst supports has remained limited to isolated examples. These include palladium complexes for carbon–carbon coupling reactions[14] and spherical polyelectrolyte brush supported nanoparticle catalysts,[15] in which it appears that only site accessibility was the strategic aim.

Here, we demonstrate how high activities through site–site cooperativity can be achieved with a new catalyst design by using an easily recoverable hybrid organic/inorganic catalyst.[16] The polymer brush architecture was employed to specifically promote the site–site interactions required by an increasing array of catalytic reactions with quasi-planar coordination complexes.[17] This site–site cooperativity is achieved through the strategic design of the pendant Co^{III}–salen active sites supported on polymer brushes to promote the cooperative bimetallic interactions required for the HKR reaction (Scheme 1). Specifically, the polymer brush architecture addresses issues of increased mobility, enhanced proximity of the catalytic sites, and facile recovery. By grafting polymer chains with pendant Co–salen sites to silica supports, the flexibility and proximity of the catalyst centers can be enhanced to produce increased activities in the HKR of epichlorohydrin,[18] and allow for simple recovery and reuse by means of the insoluble support. In addition to demonstration of the use of polymer brushes as a catalyst support, this work highlights catalyst recyclability and investigates causes of catalyst deactivation.



Scheme 1. HKR of epichlorohydrin.

Results and Discussion

The polymer brush Co–salen catalyst was synthesized from a series of steps (Scheme 2), starting with the immobilization of an atom transfer radical polymerization (ATRP) initiator to the surface of CAB-O-SIL silica.[19] Thermogravimetric analysis (TGA) indicated a loading of 0.24 mmol g^{-1} of the initiator on the silica surface. The CAB-O-SIL silica displayed a fractal-like structure with particle thicknesses of roughly 20 nm by using TEM (Figure 1). Styrene and styryl-modified salen ligands (**1a,b**)[6,20] were copolymerized from the surface initiators (**2**) forming the polymer brushes (**3a**,**b**).[21] Calculations indicated that roughly 17% of the surface initiator sites resulted in polymer chains, a result consistent with prior reports of low initiator efficiencies for polymer-brush systems.[22] Two different styryl–salen monomers were synthesized to highlight the differences in activities resulting from contrasting hydrophilicities and flexibilities of the salen–styrene linker. TGA indicated organic components of the polymer brushes **3a**,**b** to be 50 and 48%, respectively. TEM displayed similar fractal-like structures for **3a**,**b** as with the bare silica, but the particle thicknesses

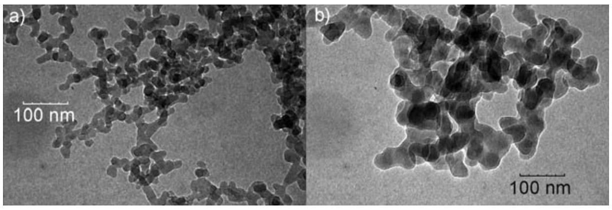
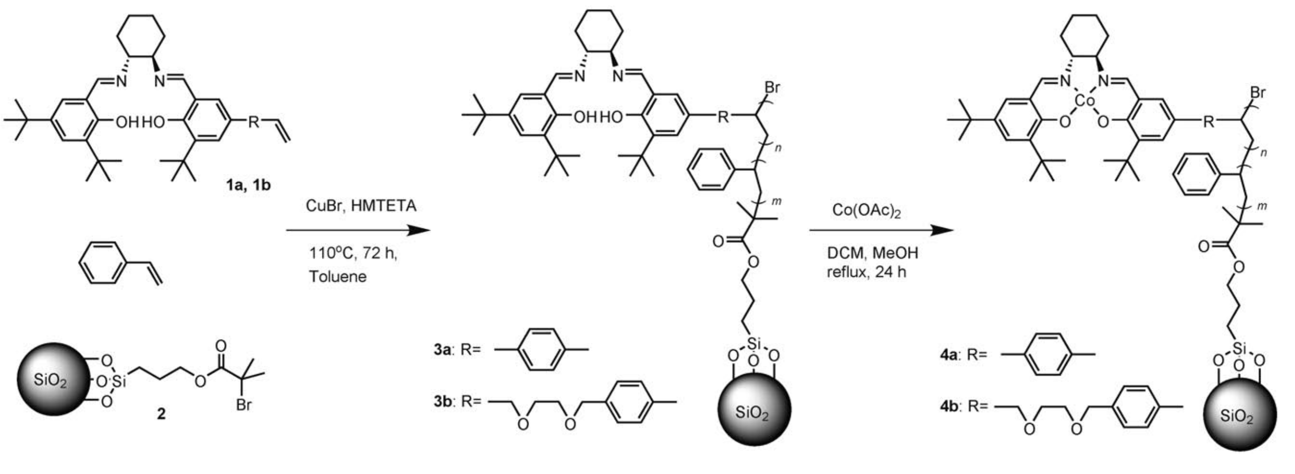


Figure 1. TEM images at 100,000× of a) CAB-O-SIL silica and b) polymer brush **3b**.



Scheme 2. Polymer brush catalyst synthesis.

increased to roughly 40 nm indicating new material was coating the silica surface. FT-IR confirmed the postulated structure of the organic species present in the solid catalyst (see the Supporting Information). Aromatic C–H stretches, not present in the immobilized ATRP initiator (**2**), were observed in each of the polymer brushes (**3a**,**b**) at $\tilde{\nu}=3086$, 3063, and 3031 cm^{-1}. A significant growth in the aliphatic C–H stretches at $\tilde{\nu}=2957$, 2934, and 2865 cm^{-1} and the imine (C=N) stretch at $\tilde{\nu}=1630\,cm^{-1}$ was also observed. The growths of the aromatic and aliphatic C–H stretches from the poly(styrene) backbone and the imine stretch from the salen ligand in the FT-IR spectra indicated that the organic loadings observed by TGA were indeed the desired styrene/styryl–salen copolymer. This formation was confirmed by means of cross-polarization magic-angle spinning (CP MAS) ^{13}C NMR spectra, which displayed peaks in the regions $\delta=25$–80 (*C*Me$_3$, *C*H$_2$, O-*C*H$_2$, cyclohexyl-*C*H$_2$, cyclohexyl *C*H), 120–145 (aromatic *C*), 160 ppm (*C*=N) (see the Supporting Information). CP MAS ^{29}Si NMR spectroscopy also indicated the presence of Q^2, Q^3, and Q^4 silicon resonances ($\delta=-90$ to -110 ppm) and resonances corresponding to reaction of 1, 2, and 3 methoxy groups of the polymer initiator to the silica surface ($\delta=-51$ to -67 ppm) in the material, confirming a covalent linkage between the silica support and surface organic functionalities. Cleavage of the polymer from the silica surface by treatment with aqueous HF allowed for analysis of the polymer by GPC and solution ^1H NMR spectroscopy. GPC indicated multimodal distributions of polymer molecular weights with number average molecular weights of 28700 Da and 21500 Da relative to poly(styrene) standards for **3a**,**b**, respectively. Integration of the imine, aldehyde, and aromatic protons in the ^1H NMR spectra yielded styrene/styryl–salen ratios of 4.1 and 4.3 for **3a**,**b**, respectively, closely matching the targeted ratio of 4.0. The polymer brushes were metalated with cobalt(II) acetate to form the Co^{II}–salen polymer brush precatalysts (**4a**,**b**). Elemental analysis indicated loadings of 0.30 and 0.28 $mmol\,g^{-1}$ on the basis of cobalt for **4a**,**b**, respectively. Calculations estimated roughly 65 % of the salen ligands were chelated to cobalt. As this work utilizes heterogeneous systems, polymer initiation and ligand metalation suffer from steric hinderance from the silica support and polymer chains. In additional studies using solely polymeric Co–salen systems, elemental analysis indicates slightly higher metalation to the Co–salen complex (70 %). This indicates that complete formation of the complex may only be possible by using small molecules rather than the polymeric or polymer brush systems.

The polymer brush catalysts were activated with acetic acid in air and evaluated in the hydrolytic kinetic resolution (HKR) of epichlorohydrin. A dramatic difference in activity was observed between **4b** and the homogeneous Co–salen catalyst at 0.01 mol % loading (Figure 2). After 20 h, the enantiomeric excesses of the polymer brush catalyst approached 85 % versus 10 % by the benchmark homogeneous Co–salen catalyst. Enantiomeric excesses surpassed 94 % at longer times (72 h, 48 % conversion). This difference in activity was attributed to enhanced cooperativity of the active sites through the polymer brush architecture. In contrast, the bimetallic interactions of the homogeneous catalyst were governed by statistical interactions of the active site in solution. These interactions became increasingly unfavorable, especially at the low 0.01 mol % catalyst concentration, leading to the low activity of the catalyst. Unlike the homogeneous catalyst, lowering catalyst concentration of the polymer brush catalysts only decreased the total mass of catalyst present, without affecting the local concentrations of active sites on the poly(styrene) brush.

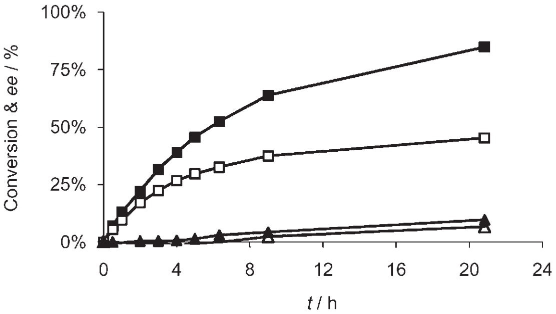


Figure 2. Kinetic data for the HKR of epichlorohydrin at 0.01 mol %: **4b** *ee* (■), **4b** conversion (□), homogeneous Co^{III}–salen *ee* (▲), and homogeneous Co^{III}–salen conversion (△).

At 0.5 mol %, activity of the homogeneous catalyst improved, owing to the increased probability of interactions of active sites in solution (Figure 3). However, **4b** still retained higher activities compared to the homogeneous Co^{III}–salen catalyst. Additionally, **4b** exhibited increased activities over **4a**, a result attributed to two improvements in design: increased flexibility and hydrophilicity of the salen–poly(styrene) linker. The flexibility of the six atom linker between the salen and poly(styrene) backbone permitted three dimensional translational and rotational freedoms, potentially leading to enhanced site–site interactions.[20] The rigid phenylene linker was hypothesized to permit rotational freedom, but restrict translational freedom of the pendant catalyst in **4a**, lessening these interactions. In addition, the hydrophilicity of the ethylene glycol linker of **4b** was envi-

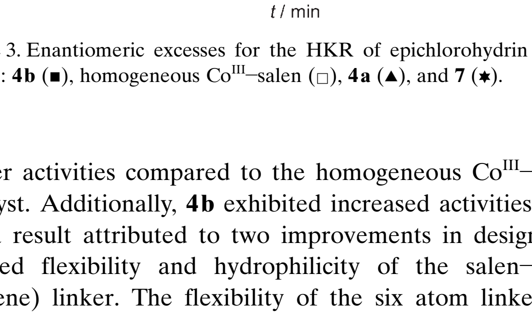


Figure 3. Enantiomeric excesses for the HKR of epichlorohydrin at 0.5 mol %: **4b** (■), homogeneous Co^{III}–salen (□), **4a** (▲), and **7** (✱).

sioned to further aid activities in this multiphase system, owing to its affinity for water near the Co^{III}–salen active sites. Additionally, the longer linker in **4b** would result in less steric hinderance from the poly(styrene) backbone than **4a**. Both catalysts displayed high enantioselectivities during the HKR reaction. Catalyst **4a** displayed 95% *ee* for epichlorohydrin and >99% *ee* for the 3-chloro-1,2-propanediol product after 120 minutes. Catalyst **4b** displayed >99% *ee* for both epichlorohydrin and the diol product after 60 minutes.

For comparison of the catalyst architectures, an analogous Co^{III}–salen catalyst was grafted (Scheme 3) onto mesoporous SBA-15 silica (**7**), similar to previous reports of silica supported salen catalysts.[23,24] Compound **1a** was reacted with 3-mercaptopropyltrimethoxysilane (MPTMS), forming salen-modified silane **5** by means of a thiol coupling. Compound **5** was metalated with cobalt(II) acetate, forming Co^{II}–salen-modified silane **6**. Compound **6** was reacted with mesoporous SBA-15, generating the silica supported Co^{II}–salen precatalyst **7**. Using nitrogen physisorption experiments, decreasing BET surface areas (888 m^{2}g^{-1} to 537 m^{2}g^{-1}) and average pore diameters (80 angstroms to 65 angstroms) were observed after grafting **5** to the silica surface, indicating the organic species were being immobilized within the mesopores. Elemental analysis confirmed a cobalt loading of 0.35 mmol g^{-1} on the silica support. After activation with acetic acid, precatalyst **7** was tested in the HKR of epichlorohydrin at 0.5 mol%. Precatalyst **7** showed greatly reduced *ee*'s of 31% at 22% conversion after 30 minutes. The low activity and selectivity of **7** versus **4a** or **4b** was attributed to poor site–site interactions and hindered Co–salen cooperativity that resulted from the inability to graft high local densities of the salen ligand on the silica surface. This is consistent with related work on epoxide ring-opening with Cr–salen catalysts.[24] Despite possessing lower cobalt loadings, polymer brushes **4a**,**b** were thought to contain higher local concentrations of the cobalt(III)–salen active site, leading to the greatly enhanced activities versus the silica grafted material **7**.

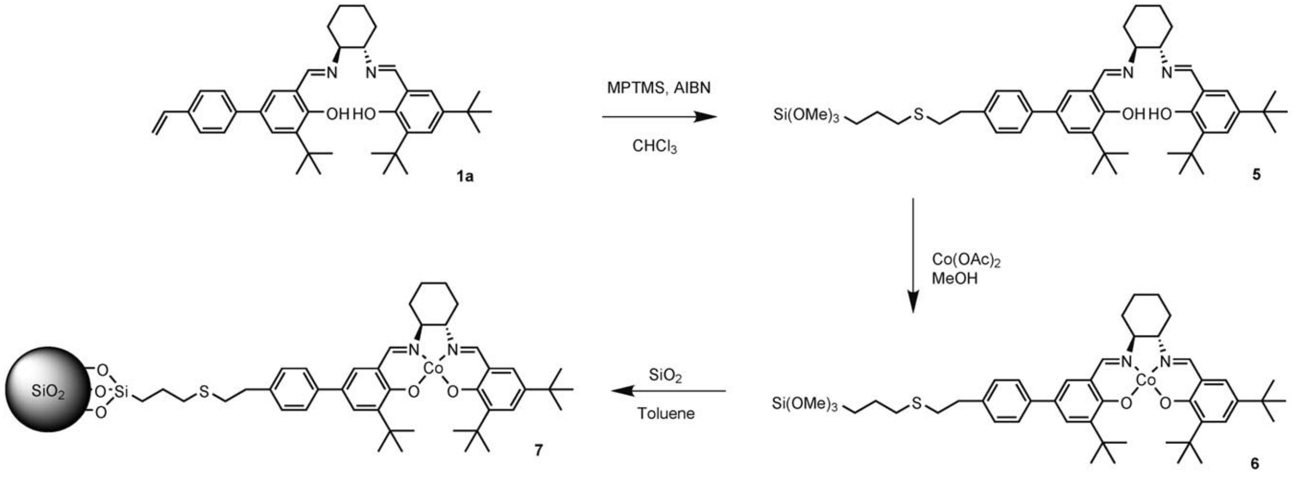
In recycle studies on the most active catalyst **4b**, high enantioselectivities of the remaining epoxide (>99%) were retained after each of five runs, however the reaction rates were observed to decrease after each subsequent run (Table 1). The time required to achieve >99% *ee*'s increased by roughly a factor of ten (45 to 420 min) and maximum initial turnover frequencies (TOFs) dropped from 30.2 to 4.1 min^{-1} after five cycles. These results echo observations by other researchers of retained high selectivities with decreasing activities (or lengthened reaction times) upon recycle of Co–salen catalysts.[6,8,25] However, the deactivation mechanism has yet to be thoroughly investigated.

Table 1. Recycle data for catalyst **4b** at 0.5 mol% catalyst.

Cycle	*t* [min]	Conv. [%]	*ee*[a] [%]	Max initial TOF [min^{-1}]
1	45	55	>99	30.2
2	60	55	>99	25.5
3	120	55	>99	9.4
4	210	55	99	4.8
5	420	52	99	4.1

[a] *ee* corresponds to the enantiomeric excess of the unreacted epichlorohydrin.

Several possibilities existed to explain the catalyst deactivation: cobalt leaching, ligand decomposition, polymer loss (non-surface-bound or cleavage of surface-bound polymer), and/or counter-ion exchange.[2,25] Elemental analysis (EA) and FT-IR of fresh and spent catalysts were compared to elucidate possible deactivation mechanisms. EA indicated significant losses of cobalt and nitrogen in the fresh versus spent catalysts (Figure 4). EA also indicated a 10% carbon loss, 6% hydrogen loss and similar silicon content after five cycles. These data indicated ligand decomposition as the underlying cause of catalyst deactivation. If cobalt leached and the salen ligand remained intact, one would not expect to observe 60% N or 10% C losses. If polymer cleavage or removal of non-surface-bound polymer were the suspected cause, one might expect to observe a linear relationship between Co, and C, H, N losses. Instead the data indicate



Scheme 3. Synthesis of the SBA-15 grafted Co^{II}–salen precatalyst.

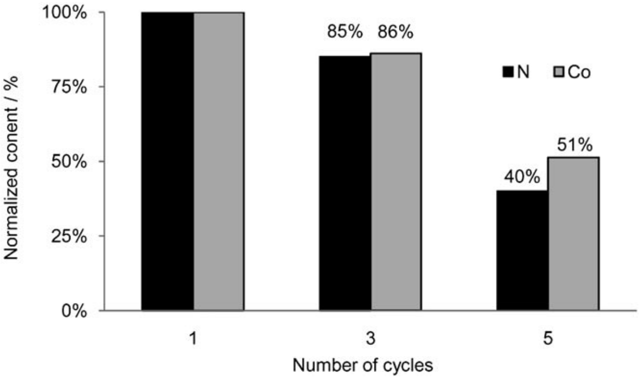


Figure 4. Retention of nitrogen and cobalt in catalyst **4b** upon recycle.

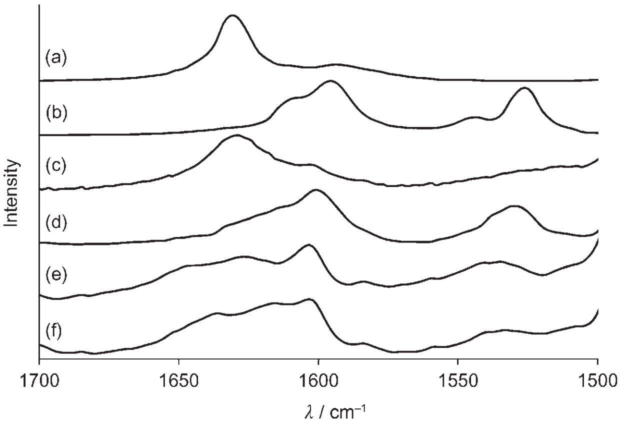


Figure 5. FT-IR spectra of a) non-metalated homogeneous salen ligand, b) homogeneous Co–salen complex, c) non-metalated polymer brush **3b**, d) Co–salen polymer brush **4b**, e) polymer brush catalyst **4b** after 1 cycle, and f) polymer brush catalyst **4b** after 5 cycles.

slight C and H losses and significant Co and N losses, an observation much more consistent with decomposition of the salen ligand. The hypothesized mechanism for this decomposition is presumed to involve cleavage of the imine bonds in the salen ligand. Imines are known to cleave in the presence of water with an acid catalyst. Any acetic acid remaining from the activation step of the Co^{II}–salen to the Co^{III}–salen could catalyze the decomposition of the Schiff base in the presence of water during the HKR reaction. Alternately, unremoved water from the HKR reaction or water vapor absorbed from the air could produce the same result during the activation step with acetic acid (although extensive washing steps with dry THF between cycles was undertaken to minimize residual water). The resulting amine and cobalt species would be removed during the THF washing steps, leading to catalyst loss and possibly explaining the EA results and observed deactivation. It may also be possible that counter-ion exchange was occurring at long reaction times, compounding the problem of salen decomposition. Jain et al. recently suggested counter-ion exchange of Co–OAc to Co–OH could lead to catalyst deactivation.[25] This is consistent with the previous report that the fastest HKR rates were observed when a roughly equal ratio of Co–X ($X = SbF_6^-$) to Co–OH was used, with the Co–OH performing the nucleophilic attack on the epoxide.[2] Therefore it is suggested that a balance of Co–OH and Co–X is required for good activity, although it should be mentioned that no report of the experimental observation or verification of Co–OH species has appeared. In the present work, decomposition of the salen ligand was the presumed cause of deactivation of catalyst **4b**, resulting in reduced rates after two cycles. As the reaction time lengthened, counter-ion exchange to high fractions of Co–OH could be compounding problems, leading to further deactivation of the catalyst. This possibility could not be discounted.

To further investigate catalyst deactivation, FT-IR was utilized to compare the fresh and spent catalysts (Figure 5). The imine bands were the main peaks of interest. Nonmetalated salen ligand displayed a large imine stretch at $\tilde{\nu} = 1631\,cm^{-1}$, which shifted to $\tilde{\nu} = 1596\,cm^{-1}$ upon incorporation of cobalt into the ligand. Unmetalated and metalated polymer brushes **3b** and **4b** displayed similar shifts from $\tilde{\nu} = 1629$ to $1601\,cm^{-1}$, respectively. After 1 and 5 cycles of catalyst **4b**, the imine stretch at $\tilde{\nu} = 1603\,cm^{-1}$ displayed a substantial decrease in intensity. Additionally, evidence of an unmetalated imine stretch in the $\tilde{\nu} = 1630\,cm^{-1}$ region began to reappear as a shoulder, although not nearly as intense as the unmetalated polymer brush **3b**. These results indicate a significant reduction in the Co–salen structure upon reuse of the catalyst. The FT-IR results support the hypothesis of cleavage of the C=N bond, accompanied by loss of cobalt from the fragmenting ligand. Since a strong imine stretch at $1630\,cm^{-1}$ did not reappear in the FT-IR spectra of the spent catalysts, it may be reasoned that just leaching of the cobalt from the intact ligand was not the underlying cause of deactivation.

Conclusion

Presented here is the first example of utilizing pendant polymer brush catalysts for enhancing cooperative catalysis. It is also one of very few examples of polymer brush catalysts in general.[14,15] Additionally, catalyst **4b** appears to be among the most active, solid, insoluble Co–salen HKR catalysts. Results indicate this novel catalyst promotes bimetallic interactions of the Co–salen catalyst, leading to high activities. This type of catalyst could be especially useful for a variety of reactions that are proposed to require cooperative catalysis.[17] This architecture could also be beneficial to obtain higher loadings and/or higher local concentrations of catalyst on insoluble supports versus traditional grafting approaches. The silica support provided for facile recovery of the catalyst in contrast to highly active, but more difficult to recover examples of oligomeric, polymeric, and dendritic materials. In addition to catalyst architecture, a flexible/hydrophilic linker was hypothesized to further aid activity. The polymer brush catalyst was observed to retain high enantioselectivities up to five cycles in the HKR of epichlorohydrin, despite a drop in activity. Cleavage of the salen ligand was the suggested cause of the catalyst deactivation as indicated by FT-IR and elemental analysis investigations of the spent catalyst.

Experimental Section

General: Reagents were used as received unless otherwise noted. Dichloromethane (DCM) was dried by passing through columns of activated alumina. Toluene and tetrahydrofuran (THF) were dried by passing through columns of activated copper oxide and alumina successively.[26] Styrene was dried over activated 3 Å molecular sieves, purified by distillation, and stored in a nitrogen glovebox. Non-porous CAB-O-SIL M5 fumed silica (BET surface areas 200 m^2g^{-1}) was purchased from Cabot Corporation (Tuscola, IL, USA), dried under vacuum (200 °C, 3 h), and stored in a nitrogen glovebox prior to functionalization. ^{1}H and ^{13}C NMR spectra were acquired with a Varian Mercury 400 MHz spectrometer, and chemical shifts (δ) were reported in ppm with reference to the corresponding residual nuclei of the deuterated solvents. Cross-polarization magic-angle spinning (CP-MAS) solid-state NMR spectra were collected by using a Bruker DSX 300 MHz instrument. Samples were packed in 7 mm zirconia rotors and spun at 6.6 kHz. Typical ^{13}C CP-MAS parameters were 3000 scans, a 90° pulse length of 4 μs, and recycle times of 4 s. Typical ^{29}Si CP-MAS parameters were 5000 scans, a 90° pulse length of 5 μs, and recycle times of 5 s. Mass spectra were analyzed using a VG 7070 EQ-HF hybrid tandem mass spectrometer. Transmission electron microscopy experiments (TEM) was performed using a Hitachi HD-2000 field emission gun microscope. Gel-permeation chromatography (GPC) analyses were performed with American Polymer Standards columns equipped with a Waters 510 pump and UV detector, using poly(styrene)s as standards for calibration and THF at a flow rate of 1.0 mL min^{-1} as the mobile phase. Enantiomeric excesses were determined by capillary gas-phase chromatography (GC) analysis on a Shimadzu GC 14 A instrument equipped with a FID detector and a Chiraldex γ-TA column (40 m × 25 mm × 0.25 μm). A Netzsch Thermoanalyzer STA 409 was used for thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10 °C min^{-1} in air. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker IFS 66 V/S or Bruker Equinox 55 spectrometers by dispersing samples in potassium bromide pellets. A Fischer Scientific FS60 H, was used for ultrasonication purposes to disperse samples in solution. Elemental analyses were performed by Desert Analytics Lab (Tucson, AZ, USA).

Synthesis of grafted ATRP initiator (2): The initiator 3-(trimethoxysilyl)-propyl 2-bromo-2-methylpropanoate was synthesized as previously reported.[19] The product was purified by distillation and stored in a nitrogen glovebox. Non-porous CAB-O-SIL M-5 fumed silica (1.00 g), which was previously dried under vacuum (200 °C, 3 h) prior to use, was suspended in dry toluene (30 mL) in a nitrogen glovebox. 3-(Trimethoxysilyl)propyl 2-bromo-2-methylpropanoate (1.00 g) was added. The mixture was sonicated (15 min) to disperse the silica and refluxed under an argon atmosphere (48 h). The solid was filtered and washed with copious amounts of toluene, hexanes, methanol, and diethyl ether. The immobilized bromoisobutyrate initiator (**2**) was dried under vacuum (150 °C, 3 h) and stored in a nitrogen glovebox. TGA of the solid revealed that approximately 0.24 mmol g^{-1} of the bromoisobutyrate initiator was grafted on the silica surface. IR (KBr): $\tilde{\nu}$ = 3430, 2953, 2852, 1727 (C=O), 1630, 1100, 815 cm^{-1}.

Synthesis of polymer brushes (3a,b): A pressure reactor (50 mL) was charged with styryl-modified salen ligand (**1a** or **1b**, 0.5 mmol), toluene (5 mL), immobilized bromoisobutyrate initiator (**2**, 0.30 g), styrene (0.21 g, 2 mmol), and 2.5 mL of a copper (I) bromide/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) mixture (2 mmol HMTETA, 1 mmol CuBr, and 30 mL toluene) in a nitrogen glovebox. The mixture was sonicated (15 min) to disperse the silica and stirred (110 °C, 72 h) under argon. The reaction mixture was cooled to room temperature, opened to air, sonicated (30 min), and the solid was isolated by centrifugation. The particles were re-dispersed in dry toluene (40 mL), sonicated (30 min), and allowed to stand overnight. The green precipitate was removed, and the polymer brushes were then recovered by centrifugation. The particles were re-dispersed in dry toluene (40 mL), sonicated until no particles were visually observed (30 min), and the washing procedure was repeated 6 times. Thermal induced polymerization of styrene likely generated polymer chains not attached to the silica surface. The extensive washing steps were undertaken to minimize free polymer chains from the solid material. The polymer brushes were dried under vacuum at room temperature overnight. TGA of **3a** indicated an organic loading of 50%. ^{13}C CP-MAS NMR (300 MHz, 25 °C): δ = 25–50 (aliphatic), 73 (CH−N), 120–145 (aromatic), 158 (C−O), 165 ppm (C=N); ^{29}Si CP-MAS NMR (300 MHz, 25 °C): δ = −110, −105, −90, −65, −60, −50 ppm; IR (KBr): $\tilde{\nu}$ = 3430, 3086, 3063, 3031, 2957, 2934, 2865, 1727 (C=O), 1630 (s, C=N), 1456, 1102, 815, 703; TGA of **3b** indicated an organic loading of 48%; ^{13}C CP-MAS NMR (300 MHz, 25 °C): δ = 25–80 (aliphatic, cyclohexyl, CH_2-O), 120–145 (aromatic), 159 (C−O), 166 ppm (C=N); ^{29}Si CP-MAS NMR (300 MHz, 25 °C): δ = −110, −102, −90; and −66, −57, −50 ppm (CP MAS ^{13}C and ^{29}Si spectra contained in the Supporting Information); IR (KBr): $\tilde{\nu}$ = 3416, 3084, 3061, 3028, 2951, 2930, 2863, 1724 (C=O), 1632 (C=N), 1456, 1104, 803, 700 cm^{-1}.

Cleavage of grafted polymer from silica: The polymer brushes (30 mg, **3a** or **3b**) were dispersed in DCM (20 mL) in a 50 mL polypropylene bottle, and the mixture was sonicated for 30 min. Using proper safety precautions, aqueous hydrofluoric acid (2 M, 20 mL) was carefully added, and the mixture was shaken vigorously for 10 min. The bottle was then allowed to stand for 15 min. The DCM phase was then recovered, washed with water (20 mL) four times, and dried over anhydrous magnesium sulfate. The solvent was roughly removed by a rotovap, and the yellow residue was dried under vacuum at room temperature overnight. The polymer was characterized by ^{1}H NMR and GPC. Cleaved polymer from **3a**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.82–2.0 (m), 1.26 (s), 1.33 (s), 1.43 (s), 3.35 (br, $2NCHCH_2$), 6.30–7.45 (aromatic), 8.35 ppm (br, C*H*=N). Traces of C*H*=O and Ar−O*H* groups were observed at 9.87 and 11.64 ppm, respectively. Integration of C*H*=N and C*H*=O indicated that approximately 5.1% of the salen ligand was hydrolyzed by hydrofluoric acid. Integration of the imine, aldehyde, and aromatic protons indicated a styrene/salen ratio of 4.1, closely matching the desired ratio of 4.0. GPC indicated a multimodal distribution of polymeric molecular weights and M_n = 28 700 Da. It was calculated that only 15% of the available surface initiator sites were converted into polymer chains using Equation (1):

$$I_{\text{eff}} = \text{Org}_{\text{TGA}}/(M_n \cdot I_{\text{loading}}) \tag{1}$$

in which I_{eff} = initiator efficiency, Org_{TGA} = TGA organic loss ($g_{\text{organic}}/g_{\text{material}}$), M_n = number average molecular weight of the cleaved polymer, and I_{loading} = initiator loading (mmol g^{-1}). Cleaved polymer from **3b**: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.8–2.0 (m), 3.31 (br, $2NCHCH_2$), 3.56 (br, OCH_2CH_2O), 4.41 (br, Ar-CH_2-O), 6.30–7.45 (aromatic), 8.35 (br, C*H*=N), 9.87 (C*H*=O), 11.64 ppm (Ar-O*H*). Integration of C*H*=N and C*H*=O indicated that approximately 7.5% of the salen ligand was hydrolyzed by hydrofluoric acid. Integration of the imine, aldehyde, and aromatic protons confirmed a styrene/salen ratio of 4.3, closely matching the desired value of 4.0. GPC studies indicated a multimodal distribution of polymeric molecular weights and M_n = 21 500 Da. Using Equation (1), it was calculated that only 19% of the available surface initiator sites were converted into polymer chains.

Synthesis of Co^{II}–salen polymer brush precatalysts (4a, 4b): A flask (100 mL) was charged with the polymer brushes (**3a** or **3b**, 400 mg) and anhydrous DCM (10 mL) in a nitrogen glovebox. A solution of anhydrous cobalt(II) acetate (80 mg) in anhydrous methanol (10 mL) was then added. A brick-red powder was observed immediately in the reaction mixture. The brick-red suspension was sonicated (30 min) to disperse the particles in the solution. The reaction mixture was refluxed (40 h) under an argon atmosphere. The suspension was then cooled to room temperature and transferred to a centrifuge tube in a nitrogen glovebox. The solid was recovered by centrifugation. Anhydrous methanol (40 mL) was added, the suspension was sonicated (30 min), and the solid was recovered by centrifugation. The washing procedure was repeated 6 times. The brick-red Co^{II}–salen precatalyst was dried under vacuum at room temperature overnight. Elemental analysis (ICP-MS) of the pre-catalyst indicated a cobalt loading of 0.30 mmol g^{-1}. for **4a** and 0.28 mmol g^{-1} for **4b**. The cobalt loading on the polymer chains were calculated from Equation (2):

$$\mathrm{Co_{exp}} = \mathrm{Co_{EA}}/\mathrm{Org_{TGA}} \tag{2}$$

in which Co$_{exp}$ = experimental polymeric cobalt loading (mmol Co g^{-1} polymer) and Co$_{EA}$ = cobalt loading of the solid catalyst as determined by means of elemental analysis (mmol Co g^{-1} solid). The theoretical maximum cobalt loading was calculated from Equation (3):

$$\mathrm{Co_{th}} = 1/(MW_{\mathrm{styrene}} \cdot R + MW_{\mathrm{salen}}) \tag{3}$$

in which Co$_{th}$ = theoretical polymeric cobalt loading assuming complete metalation of the salen monomers (mmol Co g^{-1} polymer), MW_{styrene} = styrene molecular weight (g mol^{-1}), R = styrene/salen ratio as determined by using ^{1}H NMR spectroscopy, and MW_{salen} = styryl–salen molecular weight (g mol^{-1}). The effectiveness of the cobalt metalation step was calculated by using Equation (4):

$$M_{\mathrm{eff}} = \mathrm{Co_{exp}}/\mathrm{Co_{th}} \tag{4}$$

in which M_{eff} = percent efficiency of the metalation procedure. From these calculations, it was determined only 62 % and 68 % of the salen ligands were metalated with cobalt for species **4a** and **4b**, respectively.

Synthesis of Co^{II}–salen grafted silica precatalyst (7): A salen ligand was grafted onto an SBA-15 support using modified methods from literature.[23] A solution of styryl-modified salen ligand (1.80 g, 3.0 mmol, **1a**) in dry chloroform was added to a solution of 3-mercaptopropyltrimethoxysilane (MPTMS, 0.72 g, 3.6 mmol) and AIBN (0.24 g, 1.5 mmol) in dry chloroform. The solution was heated at 80 °C for 24 h and then cooled to room temperature. The solvent was removed under vacuum. Flash chromatography of the crude product with ethyl actetate/hexanes afforded the compound **5** as yellow oil. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 14.15 (brs, 1H; -OH), 13.60 (brs, 1H; -OH), 8.41 (s, 1H; N=CH), 8.18 (s, 1H; N=CH), 7.48 (d, J = 2.4 Hz, 1H; ArH), 7.40 (s, 1H; ArH), 7.38 (s, 1H; ArH), 7.32 (d, J = 2.4 Hz, 1H; ArH), 7.24 (s, 1H; ArH), 7.23 (s, 1H; ArH), 7.20 (d, J = 2.4 Hz, 1H; ArH), 6.99 (d, J = 2.4 Hz, 1H; ArH), 3.59 (s, 9H; OMe), 3.36–3.23 (m, 2H; CH$_2$), 2.93–2.89 (m, 2H; CH$_2$), 2.82–2.78 (m, 2H; CH$_2$), 2.62–2.58 (m, 2H; CH$_2$), 2.04–1.97 (m, 2H; CH$_2$), 1.90–1.88 (m, 2H; CH$_2$), 1.77–1.73 (m, 4H; CH$_2$), 1.47 (s, 9H; CMe$_3$), 1.48–1.46(m, 2H; CH$_2$), 1.43 (s, 9H; CMe$_3$), 1.23 (s, 9H; CMe$_3$), 0.81–0.78 ppm (m, 2H; CH$_2$); ^{13}C NMR (100.6 MHz, CDCl$_3$, 25 °C): δ = 165.72, 165.31, 159.56, 157.66, 139.68, 138.97, 138.65, 137.18, 136.09, 130.37, 128.56, 128.02 127.85, 126.62, 126.52, 125.80, 118.52, 117.60, 72.33, 72.28, 50.56, 36.01, 35.19, 34.95, 34.05, 33.49, 33.20, 31.44, 29.44, 27.62, 24.39 23.05, 8.69, 8.32 ppm (^{1}H and ^{13}C NMR spectra can be found in the supporting information); MS(ESI): m/z: 789 [M^+].

A solution of the salen-modified silane **5** (2.06 g, 2.6 mmol) in dry chloroform was added to a solution of cobalt(II) acetate (0.46 g, 2.6 mmol) in dry methanol. The solution was stirred at room temperature for 4 h and then filtered to afford 6 as a red colored solid. MS(ESI): m/z: 846 [M^+]; elemental analysis calcd (%) for $C_{46}H_{66}N_2SSiO_5Co$: C 65.30, H 7.86, N 3.31, Co 6.97; found: C 65.74, H 7.63, N 3.56, Co 6.22.

SBA-15 was synthesized by a slightly modified method[27] based on published procedures.[28] A solution of (2.0 g) of compound **6** in dry toluene was added to a mixture of SBA-15 (2.0 g) in dry toluene in a nitrogen glovebox. The reaction was stirred under reflux conditions for 24 h, filtered and washed with toluene and hexanes. The red solid obtained was soxhlet extracted with dichloromethane for 12 h, and the resulting solid was dried under vacuum at 50 °C, overnight. Elemental analysis of precatalyst **7** indicated a cobalt loading of 0.35 mmol g^{-1}; IR (KBr): $\tilde{\nu}$ = 2952, 2863, 1610, 1521, 1434, 1388 cm^{-1}; UV/Vis: $\lambda_{\max}$ (ε) = 375, 420 nm.

Procedure for the hydrolytic kinetic resolution of epichlorohydrin: To test the catalyst at 0.5 mol %, a 5 mL pear shaped flask was charged with the Co^{II}–salen polymer brush precatalyst (0.015 mmol using a cobalt basis, **4a**, **4b**, or **7**), DCM (1 mL), glacial acetic acid (0.1 mL), and a triangular stir bar. The flask was sonicated (5 min) to disperse the particles and stirred under air (30 min). The solvent and acetic acid were removed by using a rotovap and dried under high vacuum (30 min) leaving the solid, brown activated Co^{III}–salen polymer brush catalyst. The catalyst was dispersed into racemic epichlorohydrin (234.6 μL, 3 mmol) and chlorobenzene (27.3 μL, internal standard) and immersed into a water bath at room temperature. Deionized water (0.6 equiv, 32.4 μL, 1.8 mmol) was added to initiate the reaction. Samples (2 μL) were periodically removed from the reaction mixture by means of a micropipette, then diluted with anhydrous diethyl ether (2 mL), and passed through a plug of silica gel in a Pasteur pipette to remove the catalyst and water. Conversions and enantiomeric excesses of epichlorohydrin were measured by GC with a Chiraldex γ-TA column with reference to the chlorobenzene internal standard.

Procedure for recycle experiments: Recycle experiments of the polymer brush catalyst were started similarly to the initial experiments. The mass of the dry flask and stir bar was recorded. Catalyst (0.025 mmol using a cobalt basis) was added (scaling other parameters appropriately) and the reaction was performed as described above. The reaction was terminated by addition of excess THF (3 mL). The solid catalyst was recovered by using a centrifuge (2500 rpm, 30 min) and the solution was decanted. Fresh THF (3 mL) was added, and the solid was dispersed by means of sonication. The washing procedure was repeated four times to remove water, chlorobenzene, 3-chloro-1,2-propanediol, and epichlorohydrin. The solid was dried under high vacuum, and the mass of the flask, stir bar, and recovered catalyst was recorded. Recycle experiments were scaled according to the mass of recovered catalyst, as the centrifuge proved insufficient to completely recover the solid particles. Reactivation of the catalyst with acetic acid was performed before each cycle, because it has been shown important for retention of high activities.[25]

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