

Polyglycerol-Supported Co- and Mn-salen Complexes as Efficient and Recyclable Homogeneous Catalysts for the Hydrolytic Kinetic Resolution of Terminal Epoxides and Asymmetric Olefin Epoxidation

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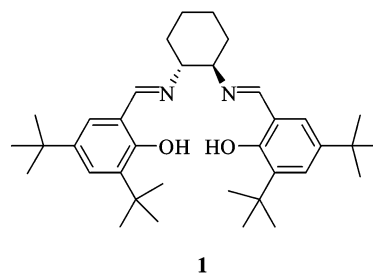
In this report we demonstrate the suitability of hyperbranched polyglycerol as high-loading support for asymmetric catalysis. A polyglycerol-supported unsymmetrical salen ligand was prepared and purified by means of ultrafiltration. The polymeric ligand was metalated with cobalt acetate to afford the corresponding supported Co-salen complex which was further utilized in the hydrolytic kinetic resolution (HKR) of terminal epoxides. Kinetic studies for HKR of 1,2-epoxyhexane using polyglycerol-supported Co-salen showed improved catalytic performance compared to the respective non-immobilized catalyst. This observation points to the presence of a positive dendrimeric effect assuming a cooper-

ative bimetallic mechanism. Furthermore, a polymer-supported Mn-salen catalyst was prepared and successfully applied in the asymmetric epoxidation of olefins. The respective dendritic catalyst was recycled by precipitation up to three times in the epoxidation of 6-cyano-2,2-dimethylchromene (ee up to 95 %). Experiments with repetitive batches revealed enhanced stability of the catalyst as a result of immobilization whereby the total turnover number increased from 23 in a single batch to around 80 for four repetitive batches.

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Introduction

Chiral derivatives of the tetradentate Schiff base^[1] known as salen [$H_2\text{salen}$ = bis(salicylidene)ethylene diamine] have attracted considerable attention in the field of asymmetric catalysis.^[2] The related structure **1**, optimized by Jacobsen and co-workers^[3] is ranked as one of the most important ligands for chiral catalysts.^[4] Over the last decade, diverse metal complexes of salen have been prepared and successfully applied for a multitude of reactions including epoxidation,^[5–8] ring opening of epoxides,^[9–15] Diels–Alder reaction,^[16–19] C–H oxidation,^[20–22] C–H amination,^[23] hydrocyanation^[24–26] aerobic oxidative coupling^[27] and oxidations of ketone silyl enol ethers.^[28–30]



Efforts for the immobilization of achiral salen ligands went on for a long time,^[31] but since the introduction of the efficient chiral types of salen ligands^[3,32–33] as well as the explosion of interest in combinatorial chemistry, this area has grown significantly. Preparation of the corresponding immobilized catalyst is expected to simplify the product recovery and to increase the catalyst stability. The advantage of enhanced stability is especially important in the case of the salen ligand since the degradation tendency is a major limitation for some low-molecular weight salen species such as manganese complexes.^[34,35] Numerous accounts for salen immobilization using diverse kinds of inorganic (e.g. silica,^[19] zeolites,^[36,37] inorganic polymers) or organic supports [e.g. polystyrene,^[15,38–41] polyamidoamine (PAMAM),^[14] poly(ethylene) glycol (PEG),^[40] or poly(norbornene)^[42]] is already outlined in the literature.

Among different classes of supports, star-shaped and hyperbranched polymers are remarkable candidates. Dendritic

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catalyst^[43] preparations are expected to lead to high-loading catalysts with good solubility due to globular shapes of the respective polymers which offer the reward of carrying out the reactions in one-phase systems. The main advantages of homogeneously soluble catalysts comprise normal reaction kinetics, facile compound characterization and absence of diffusion limitations (which is very often the case with heterogenized catalysts). Furthermore, preparation of the corresponding homogeneous polymeric catalyst features the possibility of catalyst recovery via appropriate procedure (e.g. precipitation, ultrafiltration, etc.) and in conclusion, leads to higher Total Turnover Numbers (TTN).

Hyperbranched polyglycerol (PG)^[44,45] is the polymeric support that is utilized in the present work. This soluble polymer is an aliphatic polyether polyol and is easily accessible via anionic ring-opening polymerization of glycidol in kilogram quantities.^[46] PG possess a chemically stable backbone against a multitude of reagents which affords the possibility of performing reactions under a wide variety of conditions.

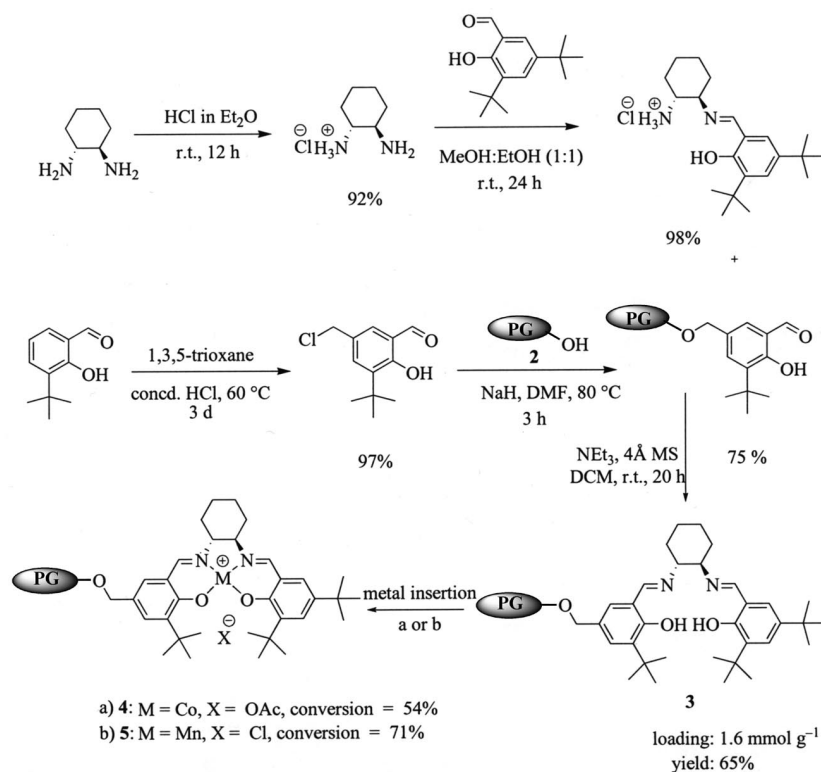
In the past, we have reported^[47] the preparation of a polyglycerol-supported Cr-salen complex and its application for an asymmetric Diels–Alder reaction as well as its retention in a membrane reactor. In this contribution, the preparation of the hyperbranched polyglycerol-supported Co- and Mn-salen complexes via unsymmetrical salen synthesis is reported. Application of the corresponding polymeric catalysts in asymmetric catalysis including hydrolytic kinetic

resolution (HKR) of terminal epoxides and olefin epoxidation is investigated. Moreover, the catalyst retainability has been inspected.

Results and Discussion

Preparation of Co- and Mn-salen Complexes Supported on Polyglycerol via Unsymmetrical salen Synthesis

Symmetrical salen preparation can be simply accomplished following its facile and general synthesis procedure, comprising the condensation of a diamine with two equivalents salicylaldehyde. In contrast, synthesis of unsymmetrical salen bearing different substituents on the two aromatic rings turned out to be problematic and therefore, it is not surprising that there are few publications mainly in the recent years dealing with this approach.^[14,29,41,42,47,48] Recently, we have reported a simple and straightforward procedure for preparation of high-loading polyglycerol salen analogues.^[47,49] The respective method using initial hyperbranched polyglycerol **2** ($M_n = 8000 \text{ g mol}^{-1}$) was applied (Scheme 1) and the final polymeric ligand **3** could be recovered in 65% yield. The NMR analysis indicated the corresponding loading of 1.6 mmol g^{-1} which already reveals the advantage of using dendritic polymer as high-loading support. The polymeric ligand was efficiently purified by means of ultrafiltration using membrane technology



Scheme 1. Preparation of polyglycerol-supported Co- and Mn-salen complexes. a) 1-Co(OAc)₂, MeOH, toluene, 2-glacial acetic acid, toluene, b) 1-Mn(OAc)₂·4H₂O, O₂, DMF, 2-LiCl.

(see Experimental Section) as an alternative for preparative GPC.^[47]

Polymeric salen was loaded with Co by introducing $\text{Co}(\text{OAc})_2$ under inert atmosphere to form red PG-salen- Co^{II} . Prior to use, the Co^{II} complex is catalytically inactive and thus has to be converted into the active Co^{III} complex **4** via one-electron oxidation with acetic acid. In accord with literature reports,^[11,41] the oxidation is accompanied by a the colour change from red to dark brown. Elemental analysis indicated a loading of 0.76 mmol g^{-1} for cobalt which means 54% of salen centers are occupied by cobalt. The final PG-salen-Co catalyst had excellent solubility properties in most of the common organic solvent such as THF, dichloromethane or toluene.

Polyglycerol-supported Mn-salen was prepared by refluxing polymeric salen with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in DMF, while air was bubbled through the reaction mixture. The resultant complex was treated with LiCl for ideal counterion substitution by stirring at room temperature for additional 12 h to afford the final catalyst **5** as brown powder. Elemental analysis showed corresponding loading of 1 mmol g^{-1} for manganese indicating that 71% of salen centers are loaded with manganese.

Hydrolytic Kinetic Resolution of Terminal Epoxides

Breinbauer and Jacobsen^[14] reported on the application of polyamidoamine (PAMAM) as dendrimeric support for salen. Application of the dendrimeric bound catalysts (PAMAM) in the HKR of terminal epoxides showed enhanced reactivity of corresponding catalysts compared to its low molecular weight analogue. This positive dendrimeric effect is probably due to a bimetallic catalysis mechanism which is believed to be followed in HKR of epoxides using salen type catalyst.^[50,51] This led the authors to the assumption that dendrimeric analogues might reinforce cooperative catalytic activity between catalytic units.

These results prompted us to investigate whether any dendrimeric effect is present in case of polyglycerol-supported salen catalyst in HKR of terminal epoxides. Therefore, 1,2-epoxyhexane **7** was chosen as the model epoxide for detailed studies. Kinetic studies for the HKR of **7** catalyzed by monomeric **6** and dendritic **4** cobalt salen catalysts were performed. As shown in Figure 1 and Table 1, a positive dendritic effect was also observed in case of dendritic polyglycerol-supported catalyst since HKR of 1,2-epoxyhexane showed enhanced reactivity of PG bound catalyst **4**, compared to low molecular weight analogue, **6**. This observation also demonstrates on cooperative bimetallic catalysis, conjecturing that the dendritic backbone increases the possibility of intramolecular cooperation between cobalt active sites by bringing the groups adjacent to each other (Figure 2).

For practical HKR, higher catalyst loadings (0.5 mol-%) were applied. HKR of different terminal epoxides was carried out using 0.55 equiv. of water in THF. Reactions were initiated at 0 °C and then warmed up to room temperature.

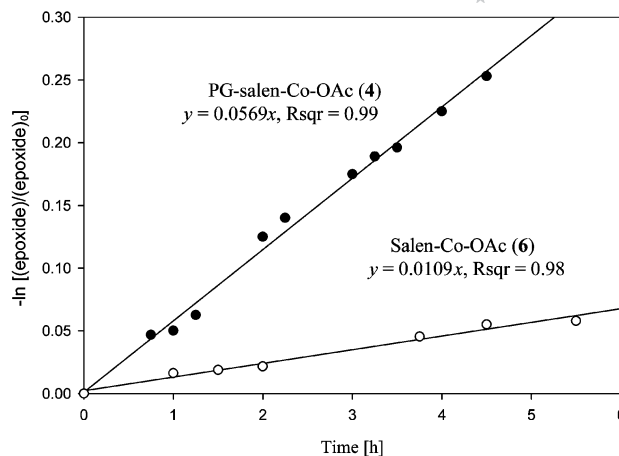


Figure 1. Time course for the HKR of 1,2-epoxyhexane **7** using 0.05 mol-% catalyst and 0.55 equiv. water in THF.

Table 1. Hydrolytic kinetic resolution of *rac*-1,2-epoxyhexane (**7**) at low catalyst loading.

Catalyst	Loading [mol-%]	Diol % <i>ee</i> ^[a]	Conversion %
salen-Co-OAc (6)	0.05	98.0	28.5
PG-salen-Co-OAc (4)	0.05	98.8	32.0

[a] Determined by chiral GC (Chiraldex G-TA).

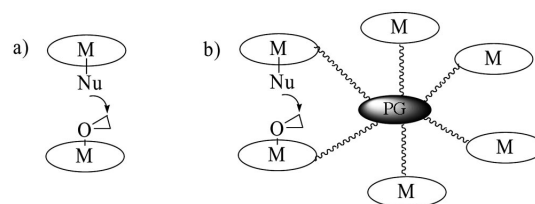


Figure 2. Schematic representation of bimetallic cooperative mechanism^[14] with a) monomeric catalyst and b) dendritic polyglycerol.

As shown in Figure 3, the enantiomeric excess is increased in the course of the reaction and the respective epoxides could be recovered in high *ee* indicating the efficiency of polyglycerol-supported salen cobalt catalyst for HKR of racemic terminal epoxides (Table 2).

Asymmetric Epoxidation of Olefins

As outlined in literature, different forms of salen ligand bearing manganese are competent catalysts for asymmetric epoxidation (AE) of olefins^[7] firstly reported by Jacobsen^[52] and Katsuki.^[53] Therefore, we were keen to check whether the polyglycerol-supported Mn-salen catalyst gives rise to any change in epoxidation reaction in solution compared to its non-immobilized analogues as it was the case for HKR. However, AE proceeds over a significantly different mechanism than HKR. The proposed mechanism of the Jacobsen–Katsuki epoxidation is based on Kochi investigations^[54] where the Mn^{V} -oxido complexes are pos-

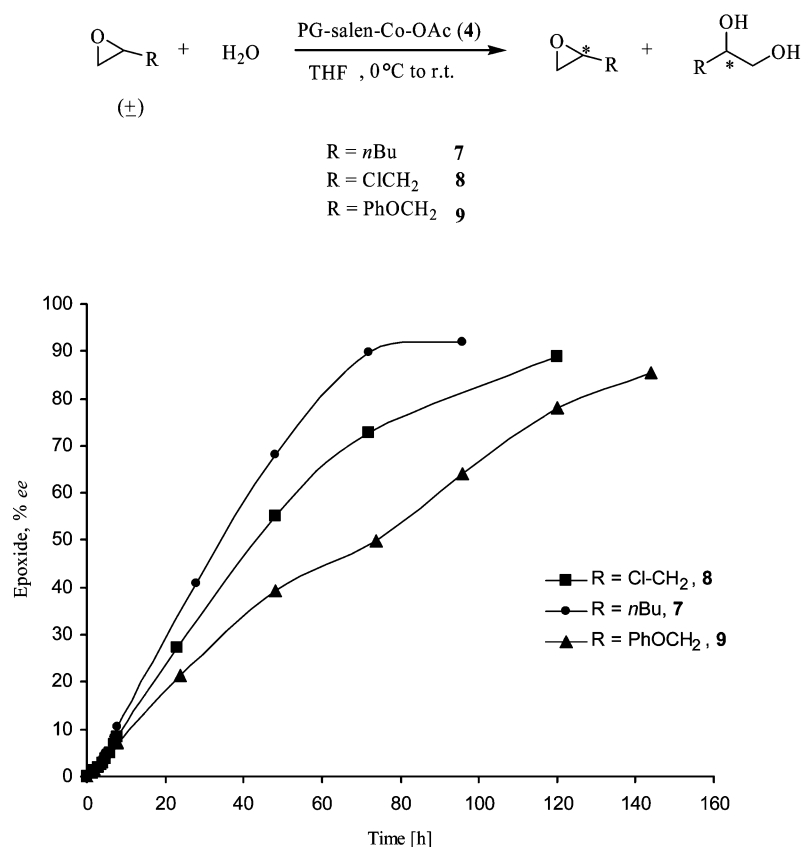


Figure 3. Time course for the enantiomeric excess of different terminal epoxides using PG-supported catalyst **4** (5 mmol epoxide, 0.55 equiv. water and 0.5 mol-% catalyst).

Table 2. Hydrolytic kinetic resolution of different terminal epoxides using PG-supported salen catalyst **4**.

Epoxide	Loading [mol-%]	Epoxide % ee ^[a]	Conversion
1,2-Epoxyhexane (7)	0.5	92.0	50.0
Epichlorohydrin (8)	0.5	90.5	52.5
Phenyl glycidyl ether (9)	0.5	85.3 ^[b]	51.5

[a] Determined by chiral GC (Chiraldex G-TA). [b] Determined by chiral HPLC (Chiral Cel OD).

tulated to be the catalytically active species. The Mn^{III}-salen complex is expected to be converted into a high-valent oxomanganese(V) species through an oxygen transfer from the oxidant. Subsequently, catalytically active oxomanganese(V) species transfer the oxygen further to the olefin double bond and is afterwards eventually converted into the Mn^{III}-salen complex. Nevertheless, beside this redox pathway, dimerization of oxidomanganese(V) with Mn^{III} can also occur, which forms catalytically inactive μ -oxidomanganese(IV) species. As a consequence, the catalyst is deactivated after a few turnovers. For this reason, immobilization has been considered as a proper pathway to enhance the catalyst stability, since it is proposed that anchoring the Mn^{III}-salen moieties to a carrier leads to lower local concentration of the catalyst and also restricted complex mobility (site isolation).^[34,55,56] As a result, the possibility of dimerization is expected to be suppressed.

Different kinds of conjugated olefins were chosen as substrates (Table 3). Following published procedures,^[57] the reactions were carried out by solving the polymeric catalyst **5**, olefin and *N*-methylmorpholine *N*-oxide (NMO) in dichloromethane followed by subsequent cooling of the mixture to the desired temperature. The epoxidation proceeds by adding *m*-chloroperbenzoic acid (*m*CPBA) to the cooled mixture in two equal portions over a period of two minutes. Initial screening and kinetic studies for epoxidation of 6-cyano-2,2-dimethylchromene already revealed significant catalytic activity of polyglycerol-supported Mn-salen since nearly quantitative conversion was reached using 4 mol-% catalyst in less than four minutes (Figure 4). Despite HKR, the presence of a racemic, non-catalytic background epoxidation was observed. Fortunately, this reaction was much slower than the catalytic one, where after 1 h less than 1% conversion is achieved.

The results for the epoxidation of different olefins catalyzed by the homogeneously soluble polyglycerol-supported Mn salen complex are shown in Table 3. All these reactions were very fast and completed in less than 10 min at 0 °C. Decreasing the temperature to –78 °C improved the enantioselectivity, but longer reaction times were needed, probably as a consequence of deficient solubility and lower activity of the polymeric catalyst at low temperatures. The values in parentheses represent reported enantiomeric excess using the free Jacobsen catalyst at –78 °C.^[55] Obviously,

Table 3. Asymmetric epoxidation of different olefins using PG-supported catalyst.

$ \begin{array}{c} \text{R}^1 \quad \text{R}^3 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{R}^2 \quad \text{R}^4 \end{array} \xrightarrow[\substack{2 \text{ equiv. } m\text{-CPBA} \\ 5 \text{ equiv. NMO, DCM}}]{4 \text{ mol-\% catalyst (5)}} \begin{array}{c} \text{R}^1 \quad \text{R}^3 \\ \diagdown \quad \diagup \\ \text{C} - \text{O} - \text{C} \\ \diagup \quad \diagdown \\ \text{R}^2 \quad \text{R}^4 \end{array} $					
0.3 mmol					
Olefin	Time	T [°C]	% Conv. ^[a]	% ee ^[b]	
1 	10	< 10 min	0	quant.	50 (86) ^[c]
2 	10	< 10 min	-20	quant.	55
3 	11	< 10 min	0	quant.	80
4 	11	< 10 min	-20	quant.	81
5 	11	4 h	-78	91	85
6 	12	< 10 min	0	quant.	95 (97)
7 	12	3 h	-78	96	96 (97)
8 	13	3 h	0	60	25
9 	14	< 10 min	0	quant.	90 ^[d] (96)
10 	15	3 h	-78	94	75

[a] Conversion calculated on the basis of GC (HP-5) data related to an internal standard. [b] Determined by chiral GC (Cyclodex-B). [c] Data in parentheses represent enantiomeric excess reported using the free Jacobsen catalyst at -78 °C. [d] Determined by measuring optical rotation.

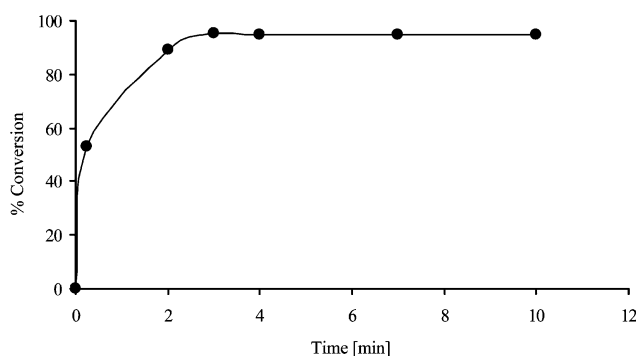
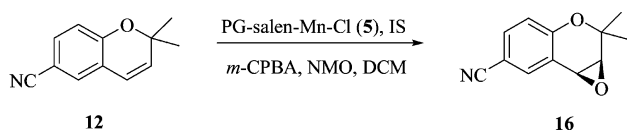


Figure 4. Asymmetric epoxidation of 6-cyano-2,2-dimethylchromene **12** with **5** (100 mM olefin, 50 mM IS, 200 mM *m*CPBA, 500 mM NMO, 4 mM catalyst **5**, 3 mL DCM, 0 °C).

the polyglycerol-supported catalyst **5** showed very high activity, most often comparable to its low molecular weight analogue (Table 3, entry 6,7), in epoxidation reaction.

Repetitive Batch Operation

One of the main advantages of catalyst immobilization is offering the possibility of catalyst recycling that is important in view of economy and applicability. Moreover, as already mentioned, a major limitation for low-molecular weight species of salen manganese complexes is their inherent degradation tendency.^[34,35] Therefore, we tried to find out whether the dendritic catalysts can be recycled and whether the polymeric catalyst preparation leads to enhanced catalyst stability.

Recycling of the dendritic catalyst in repetitive batch experiments was realized by precipitation with hexane. Polyglycerol-supported salen-Mn-Cl, **5**, used in the epoxidation of 6-cyano-2,2-dimethylchromene, could be recycled via this procedure up to three times (see Table 4). The maximum conversion was decreased with each catalyst recycling step, but nevertheless the second run showed nearly identical results to the first run in terms of conversions and 75% conversion could be still achieved in the forth run after 10 min. The *ee* values of each run showed a decrease after each recycling step from 95% for the first run to 88% in the forth run. Most probably metal leaching is the reason for loss of catalyst efficiency in the current experiment since the dark brown colour of the polymeric catalyst faded by each recycling step as similar observation is documented in the literature.^[40] As a consequence the racemic side reaction became more prominent.

Table 4. Repetitive batch operation of catalyst **5** in epoxidation of 6-cyano-2,2-dimethylchromene **12** at 0 °C.

Cycle	Time [min]	% Conversion ^[a]	% ee ^[b]
1	< 5	98	95
2	< 5	96	92
3	< 5	90	91
4	< 5	75	88

[a] Conversion calculated on the basis of GC (HP-5) data related to 2-naphthonitrile as internal standard. [b] Determined by chiral GC (Cyclodex-B).

In order to assure the absence of catalyst cleavage from the polymeric backbone, a control experiment was carried out: after separation of the polymeric catalyst by filtration, the remnant of the reaction mixture was reused by addition of substrate without appending any fresh catalyst. Since no further formation of epoxide could be detected, the hypothesis of salen catalyst release from the polyglycerol backbone can be excluded. The Total Turnover Number (TTN) is calculated to be increased from 23 for a single batch to around 80 for four repetitive batches which already represent increased catalyst stability as a result of recycling possibility.

Conclusions

In this contribution, the suitability of hyperbranched polyglycerol as high-loading support is evaluated. An unsym-

metrical salen ligand was prepared through a simple and straightforward procedure and subsequently bound to the preformed polyglycerol. The high-loading polyglycerol salen analogue was successfully purified by means of ultrafiltration. The corresponding cobalt- and manganese-loaded catalysts showed very high activity and selectivity in HKR of racemic epoxides and olefin epoxidation. Interestingly, kinetic studies revealed the presence of a positive dendrimeric effect for dendritic polyglycerol, since HKR of 1,2-epoxyhexane showed enhanced reactivity for the PG-bound catalyst, compared to the low molecular weight analogue. This observation supports a cooperative bimetallic mechanism.

The polymer-supported Mn-salen catalyst used in epoxidation of 6-cyano-2,2-dimethylchromene could be recycled by precipitation up to three times. The results of repetitive batches operation confirmed the fact that immobilization simplifies product recovery and led to increased catalyst stability (TTN). The advantage of enhanced stability is of utmost importance in the case of the salen manganese complex since the degradation tendency is a major limitation for its low-molecular weight analogues.

Experimental Section

General: Starting materials were purchased from Aldrich, Fluka or Acros and used without further purifications unless mentioned otherwise. The solvents used in the reactions were of p.a. quality or purified and dried according to standard methods. ^1H NMR Spectra: Varian Unity Plus 600 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform; ^1H : 7.24 ppm). IR spectra: Bruker IFS 28-Spectrometer or a Digilab FTS 4000. Capillary gas chromatography (GC) for determination of enantiomeric excess or conversion calculation (related to an internal standard): Hewlett–Packard (Agilent) GC, HP 6890, column: achiral HP-5 (30 m $\times$ 0.32 mm $\times$ 0.25 μm), detector: FID, carrier gas: H_2 ; Hewlett–Packard (Agilent) GC, HP 5890, column: Supelco[®] β -DEX 120 (30 m $\times$ 0.25 $\times$ 0.25 mm) from Whisky and Cognac lacton or ChiralDEX G-TA (30 m $\times$ 0.25 mm) from Advanced Separation Technologies Inc., detector: FID, carrier gas: H_2 . High Performance Liquid Chromatography (HPLC): Hewlett–Packard (Agilent) HPLC, HP 1100, binary pump, column: Chiralcel[®] OD (250 mm $\times$ 4.6 mm) from DAICEL Chemical Industries, LTD, detector: UV. Atomic Absorption Spectroscopy (AAS): Video 22, AA/AE spectrometer from Instrumentation Laboratory.

Polyglycerol-Supported salen Ligand 3: Preparation from hyperbranched polyglycerol ($M_n = 8000 \text{ g mol}^{-1}$, OH group loading: 13.5 mmol g^{-1}) according to ref.^[47] Purification of the crude product via ultrafiltration (as an alternative for preparative GPC) described below led to pure **3** with 1.6 mmol g^{-1} ligand loading as determined by NMR spectroscopy.

General Procedure for Purification of Crude Polymeric Ligand 3 via Ultrafiltration: A stainless steel ultrafiltration cell, with a reaction volume of 10 mL was applied. Toluene was used as the solvent and was pumped through the reactor using a piston pump (Pharmacia P 500). The membranes [Starmem 120 ($\text{MWCO} = 200 \text{ g mol}^{-1}$)] from Membrane Extraction Technology^[58] were preconditioned in the solvent overnight before being installed in the reactor. Prior to addition of crude polymeric ligand **3** the membrane was thoroughly rinsed with solvent (flow rate: 50 mL h^{-1}) until a constant pressure of 1 MPa was reached. Then polymer (ca. 0.5 g) was charged to

the reactor and volume fractions were collected at the reactor outlet. Solvent was flushed through the reactor until 35 residence times were collected. Then the reactor outlet was connected to the second inlet of the reactor and the retained polymer was collected for up to 5 residence times. Evaporation of the solvent delivered (ca. 0.3 g) of pure **3**; yield 60%.

Complex 4: In a one-necked Schlenk flask, purple solution of $\text{Co}(\text{OAc})_2$ (0.085 g, 0.48 mmol, 1.5 equiv.) in dry MeOH (5 mL) was dropped into the yellow solution of **3** (0.2 g, 1.64 mmol g^{-1} , 0.32 mmol) in dry and degassed toluene (15 mL) under Ar where the solution turned dark red over orange. The mixture was stirred for 24 h. Then the mixture was concentrated and the residue was dissolved in p.a. DCM and was filtered in order to remove surplus cobalt acetate. Concentration of the filtrate gave the cobalt(II) complex as a dark red solid. IR (neat): $\tilde{\nu} = 2949, 2920, 2857, 1597, 1530, 1438, 1383, 1318, 1256, 1203, 1165, 1085, 1042, 940, 897, 787, 730, 694, 641, 568 \text{ cm}^{-1}$.

The Co^{II} complex was dissolved in toluene (10 mL) and treated with glacial acetic acid (37 μL , 0.6 mmol). The mixture was stirred without exclusion of air for 2 h during which time the colour turned to brown. Concentration of the solution under vacuum afforded **4** as a brown solid. According to AAS measurements, loading of 0.76 mmol g^{-1} for cobalt was found; conversion: 54%. ^1H NMR (CDCl_3 , 600 MHz): $\delta = 7.3\text{--}7.15$ (br. s, 2 H, $\text{CH}=\text{N}$), 7.1–6.9 (br. m), 3.0 (br., 2 H), 2.6–2 (br. m, PG backbone), 1.9–0.8 (br. m, 38 H) ppm. IR (neat): $\tilde{\nu} = 2959, 2864, 1608, 1528, 1436, 1385, 1320, 1258, 1167, 1086, 1016, 867, 796, 693, 568 \text{ cm}^{-1}$.

Complex 5: A solution of the polymer-bound ligand **3** (0.3 g, 1.64 mmol g^{-1} , 0.48 mmol) in DMF (150 mL) was heated to 90°C . Upon addition of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.58 g, 2.4 mmol, 5 equiv.) the colour of the mixture changed from yellow to dark brown. Heating was continued for another 3 h during which time air was bubbled through the solution by means of a glass tube pipe. Afterwards, LiCl (0.2 g, 4.8 mmol, 10 equiv.) was added and the mixture was cooled down. After stirring the solution for 1 h at room temperature, the mixture was filtered and the solvent removed under reduced pressure. Then DCM (150 mL) was added and the brown organic layer was washed with brine and H_2O , respectively. The organic layer was dried with Na_2SO_4 , filtered and evaporated to afford **5** as a brown powder. According to AAS measurements the metal loading was 1 mmol g^{-1} for Mn; conversion: 71%. IR (KBr): $\tilde{\nu} = 2961$ (m), 2870, 1655, 1616 (s, $\text{C}=\text{N}$), 1542, 1437, 1261 (s), 1096 (m), 1026 (s, PG backbone), 864, 802 (m), 699, 568 cm^{-1} .

General Procedure for Hydrolytic Kinetic Resolution of Racemic Terminal Epoxides: The exact amount of the catalyst was dissolved in THF (2 mL). After the addition of epoxide (5 mmol, 1 equiv.), the mixture was cooled to 0°C . After 1 h, deionized H_2O (3.5 mmol, 63 μL , 0.7 equiv.) was added and the mixture was left to warm up to room temperature. Progress of reaction was monitored via GC (for **7** and **8**, Cyclodex γ -TA) or HPLC (for **9**, ChiralCel OD, hexane/*i*PrOH used as eluent).

General Procedure for Kinetic Experiments: The proper catalyst (0.012 mmol based on cobalt), *rac*-1,2-epoxyhexane **7** (3 mL, 25 mmol) and 1-(2-methylbutyl)benzene (200 μL ; as internal standard) were dissolved in 4 mL of THF. After the reaction mixture was stirred for 1 h at $0\text{--}4^\circ\text{C}$, H_2O (250 μL , 14 mmol, 0.55 equiv.) was added. 10 μL samples were withdrawn at certain times. In order to remove H_2O and the polymeric catalyst, samples were passed through a thin layer of silica using Et_2O as eluent. Then the samples were analyzed by GC. [HP-5, inj. temp. 300°C , det. temp.: 300°C , flow rate: 25 mL min^{-1} , $50^\circ\text{C}/0 \text{ min}/10^\circ\text{C min}^{-1}/300^\circ\text{C}$, t_R

(epoxide) = 3.2 min, t_R (internal standard) = 5.8 min, t_R (diol) = 6.1 min].

General Procedure for Epoxidation of Unfunctionalized Olefins: To a solution of salen-Mn-Cl type catalyst (0.0123 mmol, 4 mol-%) in DCM (3 mL), olefin (0.31 mmol), internal standard (0.16 mmol, 0.5 equiv.) and NMO (0.18 g, 1.54 mmol, 5 equiv.) were added. When the reaction mixture was cooled down to the desired temperature, *m*CPBA (0.15 g, 0.6 mmol, 2 equiv.) was added. After the reaction was complete 1 N KOH and DCM were added. Drying the organic layers with $MgSO_4$ and removal of the solvent yielded crude epoxide.

General Procedure for Repetitive Batch Experiments: To a solution of PG-supported Mn-salen (0.022 g, 0.55 mmol Mn g⁻¹, 0.0123 mmol metal, 0.04 mol-%), 2,2-dimethyl-2H-1-benzopyran-6-carbonitrile (0.057 g, 0.31 mmol) and 2-naphthonitrile as internal standard (0.022 g, 0.15 mmol) in DCM, NMO (0.18 g, 1.54 mmol, 5 equiv.) was added. After cooling the reaction mixture to the desired temperature, *m*CPBA (0.15 g, 0.6 mmol, 2 equiv.) was added. After 5 min, the reaction was completed and H₂O as well as DCM were added. After drying the organic layers with $MgSO_4$, the solvent was removed and the catalyst was precipitated from hexane. The recovered catalyst was reused in the next batch under the same condition as previously for the first step.

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