Formation and Structure of Conjugated Salen-Cross-Linked Polymers and Their Application in Asymmetric Heterogeneous Catalysis

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A new type of cross-linked condensation polymer was obtained by the reaction of 1,3,5-tris[(5-*tert*-butyl-3-formyl-4-hydroxyphenyl)ethynyl]benzene (**1**) with ethylenediamine. Solid-state $^{13}C\{^1H\}$ CP/MAS NMR analysis showed that the polymer was pure and highly cross-linked and powder synchrotron X-ray diffraction indicated some degree of local structural order in the polymer. A chiral manganese–salen-bridged polymer was obtained by the condensation of **1** with (1*R*,2*R*)-1,2-diphenyl-1,2-diaminoethane (**3a**) or (1*R*,2*R*)-1,2-diaminocyclohexane (**3b**) in the presence of $Mn(OAc)_2$. These rigid chiral metal–salen polymers can catalyze the epoxidation of *cis*-2-methylstyrene with high conversion, diastereoselectivity and enantioselectivities of up to 67% *ee*. The polymeric catalyst can be reused several times without reduced activity or selectivity.

Introduction

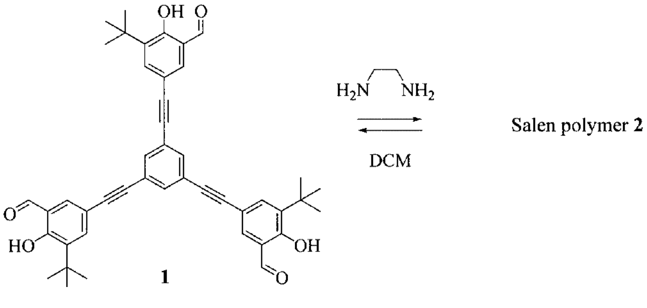
Crystalline solid-state organic and metal−organic frameworks are well known in supramolecular chemistry.[1,2] The formation of covalently linked organic polymers that possess the same degree of structural order has, on the other hand, rarely been reported. Highly conjugated all-carbon or carbon-rich 2D or 3D polymers are of immense interest owing to their use as organic conductors.[3,4] Such materials also have potential applications as catalysts. Heterogeneous chiral metal−organic catalysts have received much attention owing to the ease of recovery and the reuse of the often expensive catalysts. Derivatives of otherwise homogeneous catalysts can be immobilized on solid supports such as organic resins[5] or in dendrimers.[6] In some cases the catalyst itself is part of the polymeric network, for example, as reported by Pu[7] and Salvadori[8] and their co-workers. Previously, we reported the synthesis of new salen complexes,[9] their immobilization on gold surfaces,[10] and their application in DNA-directed coupling reactions.[11,12]

In this paper we report the formation and structure of a new type of condensation polymer formed by the condensation of a rigid trialdehyde with ethylenediamine. The condensation of this trialdehyde with chiral diamines and manganese acetate led to the formation of chiral manganese−salen-linked polymers. The catalytic properties of these chiral manganese−salen-linked polymers in epoxidation reactions have been explored.

Results and Discussions

Salen-Linked Polymer

The metal-free polymer **2** was formed by condensation of trisalicylaldehyde **1** with ethylenediamine (EDA). The trisalicylaldehyde **1** is a rigid compound in which the conformational freedom is limited to rotation around the bonds of the ethynyl and *tert*-butyl groups. It was obtained in a few synthetic steps from 1,3,5-triethynylbenzene and 3-*tert*-butyl-5-iodosalicylaldehyde.[13] Compound **1** was treated with ethylenediamine in dichloromethane and salen polymer **2** was formed (Scheme 1).



Scheme 1

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Polymer **2** was obtained as a yellow gel after filtration and contains a substantial amount of solvent (DCM). On drying under ambient conditions for a couple of hours the solvent was evaporated and **2** formed a hard solid which did not swell again on addition of DCM or other solvents. The salen-forming reaction is reversible in excess ethylenediamine and in the absence of metals.[9,14] In a test reaction we observed that the polymer dissolves in a DCM solution containing 0.15 M EDA. The product obtained by the dissolution of **2** in the presence of EDA was the tris-EDA-monoimine of **1**, as verified by ^{1}H NMR spectroscopy and mass spectrometry. Equilibrium conditions favor the formation of the thermodynamically most stable and structurally most ordered polymer. Compound **1** is a rigid planar building block and the salen complexes that connect the monomers may adopt a coplanar structure. In the ideal case polymer **2** would adopt a planar hexagonal structure, as depicted in Figure 1 (a), but we believe that hexagons only appear locally in the polymer. To analyze the structure of polymer **2**, solid-state ^{13}C{^{1}H} cross-polarization (CP) magic-angle spinning (MAS) NMR spectroscopy and powder synchrotron X-ray diffraction (Figure 1 and Figure 2) were employed. The ^{13}C{^{1}H} CP/MAS NMR spectrum of the salen polymer **2** (see d in Figure 1) shows a number of close and rather broad resonances, typical of a polymer with mobile side-chains bonded to a nonflexible backbone that consists of a quaternary and protonated carbon skeleton. Since the ^{13}C MAS NMR spectrum was acquired by using cross-polarization, the relative intensities of the individual resonances might not be quantitatively correct. However, a single-pulse ^{13}C MAS NMR spectrum of the salen polymer confirmed that resonances from all of the ^{13}C sites in the polymer sample are observed in the ^{13}C{^{1}H} CP/MAS NMR spectrum.

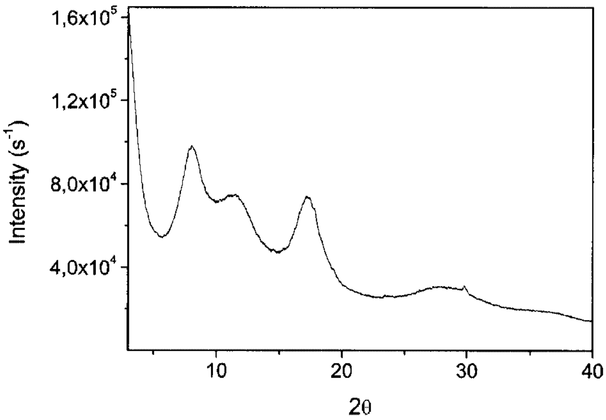


Figure 2. Powder synchrotron X-ray diffraction[16] of polymer **2** loaded in a quartz capillary (0.7 mm), λ = 1.0829 Å

The ^{13}C resonances were assigned to the 14 distinct carbon atoms in the asymmetric unit (Figure 1, a) by employing additional information obtained from ^{13}C{^{1}H}

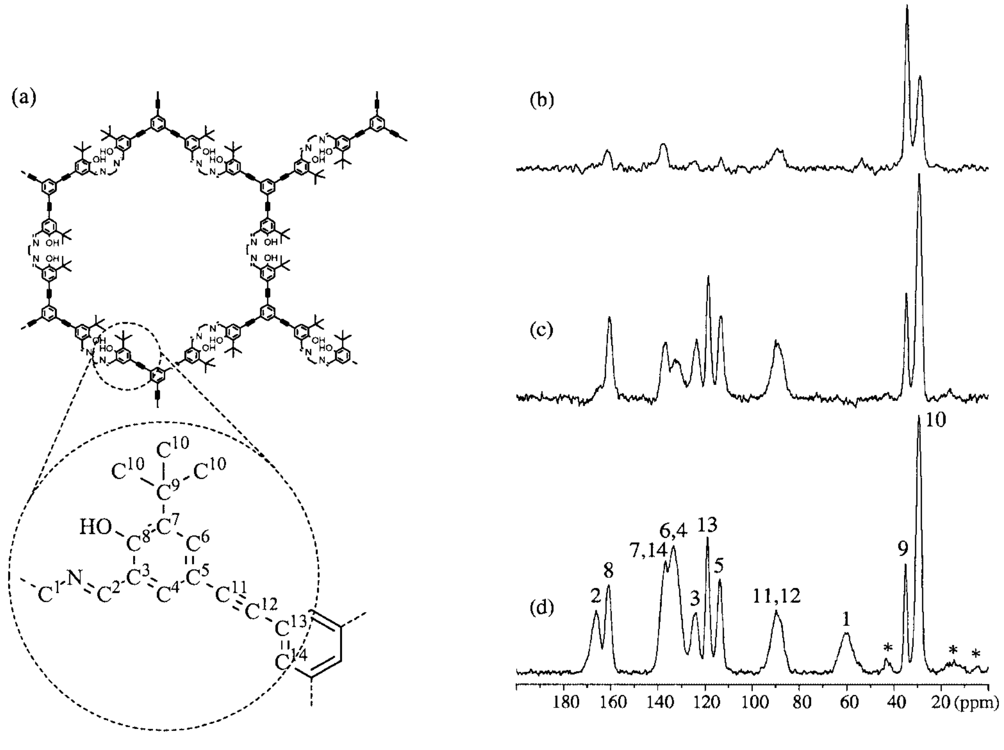


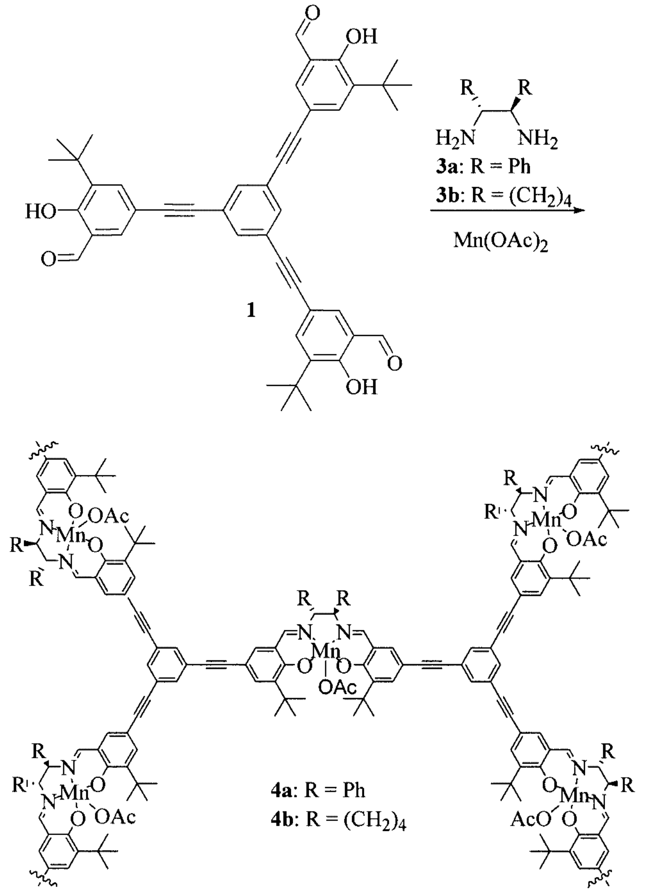
Figure 1. (a) Fragment of an ideal hexagonal structure of salen polymer **2** and assignment of the carbon atoms in the asymmetric unit; (b)–(d) ^{13}C{^{1}H} MAS NMR spectra (7.05 T) of **2** recorded with a spinning speed of 9.0 kHz; (b) spin-echo MAS spectrum obtained without decoupling during the echo period (2τ = 7.14 ms), a 15 s repetition delay, and 5200 scans; (c) cross-polarization-depolarization (CPD) MAS spectrum recorded with a CP contact time of 5.0 ms, a CPD depolarization time of 80 μs, a repetition delay of 5 s, and 1024 scans; (d) standard CP/MAS NMR spectrum obtained with a CP contact time of 5.0 ms, a repetition delay of 5 s, and 2048 scans; the asterisks indicate spinning sidebands while the numbers give the assignment of the resonances to the individual carbon atoms in the asymmetric unit shown in part (a)

cross-polarization-depolarization (CPD)[15] experiments combined with ^{13}C chemical shift−structure relationships established by liquid-state NMR spectroscopy. In the $^{13}C\{^1H\}$ CPD/MAS NMR spectrum (Figure 1, c) recorded with a short depolarization time (τ_{CPD} = 80 μs), the resonances from the CH and CH_2 groups vanish completely, which allows the resonances at δ = 59.6 and 166.2 ppm to be assigned to the C^1 and C^2 atoms of the polymer (Figure 1, a). The unsubstituted aromatic carbon atoms (C^4, C^6, and C^{14}) are observed as partly overlapping resonances in the range of 133−137 ppm. The complete assignment of the resonances in the $^{13}C\{^1H\}$ CP/MAS NMR spectrum to the carbon atoms in the asymmetric unit of polymer **2** is shown above in the spectrum in Figure 1, d. Most importantly, the absence of a resonance from an aldehyde group ($\delta_{iso} \approx$ 185−210 ppm) demonstrates that residues of monomer **1** used in the synthesis are not present in polymer **2**. The clear distinction between CH, CH_2 and C, CH_3 groups in the $^{13}C\{^1H\}$ CPD/MAS experiment indicates that a rigid polymer framework structure exists with rotating *t*Bu groups. This is further supported by the $^{13}C\{^1H\}$ spin-echo MAS NMR spectrum (Figure 1, b) obtained without ^1H decoupling during the full echo period (2τ = 7.14 ms) in which signals are suppressed for all carbon resonances except for the aliphatic C^9 and C^{10} atoms. This is caused by dipolar dephasing for all rigid carbon atoms during the quite long spin-echo period. Finally, this spectrum demonstrates that the *t*Bu groups exhibit a high degree of mobility (i.e., rotation around the C^7−C^9 axis).

Powder synchrotron X-ray diffraction was also performed on polymer **2**. The polymer displayed diffraction which indicates some degree of local order in the polymer. However, the broadness of the diffraction peaks makes it impossible to unequivocally index the peaks. The structural correlation length was estimated to be approximately 30 Å from the full width at half maximum of the observed diffraction peaks. This low structural correlation length suggests that ordered local domains are very small.

Chiral Metal−Salen Polymers

Salen ligands have been used with tremendous success with a wide range of metals in the preparation of stable homogeneous metal−ligand complexes.[17] In particular chiral manganese−salen complexes have proven successful in the Jacobsen asymmetric epoxidation.[14] Thus, with the achiral polymer described above at hand, the next target was to explore the applicability of chiral derivatives of this new type of polymer as a ligand for chiral catalysts. The manganese−salen-linked polymers **4a,b** were obtained by the condensation of **1** with the amines **3a**,**b** in the presence of $Mn(OAc)_2$ (Scheme 2). Trialdehyde **1** and $Mn(OAc)_2$ were mixed and stirred in CH_2Cl_2. The diamine of choice was added and the reaction mixture was stirred for 48 hours and the polymer was filtered off, washed, and dried under argon. Pentane (1 mL) was then added to facilitate an immediate precipitation of the polymer as a black solid. In contrast to the application of EDA, no precipitate was observed in the absence of $Mn(OAc)_2$ when using the chiral diamines **3a** or **3b**.

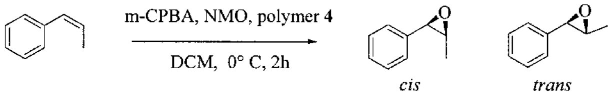


Scheme 2

The polymers **4a** and **4b** precipitate as hard solids and do not swell in organic solvents. In contrast to polymer **2** formed from **1** and ethylenediamine in the absence of a metal, the metal-containing polymers **4a** and **4b** exhibit no powder X-ray diffraction pattern. Apparently, the polymer formed in the presence of $Mn(OAc)_2$ lacks the order observed in the pure organic polymer **2**.

Asymmetric Epoxidation with Mn−Salen Polymers

Polymers **4a,b** were used as chiral catalysts in the asymmetric epoxidation of alkenes (Scheme 3). The test reaction of choice was the epoxidation of *cis*-2-methylstyrene with *m*-CPBA as the oxygen source and *N*-methylmorpholine *N*-oxide (NMO) as the co-oxidant at 0 °C. The reactions have been performed on a 0.1 mmol scale with 2 equiv. of *m*-CPBA and 5 equiv. of NMO in DCM. Mn−salen polymers **4a**,**b** were crushed in a mortar and a catalyst loading of 15 mol % was employed. The actual loading is presumably considerably lower because of the inaccessibility of catalytic sites in the core of the polymeric material. After 2 h the reaction mixture was diluted with diethyl ether to lower the density of the solvent and the reaction was stopped by precipitating the catalyst by centrifugation and decantation of the solution. Analysis of the crude product by ^1H NMR spectroscopy revealed a conversion of 73% (Table 1, entry 1). A *cis*/*trans* ratio of 12:1 was obtained which indicates that the reaction proceeds with high diastereoselectivity. The enantioselectivity for the *cis* isomer was shown to be 57% *ee* by GC analysis, which is approximately 30% lower than that obtained in reactions of the corresponding homogeneous catalyst.[9,14]



Scheme 3

The reaction was also performed without grinding the polymeric catalyst **4a** in a mortar, which presumably would lead to a significantly lower number of catalytic sites. In this case the conversion as well as the enantioselectivity dropped dramatically, probably because the catalyzed reaction path was slowed significantly, while the noncatalyzed reaction path continued at the same rate.

The solid polymer **4a** or **4b** left in the test-tube after filtration and decanting of the solution could be used again in repeated epoxidation reactions. The results of six or four epoxidation reactions using the same batch of polymer **4a** or **4b** are collected in Table 1. As the data in Table 1 clearly indicate, the yields and selectivities are consistent during the catalyst-recycling experiments. Because there is no filtration in this procedure and since the polymeric catalyst is kept in the same tube during the repeated experiments there is no loss of material, which in part explains the results obtained. The fact that the levels of reactivity and selectivity of the polymers were maintained in the catalyst-recycling experiments also shows that the polymers have a high stability. Furthermore, the catalysts **3a** or **3b** used in the experiments described above could be stored for three months and reused without a decrease in the reactivity and selectivity of the reaction. To test for any leaking of catalytically active species from the polymer into solution a series of experiments were performed. In the main experiment the polymeric catalyst was filtered off after 30% conversion, as observed by GC. No further conversion was observed after removal of the solid catalyst, whereas the control experiment containing the solid catalyst **4a** showed 73% conversion after 2 h.

The mechanism of the asymmetric Jacobsen epoxidation has been the subject of some debate.[18,19] It has been argued that in the key intermediate of the reaction, one of the salicylimine groups of the salen ligand changes conformation.[18,19a] It is most unlikely that the manganese−salen complexes in the highly cross-linked polymers **4a** and **4b** can undergo the structural changes required for such a conformal change. The fact that the reaction still proceeds, although with lower selectivities than in the homogeneous reaction, indicates that the structural change described above is not a prerequisite for the epoxidation reaction.

In summary, we have synthesized a new type of highly cross-linked condensation polymer from a rigid trialdehyde and ethylenediamine. The solid-state ^{13}C MAS NMR experiments demonstrate that this new type of salen-linked polymer is highly cross-linked while powder synchrotron X-ray diffraction data indicate that the polymer may have locally ordered domains. The polymer has few open ends, as demonstrated by the absence of signals from terminal amino and salicyl moieties in the NMR spectra. This polymer network may have unique properties with respect to inclusion of guest molecules and metal ions in its structure and as a conducting material. The two chiral manganese−salen linked polymers **4a** and **4b** are amorphous, however they catalyze the asymmetric epoxidation of an alkene to give up to 67% *ee*. The catalysts can be recovered by centrifugation and used repeatedly in up to six consecutive reactions with no significant drop in selectivity or reactivity. In future investigations on this new type of condensation polymer we will optimize and further study the properties of this new material.

Experimental Section

General Conditions: Standard Schlenk and vacuum line techniques were employed using argon as the inert atmosphere for all manipulations of air- or moisture-sensitive compounds. Yields refer to chromatographically isolated and spectroscopically homogeneous materials, unless otherwise stated. Commercially available starting materials were used without further purification. Solvents were

Table 1. Consecutive use of **3a** or **3b** as catalysts in the asymmetric epoxidation of *cis*-2-methylstyrene (reagents: *cis*-2-methylstyrene, *m*-CPBA and *N*-methylmorpholine *N*-oxide in CH_2Cl_2 at 0 °C)

Entry	Catalyst/cycle	Conversion [%]	*cis*/*trans* ratio	*ee* (*cis*) [%]	*ee* (*trans*) [%]
1	**3a**/1	73	12.0	57	20
2	**3a**/2	51	10.1	49	12
3	**3a**/3	52	10.1	53	12
4	**3a**/4	67	14.9	62	23
5	**3a**/5	78	17.0	67	23
6	**3a**/6	84	14.4	64	21
7	**3b**/1	56	6.3	46	34
8	**3b**/2	59	7.8	51	43
9	**3b**/3	64	8.4	56	44
10	**3b**/4	83	8.0	60	48

dried according to standard procedures. The products were purified by flash chromatography (FC) using Merck silica gel 60 (230–400 mesh). The liquid-state ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Varian Mercury (9.4 T) spectrometer with $CDCl_3$ as the solvent. The chemical shifts are reported in ppm downfield from TMS (δ = 0.00 ppm) in the ^{1}H NMR spectra and relative to the central $CDCl_3$ resonance (δ = 77.00 ppm) in the ^{13}C NMR spectra. Mass spectra and high-resolution mass spectra were obtained on an LC-TOF spectrometer (Micromass).

Materials: Triethylamine was distilled from CaH_2 under argon prior to use. Bis(triphenylphosphine)palladium(II) chloride was purchased from Aldrich. 3-*tert*-Butyl-5-iodosalicylaldehyde[9] and 1,3,5-triethynylbenzene[20] were synthesized according to literature procedures.

1,3,5-Tris[(5-*tert*-butyl-3-formyl-4-hydroxyphenyl)ethynyl]benzene (1): Bis(triphenylphosphane)palladium(II) chloride (288 mg, 0.41 mmol) and copper iodide (156 mg, 0.82 mmol) were stirred in a Schlenk flask under vacuum for 30 min. 5-Iodo-3-*tert*-butylsalicylaldehyde (2.60 g, 8.55 mmol), 1,3,5-triethynylbenzene (306 mg, 2.04 mmol), and NEt_3 (30 mL) were added and the reaction mixture was stirred under argon at 50 °C for 21 h. The reaction mixture was poured into 10% aqueous NH_4Cl (40 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic fractions were washed with water, dried over $MgSO_4$, and concentrated. The crude product was purified by flash chromatography on silica gel (CH_2Cl_2/pentane, 1:1 → 3:2) to yield **1** as white crystals (841 mg, 61%): ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.44 (s, 27 H), 7.61 (s, 3 H), 7.64 (s, 3 H), 7.66 (s, 3 H), 9.87 (s, 3 H), 11.97 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.3, 35.2, 87.0, 89.9, 114.0, 120.7, 124.2, 134.0, 135.5, 137.3, 139.3, 161.8, 196.9 ppm.

Polymer 2: Compound **1** (200 mg, 0.29 mmol) was dissolved in CH_2Cl_2 (20 mL) in a Schlenk flask. Ethylenediamine (36 mg, 0.435 mmol) was added and the reaction mixture was stirred at room temperature for 19 hours. The resulting yellow polymeric material was filtered off, washed with CH_2Cl_2 (2 × 5 mL), and dried under argon to yield **2** as a hard yellow polymer (209 mg). The polymer was characterized by solid-state ^{13}C NMR spectroscopy; no signals due to an aldehyde group were observed.

Polymer 4a: Trialdehyde **1** (100 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (20 mL) in a Schlenk flask. (1*R*,2*R*)-1,2-Diphenyl-1,2-diaminoethane (**3a**) (47 mg, 0.22 mmol) and manganese acetate tetrahydrate (55 mg, 0.22 mmol) were added and the reaction mixture was stirred at room temperature for 48 hours. The resulting black polymeric material was filtered off, washed with CH_2Cl_2 (2 × 5 mL), and dried under argon to yield **4a** as a black polymer (200 mg). The polymer was used without further purification.

Polymer 4b: Trialdehyde **1** (100 mg, 0.15 mmol) was dissolved in CH_2Cl_2 (20 mL) in a Schlenk flask. (1*R*,2*R*)-1,2-Diaminocyclohexane (**3b**) (25 mg, 0.22 mmol) and manganese acetate tetrahydrate (55 mg, 0.22 mmol) were added and the reaction mixture was stirred at room temperature for 48 hours. The resulting black polymeric material was filtered off, washed with CH_2Cl_2 (2 × 5 mL), and dried under argon to yield **4b** as a black polymer (201 mg). The polymer was used without further purification.

Asymmetric Epoxidation using 4a or 4b as the Catalyst: NMO (58 mg, 0.5 mmol) and (*Z*)-2-methylstyrene (12 µL, 0.1 mmol) was added to a suspension of polymer **4a** (11 mg) or **4b** (10 mg) in CH_2Cl_2 (3 mL). The suspension was cooled to 0 °C and *m*-CPBA (58 mg, 57–86% w/w, 0.2 mmol) was added. After stirring the reaction mixture at 0 °C for 2 h, diethyl ether (1 mL) was added, the mixture was centrifuged, and the polymeric material isolated by decanting off the liquid phase. NaOH (0.5 mL, 1 M) was added to the liquid phase, the organic layer was separated, washed with brine (1 mL) and water (1 mL), and dried over $MgSO_4$. The enantiomeric excess and diastereomeric ratio were determined by chiral GC-MS by using an Astec B-DM column. A 1 mM solution was injected into the GC apparatus and an initial column temperature of 70 °C was maintained for 5 minutes, after which it was increased at a rate of 5 $°C{\cdot}min^{-1}$ for 15 min. The retention times were t_R (*cis*-epoxide) = 11.8 (major) and 12.5 min (minor) and t_R (*trans*-epoxide) 11.3 and 11.4 min. After decanting off the liquid phase the Mn–salen polymer could be reused in another experiment without further purification.

Solid-State ^{13}C{^{1}H} MAS NMR Experiments: Solid-sate ^{13}C{^{1}H} MAS NMR experiments were performed on a Varian INOVA-300 (7.05 T) spectrometer using a home-built CP/MAS NMR probe for 5 mm o.d. zirconia (PSZ) rotors. The ^{13}C{^{1}H} CP and CPD/MAS experiments were performed with a repetition delay of 5 s, a CP contact time of 5.0 ms, rf field strengths of $\gamma_C B_{1C}/2\pi = \gamma_H B_{2H}/2\pi \sim 40$ kHz for the Hartmann–Hahn match during the CP and CPD contact periods, and $\gamma_H B_{2H}/2\pi = 100$ kHz for the 90° ^{1}H pulse and the ^{1}H decoupling rf field strength. The ^{13}C{^{1}H} spin-echo MAS experiment was performed with a repetition delay of 15 s, a rf field strength of $\gamma_C B_{1C}/2\pi = 60$ kHz for the 90° and 180° ^{13}C pulses, and a ^{1}H decoupling rf field strength of $\gamma_H B_{2H}/2\pi = 100$ kHz. The chemical shifts in the ^{13}C NMR spectra are referenced to TMS and an external sample of hexamethylbenzene was used as a secondary reference (δ_{iso} = 17.20 ppm for the aliphatic carbon atoms). In the ^{13}C{^{1}H} CP/MAS NMR spectrum (Figure 1, d) of polymer **2**, the ^{13}C resonances are observed at 29.6 (C^{10}), 35.2 (C^9), 59.6 (C^1), 89.3 (C^{11}, C^{12}), 113.7 (C^5), 119.0 (C^{13}), 124.3 (C^3), 133.4 (C^4, C^6), 136.8 (C^7, C^{14}), 160.8 (C^8), and 166.2 ppm (C^2), with the assignment to the carbon atoms in the asymmetric unit of polymer **2** (see a in Figure 1) given in parentheses.

Powder Synchrotron X-ray Diffraction: Powder synchrotron X-ray diffraction data were collected at beamline I711 at the Max II synchrotron in Lund, Sweden, as described in detail elsewhere.[16a] A monochromatic beam was selected by using a Si(111) monochromator single crystal and the wavelength was refined by using a Si sample as standard, λ = 1.08286(1) Å. Powder diffraction data were obtained in transmission geometry mode by using a Huber G670 imaging-plate Guinier powder diffraction camera.[16b] Data were collected from a sample of the polymer mounted in a quartz capillary (0.7 mm) at room temperature with an exposure time of 300 s. The background was corrected by subtracting the scattered intensity from an empty quartz capillary measured with the same exposure time.

Acknowledgments

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[1] J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, **1995**.
[2] M. Ohkita, M. Kawano, T. Suzuki, T. Tsuji, *Chem. Commun.* **2002**, 3054–3055.

[3] U. H. F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* **1999**, *28*, 107−119.

[4] J. Roncali, *Chem. Rev.* **1997**, *97*, 173−205.

[5] [5a] H. Sellner, J. K. Karjalainen, D. Seebach, *Chem. Eur. J.* **2001**, *7*, 2873−2887. [5b] D. A. Annis, E. N. Jacobsen, *J. Am. Chem. Soc.* **1999**, *121*, 4147−4154.

[6] D. Astruc, F. Chardac, *Chem. Rev.* **2001**, *101*, 2991−3023.

[7] K. B. Simonsen, K. A. Jørgensen, Q. S. Hu, L. Pu, *Chem. Commun.* **1999**, 811−812.

[8] F. Minutolo, D. Pini, A. Petri, P. Salvadori, *Tetrahedron: Asymmetry* **1996**, *7*, 2293−2302.

[9] M. Nielsen, K. V. Gothelf, *J. Chem. Soc., Perkin Trans. 1* **2001**, 2440−2444.

[10] M. Nielsen, N. B. Larsen, K. V. Gothelf, *Langmuir* **2002**, *18*, 2795−2799.

[11] K. V. Gothelf, A. H. Thomsen, M. Nielsen, E. Cló, R. S. Brown, *J. Am. Chem. Soc.* **2004**, *126*, 1044−1046.

[12] J. L. Czlapinski, T. L. Sheppard, *J. Am. Chem. Soc.* **2001**, *123*, 8618−8619.

[13] M. Nielsen, A. H. Thomsen, K. V. Gothelf, *J. Org. Chem.* **2004**, *69*, 2240−2250.

[14] M. Palucki, N. S. Finney, P. J. Pospisil, M. L. Güler, T. Ishida, E. N. Jacobsen, *J. Am. Chem. Soc.* **1998**, *120*, 948−954.

[15] [15a] X. Wu, Z. Shanmin, X. Wu, *J. Magn. Reson.* **1988**, *77*, 343−347. [15b] D. G. Cory, *Chem. Phys. Lett.* **1988**, *152*, 431−434. [15c] R. Sangill, N. Rastrup-Andersen, H. Bildsøe, H. J. Jakobsen, N. C. Nielsen, *J. Magn. Reson. A* **1994**, *107*, 67−78.

[16] [16a] Y. Cerenius, K. Ståhl, L. A. Svensson, T. Ursby, Å. Oskarsson, J. Albertsson, A. Liljas, *J. Synchrotron Rad.* **2000**, *7*, 203−208. [16b] K. Ståhl, *J. Appl. Cryst.* **2000**, *33*, 394−396.

[17] [17a] M. D. Hobday, T. D. Smith, *Coord. Chem. Rev.* **1973**, *9*, 311−337. [17b] T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299*, 1691−1693. [17c] L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, *28*, 85−93.

[18] P. Norrby, C. Linde, B. Åkermark, *J. Am. Chem. Soc.* **1995**, *117*, 11035−11036.

[19] [19a] N. S. Finney, P. J. Pospisil, S. Chang, M. Palucki, R. G. Konsler, K. B. Hansen, E. N. Jacobsen, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1720−1723. [19b] T. Linker, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2060−2062. [19c] C. Linde, N. Koliaï, P. Norrby, B. Åkermark, *Chem. Eur. J.* **2002**, *8*, 2568−2573.

[20] E. Weber, M. Hecker, E. Koepp, W. Orlia, M. Czugler, I. Csöregh, *J. Chem. Soc., Perkin Trans. 2* **1988**, 1251−1257.

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