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Highly efficient heterogeneous polymer-supported Sharpless alkene epoxidation catalysts

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Abstract

More widespread, and cost effective, use of soluble transition metal complex asymmetric catalysts would be achieved if highly efficient heterogeneous analogues could be developed. We now report the synthesis of branched/crosslinked poly(tartrate ester)s and their use as heterogeneous ligands for the complexation of $Ti(O^iPr)_4$, and use of the resulting insoluble catalysts in the asymmetric epoxidation of a range of *trans*-allylic alcohols employing *t*-butylhydroperoxide (*t*BHP) as the oxidant. Isolated yields of epoxides of up to 80%, with enantiomeric excesses up to 98% have been achieved. Removal and recovery of the polymer catalyst is by simple filtration at the end of reactions. The influence of the ratio of polymer-ligand–titanium, and the polymer backbone molecular architecture on the activity and enantioselectivity of the catalysts has been assessed. Typically polymer branching ratios of 3–11% and a polymer-ligand:titanium ratio of 2:1 yield the optimum results. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

The numerous advantages of polymer-supported systems have been well recognized[1] but unfortunately in the case of asymmetric catalysts the supported systems often suffer from a significant drop in enantioselectivity compared to the corresponding low molecular weight species.[2] Recently attention has focussed on polymer-supported asymmetric alkene oxidation catalysts.[3] Some approaches to the production of a heterogeneous Sharpless-type epoxidation catalyst have also been published[4] but the level of asymmetric induction achieved was generally only modest. We have previously reported on the synthesis of a group of linear soluble poly(tartrate ester) ligands and their use as homogeneous catalysts with titanium tetraisopropoxide and *tert*-butyl hydroperoxide (*t*BHP) as the oxidant in epoxidising *trans*-hex-2-en-1-ol in high chemical yield and with good enantioselectivity.[5] Although the enantiomeric

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excesses are in general a little lower than those achieved using monomeric tartrate esters, they are still significantly better than those from previously reported polymer-supported systems[4] as well as those from some homogeneous Sharpless-type modified systems.[6] We believe therefore that our results are important not only in methodological (and potentially technological) terms, but also scientifically since they offer the prospect of new information regarding the structure of the active species and its mechanistic role, and provide design criteria for new catalysts.

We have now synthesized a number of insoluble branched and/or crosslinked poly(tartrate ester)s and have studied their use as heterogeneous optically active ligands in asymmetric epoxidations of a number of *trans*-allylic alcohols with titanium tetraisopropoxide and *t*BHP. We have investigated the effect of the ratio of polymer-ligand to titanium on the enantioselectivity and yields, and the influence of the polymer backbone molecular architecture on asymmetric induction. Furthermore we also present our preliminary ideas explaining the various polymer effects we have observed and will report in more detail on these later, along with molecular modelling studies.

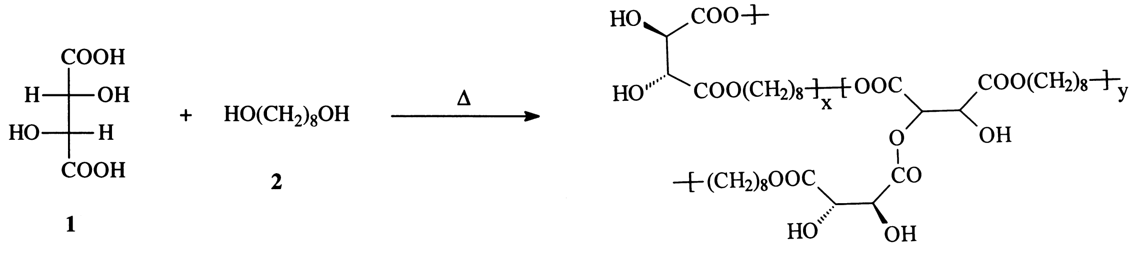
2. Results and discussion

The engineering of processes utilising structurally well-defined soluble metal complex catalysts[7] can be difficult and costly. Attachment of such species to linear macromolecules which remain homogeneous improves the situation somewhat, but the use of insoluble polymer-supports as the basis for heterogeneous catalysts really transforms the prospects for exploitation of such metal complexes in catalysis.[8,9]

In recent publications we have described the synthesis of linear optically active polyesters which were obtained by bulk or phase transfer catalysed polycondensation of diacids with diols.[5] We have now developed the bulk polymerisation further. In general, it is difficult to prepare linear polyesters by melt polycondensation having pendant functional groups, such as hydroxyl groups, on a main-chain since the pendant groups tend to participate in the reaction leading to crosslinking.[10] Indeed, we were surprised in our earlier studies not to detect any branching/crosslinking but the ^{1}H NMR spectra of these products confirmed the absence of branching/crosslinking.[11] However we have now synthesized some branched/crosslinked optically active polyesters using an elevated reaction temperature and prolonged reaction time. These gel-type polyester ligands have from 3% up to a 15% degree of branching/crosslinking but they all swell enough in the catalysis solvent (CH_2Cl_2) to form a complex with titanium tetraisopropoxide, thus allowing them to be used heterogeneously in asymmetric epoxidation reactions.[12]

2.1. Synthesis of branched/crosslinked optically active poly(tartrate ester)s

The branched/crosslinked C_8-alkyl group-containing poly(tartrate ester) gels **3** were synthesised from L-(+)-tartaric acid **1**, 20 mol% excess of 1,8-octanediol **2** and 3 wt% *p*-toluene sulfonic acid as a catalyst, as shown in Scheme 1.[13] The C_8-diol was chosen because the linear poly(tartrate ester) derived from this had earlier proven to be the most enantioselective ligand, probably because of easy access of Ti to the tartrate groups,[14] and because this polymer can most easily adopt the conformation for formation of the active metal complex.[15] The polymerisation conditions used were anaerobic and more forcing than in earlier preparations[5] and this seems to be the origin of the branching/crosslinking. Elemental microanalysis of **3** typically yielded C, 55.3; H, 8.5; and the theoretical values for a linear version of **3** are C, 55.4; H, 7.75. The FTIR spectrum of **3** displayed the expected bands 1743 (C=O) and 3500 (OH) cm^{-1}. The exact structure and architecture of **3** varied with different batches. Most were soluble either in hot pyridine, hot THF or hot Me_2SO and thus are probably branched rather than crosslinked.[16] All the polymers which were soluble in hot THF, displayed a positive optical rotation with $[\alpha]_D^{25}=+9$ typically. This value compares with one of +17 for the earlier linear version of **3**.[5,17] The presence of a CH_2OH signal in the ^1H NMR spectra of these soluble polymers confirmed the presence of these end groups, but the intensity was generally too high to be accounted for by a linear polymer structure. The occurrence of significant chain branching however is consistent with this observation. Indeed the molecular structure of the polymers was deduced from both ^1H and ^{13}C NMR spectra, and the degree of branching/crosslinking was calculated by integration of approriate signals in the former spectra.[18] In the ^{13}C-{^1H}-spectra a diagnostic methine (*C*H–OH) signal from the linear part of the polymer chain was found at δ 72 ppm. Small but clear signals from the branched/crosslinked segments of the polymer chain were also found at δ 80 ppm (–OOC–*C*H(CH–OH)–OCO–; in repeat unit y in Scheme 1). The proton coupled carbon spectrum shows the small signal at δ 80 ppm to be a doublet hence confirming the structure assignment. The degree of branching varied from 3 to 15% of all segments as determined by integration of the appropriate characteristic signals in the ^1H spectra[18] and those samples which proved to be insoluble in hot solvents were assumed to be crosslinked with a level of crosslinking $\gg$15%. The effect of the polymer backbone architecture (branching/crosslinking degree) on asymmetric induction in epoxidation reactions was investigated.

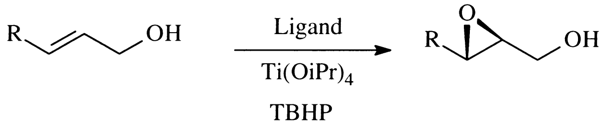


3

Scheme 1. *Reagents and conditions*: toluene *p*-sulfonic acid (3 mass%), 20 mol% excess of diol **2**, *ca*. 130°C, 4 days

2.2. *Asymmetric epoxidation of* trans-*hex-2-en-1-ol using heterogeneous poly(tartrate ester) ligands* **3** *(Scheme 2)*

Polymer-ligand **3** did not form CH_2Cl_2 soluble complexes with $Ti(O^iPr)_4$. Inevitably between 70 and 100% of the polymer was recovered from reaction mixtures by simple filtration. Recovered polymer was washed thoroughly with CH_2Cl_2 and dried under vacuum at room temperature and IR spectroscopic analysis showed the polymer to have the same characteristic bands at 3400–3500 cm^{-1} and 1750 cm^{-1} as before the reaction, indicating that in principle the polymer-ligand might be reused.[19] The results of epoxidations of *trans*-hex-2-en-1-ol are summarised in Table 1. Enantiomeric excesses were determined as derived acetates with chiral shift reagents or as Mosher esters using ^1H NMR.[12] Some non-GC-detectable side products were apparent from a shortfall (~20–30%) in the mass balance so dodecane was used an internal GC standard to determine the actual yields. It seems most likely that these side-products are formed via oligomeratisation of the epoxy alcohol products since they did not emerge from the GC column employed.[20] More often than not heterogeneously catalyzed processes are more complex than homogeneously catalysed ones since the catalyst is not uniformly distributed thoughout the reaction medium and a distribution (spatial and chemical) of active sites are generally found in heterogeneous catalysts.[21]



R = C_3H_7 **4**

C_8H_{17} **5**

Phenyl **6**

Scheme 2. *Reagents and conditions*: poly(tartrate ester), $Ti(OPr^i)_4$, Bu^tOOH (2 equiv.), 4 Å molecular sieves, CH_2Cl_2

Table 1
Epoxidation of *trans*-hex-2-en-1-ol with *t*BHP by L-(+)-polyester **3** and $Ti(OPr^i)_4$

Entry	Ligand **3** [(%), branching/ crosslinking]	Molar ratio substrate:Ti: tartrate	T / °C	Reaction time / h[a]	Epoxide yield (%), GC[b]	Isolated yield (%)[c]	Ee%[e]
1[i]	**DET**[h]	100:5:6	-20	2.5	-	85	94[g]
2	**3** (3 %)	100:40:50	-20	6	88	72	72
3	**3** (3 %)	100:25:50	-20	6	87	53	87
4	**3** (6 %)	100:20:60	-30	12	46	23	40
5	**3** (9 %)	100:15:20	-20	5.5	64[f]	44	58[g]
6	**3** (9 %)	100:25:50	-20	5.5	62[f]	58	76
7	**3** (11 %)	100:20:50	-20	10	86	57[d]	78[g]
8	**3** (11 %)	100:6:20	-20	11	87	47	40
9	**3** (>>15 %)	100:17:20	0	3	75	38	38
10	**3** (>>15 %)	100:4.5:5	-20	4.5	56	32	26

[a] From addition *trans*-hex-2-en-1-ol. [b] From GC analysis without internal standard dodecane.
[c] After additional 12 h in freezer, work-up and flash-chromatography. [d] After additional 12 h in freezer, work-up and Kugelrohr-distillation. [e] ee% determined ^1H NMR shift analysis of the derived acetate with $Eu(hfc)_3$ in benzene-d_6. [f] From GC analysis with internal standard dodecane correcting for response factors.
[g] (2S-*trans*)-3-Propyloxiranemethanol ee% determined by ^1H NMR analysis of the derived MTPA ester in benzene-d_6. [h] DET = L-(+)-diethyl tartrate.
[i] Results of monomeric system from reference 12.

Epoxidation of *trans*-hex-2-en-1-ol using polymer **3** gave similarly high chemical yields to those with soluble C_8-poly(tartrate ester)[5] but surprisingly a better enantioselectivity was obtained (Table 1, entry 3, 87% compared to 70% ee earlier). The influence of the ligand:Ti ratio was investigated and also a series of experiments using different substrate:catalyst ratios was performed. The enantioselectivities varied a lot with different ligand:Ti ratios as well as depending strongly on the polymer architecture. In Table 1, the reactions shown as entries 9 and 10 were performed using the same polymer-ligand with a degree of branching or crosslinking $\gg$15%. This polyester is presumably highly crosslinked rather than branched since it did not dissolve in any hot solvents. The asymmetric induction observed is only modest, 26–38% ee, even though the polymer swelled well in CH_2Cl_2. The reactions shown as entries 2 and 3 were performed using the polymer-ligand with ~3% of branching/crosslinking units. The best result was obtained using a ligand:Ti ratio of 2:1 (87% ee, entry 3). The use of a large excess of ligand and a lower reaction temperature retarded the reaction (entry 4) although this polymer-ligand also has a branching/crosslinking ratio of ~6%. Generally therefore it is quite obvious that different levels of branching/crosslinking have a significant effect on the degree of asymmetric induction achieved.

Table 2
Epoxidation of *trans*-2-undecen-1-ol with *t*BHP by L-(+)-polyester **3** and $Ti(OPr^i)_4$

Entry	Ligand **3** [(%), branching/ crosslinking]	Molar ratio substrate:Ti: tartrate	T / °C	Reaction time / h[a]	Epoxide yield (%), GC[b]	Isolated yield (%)[c]	Ee%[e]
1[i]	**DET**[h]	100:5:6	-10	1.5	-	78	94[f]
2	**3** (3 %)	100:50:100	-20	6	87	50	88[f]
3	**3** (6 %)	100:20:60	-15	12	54	40[d]	98
4	**3** (>>15 %)	100:17:20	0	6	58	30	14
5	**3** (>>15 %)	100:12:40	-15	4	94[g]	35	25[f]
6	**3** (>>15 %)	100:17:20	-20	6	16	25	34

[a] From addition *trans*-2-undecen-1-ol. [b] From GC analysis without internal standard dodecane. [c] After additional 12 h in freezer, work-up and flash-chromatography. [d] After additional 12 h in freezer, work-up and Kugelrohr-distillation. [e] (2S-*trans*)-3-Octyloxiranemethanol ee% determined ^1H NMR shift analysis of the derived acetate with $Eu(hfc)_3$ in benzene-d_6. [f] ee% determined by ^1H NMR analysis of the derived MTPA ester in benzene-d_6. [g] From GC analysis with internal standard dodecane correcting for response factors. [h] DET = L-(+)-diethyl tartrate. [i] Results of monomeric system from reference 12.

The reactions shown as entries 5–8 in Table 1 were performed using polymer-ligands with ~9–11% branching/crosslinking. These results are quite consistent and show that the enantioselectivity varies only according to the ligand:Ti ratio used. Furthermore it is clear that a polymer with branching/crosslinking levels of up to 11% can be used quite successfully in asymmetric epoxidation by an appropriate choice of the ligand:Ti ratio.

The complexity of these Ti–polymer-ligand systems makes it difficult to define the optimium polymer-ligand structure which in turn will allow the the best ligand:Ti ratio to be defined. However surprisingly, the findings so far suggest that the most efficient heterogeneous polymer–titanium complex has a 2:1 structure instead of the Sharpless low molecular weight 2:2 dimer. In principle, the reactivity or effectiveness of a particular functional group or ligand on a polymer can depend upon whether it is located at or near a crosslinking point or somewhere on the chain well removed from such a point.[14] Some of the tartrate residues in the 2:1 structures may not therefore play a functional role, and the real structure may indeed be an analogue of the 2:2 soluble dimer.

2.3. Asymmetric epoxidation of other allylic alcohols using poly(tartrate ester) ***3*** *(Scheme 2)*

With the successful epoxidation of *trans*-hex-2-en-1-ol using polymer-ligand **3** we were encouraged to perform a series of epoxidation reactions of *trans*-allylic alcohols using this heterogeneous system. The results are summarized in Tables 2–4.

In order to investigate the effect of reaction temperature, some reactions were carried out at room temperature, 0, −20 and −30°C. A mixture of unidentified compounds was generally obtained when each reaction was performed at room temperature, although typically ~20% of the target epoxy alcohol was also present. Enantioselectivities were in general ~10–20% ee when the reactions were carried out at 0°C (Table 1, entry 9 and Table 2, entry 4, Table 4, entry 9) but also lowering the reaction temperature much below −20°C did not bring any advantage (Table 1, entry 4).[22]

The results of the epoxidation of *trans*-2-undecen-1-ol in Table 2 show the same effect of the polymer architecture on asymmetric induction as observed before with *trans*-hex-2-en-1-ol. The reactions shown as entries 4–6 (Table 2) were carried out using the highly crosslinked (≫15%) polyester, and the

Table 3
Epoxidation of *trans*-cinnamyl alcohol with *t*BHP by L-(+)-polyester **3** and $Ti(OPr^i)_4$

Entry	Ligand **3** [(%), branching/ crosslinking]	Molar ratio substrate:Ti: tartrate	T / °C	Reaction time / h[a]	Epoxide Isolated yield (%)[b]	Ee%[d]
1[g]	**DIPT**[f]	100:5:7.5	-20	3	89	>98[e]
2	**3** (3 %)	100:17:20	-20	6	48	80
3	**3** (6 %)	100:25:50	-20	6.5	38	89
4	**3** (6 %)	100:20:60	-30	7.5	13	58
5	**3** (11 %)	100:20:50	-20	3	45[c]	74
6	**3** (11 %)	100:6:20	-20	5.5	16[c]	76
7	**3** (>>15 %)	100:17:20	0	6	31	40

[a] From addition *trans*-cinnamyl alcohol. [b] After additional 12 h in freezer, work-up and flash-chromatography. [c] After additional 12 h in freezer, work-up and Kugelrohr-distillation. [d] (2S-*trans*)-3-Phenyloxiranemethanol ee% determined by ^{1}H NMR analysis of the derived MTPA ester in benzene-d_6. [e] ee% reported for recrystallized material. [f] DIPT = L- (+)- diisopropyl tartrate. [g] Results of monomeric system from reference 12.

Table 4
Epoxidation of *trans*-geraniol with *t*BHP by L-(+)-polyester **3** and $Ti(OPr^i)_4$

Entry	Ligand **3** [(%), branching/ crosslinking]	Molar ratio substrate:Ti: tartrate	T / °C	Reaction time / h[a]	Epoxide yield (%), GC[b]	Isolated yield (%)[c]	Ee%[e]
1[h]	**DET**[g]	100:5:7.4	-20	0.75	-	95	91
2	**3** (6 %)	100:25:50	-20	6	98	66	72
3	**3** (6 %)	100:20:60	-30	6	76	58	48
4	**3** (11 %)	100:20:50	-20	4	100	33[d]	62
5	**3** (11 %)	100:10:50	-20	4	72	75[d]	34
6	**3** (15 %)	100:25:50	-20	4	74[f]	53	40
7	**3** (15 %)	100:20:50	-20	4	74[f]	56	52
8	**3** (15 %)	100:15:20	-20	3	100[f]	72	50
9	**3** (>>15 %)	100:17:20	0	3	66	53	16
10	**3** (>>15 %)	100:40:50	-20	6	71	65	40

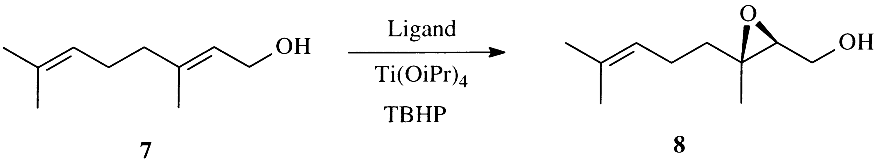
[a] From addition *trans*-geraniol. [b] From GC analysis without internal standard dodecane. [c] After additional 12 h in freezer, work-up and flash-chromatography. [d] After additional 12 h in freezer, work-up and Kugelrohr-distillation. [e] (2S-*trans*)-3-Methyl-3-(4-methyl-3-pentenyl)oxiranemethanol ee% determined ^{1}H NMR shift analysis of the derived acetate with Eu(hfc)$_3$ in benzene-d_6. [f] From GC analysis with internal standard dodecane correcting for response factors. [g] DET = L-(+)-diethyl tartrate. [h] Results of monomeric system from reference 12.

enantioselectivities are very low compared to those obtained using the polymer with only 3–6% of branched/crosslinked units (entries 2 and 3). In the latter cases the enantioselectivities are excellent (88–98% ee) and are combined with reasonable non-optimised isolated yields (40–50%). Even using a stoichiometric amount of polymer-ligand relative to substrate (entry 2) the polymer could be easily filtered off from the reaction mixture. These results show clearly the synthetic potential of these heterogeneous asymmetric epoxidations.

With the sensitive substrate *trans*-cinnamyl alcohol some difficulties were observed. The results in Table 3 show that the chemical yields drop significantly. Titanium isopropoxide is a potential polymerization catalyst[23] and these low yields may arise from epoxide polymerization.

Nevertheless the effect of the polymer architecture is seen again in the data in Table 3. The best enantioselectivity was obtained using the 6% branched/crosslinked polymer-ligand with a ligand:Ti ratio of 2:1 (89% ee, entry 3). The polymer with a lower degree of branching/crosslinking (3%) did not give a better enantioselectivity even using a ligand:Ti ratio of 1.18:1 (entry 2). This again indicates the importance of an appropriate ligand:Ti ratio.

Several ligand:Ti ratios with different polymer batches were studied in the case of *trans*-geraniol as the substrate (Scheme 3). The results in Table 4 show again that the best polymer-ligand:Ti ratio is 2:1 using the polymer with a degree of branching/crosslinking of 6% (entry 2). The level of asymmetric induction drops significantly (~30%, entries 2 and 6) when the branching/crosslinking is increased to $\gg$15%. The highest enantioselectivity obtained is 72% (entry 2) which is somewhat lower than that achieved with other substrates but higher than that reported with an earlier polymer-supported catalyst.[4] This poorer performance with this substrate is not too surprising however since Sharpless et al. have also observed that using the monomeric tartrate with this substrate the enantioselectivity is reduced (Table 4, entry 1).[24]



7 **8**

Scheme 3. *Reagents and conditions*: poly(tartrate ester), Ti(OPr^i)$_4$, Bu^{t}OOH (2 equiv.), 4 Å molecular sieves, CH_2Cl_2

Overall the results of experiments with four allylic alcohols show that the optimium asymmetric induction is obtained with heterogeneous polymer-ligands with a degree of branching/crosslinking of 3–6%, when used in a polymer-ligand:Ti ratio of 2:1.

2.4. *Effect of leached titanium on asymmetric induction*

The influence of leached Ti on enantioselectivity has also been investigated. Typically when polymer-ligand **3** was removed by filtration from the reaction solution with a polymer-ligand:Ti ratio of 2:1 recoveries were ~90–100%. Atomic absorption spectroscopic analysis indicates that generally about 80% of Ti was bound to the polymer-ligand and the remaining 20% is uncomplexed or complexed with tartrate monomer or oligomer in a solution.[25] To examine the activity of this 20% 'free' titanium, a control epoxidation reaction was carried out. A Ti–polymer-ligand catalyst was prepared using the standard procedure but the Ti–polymer complex was filtered off before adding the substrate; *trans*-hex-2-en-1-ol. The reaction proceeded slowly (GC analysis) and after 10.5 hours stirring at −20°C and storing in a freezer for over 2 weeks the yield of epoxide was 23%.[26] The epoxide was isolated by Kugelrohr distillation to determine the enantioselectivity of the reaction which was very low (4% ee). This data shows that the catalytic activity of the free Ti is very low and that this component is probably not tartrate complexed. This is confirmed by the low % ee seen which again suggests an absence of any optically active monomer or oligomer in solution. Polymer **3** therefore appears not to contain any significant CH_2Cl_2 soluble component.

3. Experimental

3.1. General

The ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker AM200 MHz or Bruker DPX400 MHz spectrometers. Chemical shifts (δ) are given in ppm relative to TMS. Gas chromatographic (GC) analysis were carried out on a Carlo Erba GCHR 5300 Mega Series employing a SGE BPX5 column or a Perkin–Elmer 8500 equipped with FID detector employing a 25 m column packed with fused silica (phase layer 0.25 μm). FTIR spectra were measured on a Bruker IFS 66 or Nicolet Impact 400d instruments, wavenumbers are in cm^{-1}. Enantiomeric ratios measured by HPLC were determined using a Daicel Chiralcel OB column (flow rate=0.5 ml/min, hexane:isopropanol=97.5:2.5). High resolution GC/MS analysis were performed by the Mass Spectrometry Laboratory of the University of Oulu, Finland. Optical rotations were determined on a Perkin–Elmer WM250 or a Perkin–Elmer 243 B polarimeter using a 1 cm^3 capacity, 1 dm path length, quartz cell. Elemental analyses were performed by the Microanalytical Laboratory of the University of Strathclyde, Scotland or by the Microanalytical Laboratory of the University of Oulu, Finland. Metal leaching was determined by atomic absorption spectrophotometry (AAS) by the Microanalytical Laboratory of the University of Oulu, Finland. Molecular weights were measured by gel permeation chromatography (polystyrene standards in THF) by RAPRA, UK. Flash chromatography was performed using Merck silica gel 60 (230–400 mesh) with diethyl ether/petrol ether (40°C–60°C) in various proportions as eluent.

3.2. Materials

Pre-activated and powdered 4 Å molecular sieves were available from the Aldrich Chemical Co. and were used as received. The dichloromethane used did not contain methanol and therefore was not distilled but was stored over $CaCl_2$. Aqueous 70% *tert*-butyl hydroperoxide (*t*BHP) was obtained from the Aldrich Chemical Co. *trans*-Cinnamyl alcohol was distilled under vacuum. All other reagents were used as obtained from Aldrich Chemical Co. or from Fluka Chemica-Biochemica (*trans*-2-undecenol). Reagents handled by syringe were measured by weight or by volume.

3.3. Anhydrous tert-*butyl hydroperoxide (*t*BHP) in* iso-*octane*[27]

To a 250 ml separating funnel was added a 70% *t*BHP/30% H_2O solution (65 ml) and reagent grade *iso*-octane (80 ml). The flask was swirled (not shaken) to avoid the formation of an emulsion. The aqueous layer was separated and the organic layer was transferred to a 250 ml round-bottomed flask equipped with a Dean Stark trap and a reflux condenser. A few boiling chips were added and the solution was refluxed. After approximately one hour of refluxing, a drying tube filled with anhydrous $CaCl_2$ was fitted and refluxing was continued for a further two hours. After the *t*BHP/*iso*-octane solution had been allowed to cool, it was transferred to a brown glass bottle and was stored over 4 Å molecular sieves.

3.4. Molarity determination of anhydrous tBHP/iso-*octane*[26]

A 0.1 M aqueous sodium thiosulphate solution was prepared by dissolving $Na_2S_2O_3\cdot5H_2O$ (12.16 g) in de-ionised water (500 ml). To a 250 ml conical flask, isopropyl alcohol (25 ml) and glacial acetic acid (2 ml) were added. A 20% solution of NaI was prepared in 100 ml of warm isopropyl alcohol and 10 ml of this solution was added to the conical flask. A quantity (0.5 ml) of the anhydrous *t*BHP *iso*-octane solution was then added and the mixture was heated to boiling and was allowed to boil for 40 seconds. After dilution with 100 ml of de-ionised water, the warm solution was rapidly titrated with the 0.1 M thiosulphate solution until the yellow iodine colour disappeared. The titration was repeated three times. The concentration was calculated from Eq. 1:

$$\text{Concentration} = \frac{(\text{molarity of titrant}) * (\text{volume of titrant added})}{(\text{volume of } t\text{BHP solution}) * 2} \qquad (1)$$

3.5. General preparation and NMR analysis of Mosher esters[12]

This method was suitable for the determination of the enantiomeric excess (ee) of all *trans*-disubstituted epoxy alcohols in particular it is the only suitable method for *trans*-epoxycinnamyl alcohol.

The reactions were run on a 0.15 mmol scale. A mixture of 18 mg (0.15 mmol, 1.0 equiv.) of 4-(dimethylamino)pyridine (DMAP) and 100 µl of triethylamine in 10.5 ml of CH_2Cl_2 was treated with the substrate. Immediately, 30 µl of neat (+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA chloride) was added. The solution became warm and turned orange. Reactions were quenched by addition of 3-(dimethylamino)propylamine (40–60 µl) and the residue was passed though a plug of silica gel in order to remove polar impurities (20% EtOAc/hexane). ^{1}H NMR analysis in C_6D_6 at 400 MHz focussed on the terminal methylene protons. These protons typically were observed as a diastereomeric pair of AB doublets (or doublets of doublets) around δ 4.0–4.3 ppm. The pair was compared by integration to determine the enantiomeric excess.

3.6. General preparation and NMR shift analysis of acetates[12]

This method was suitable for nearly all *trans*-disubstituted epoxy alcohols and for 2,3-epoxygeraniol. Acetates were prepared as described above for Mosher esters, using acetyl chloride (0.30 mmol scale). ^{1}H NMR analysis involved sequential treatment of a solution of about 10 mg of an acetate in 0.5 ml of C_6D_6 with 0.05–0.1 mol equiv. portions of a solution of 0.14 g of europium(III) tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorate], Eu(hfc)$_3$, in 2 ml of C_6D_6 and observation of the acetate CH_3.

3.7. Absolute configurations

Absolute configurations were determined by comparison of the observed rotation by polarimetry with the literature value.

3.8. AAS-measurements

The leaching of titanium from the polymer-support was determined by AAS analysis. After filtration the polymer-ligand was washed throughly with dichloromethane and the sample from the filtrate (known reaction volume) was taken for AAS-measurements. The results are expressed as mg titanium/L.

3.9. General preparation of branched/crosslinked optically active polyesters[13] (**3**, Scheme 1)

An oven-dried 100 ml three-necked round-bottomed flask equipped with a magnetic stir bar, nitrogen inlet and bubbler was charged with L-(+)-tartaric acid (10 g, 0.067 mol), 20 mol% excess of 1,8-octane diol (11.67 g, 0.080 mol) and ~3 wt% *p*-toluene sulphonic acid (0.6 g) (excess of diol was employed to account for possible loss of this component in the N_2 stream at high temperature). The temperature was raised to between 140 and 150°C to achieve a homogeneous mixture and then it was stirred at 120–130°C for between 3 and 4 days under the nitrogen. Water and unreacted diol were removed by distillation under high vacuum at the end of reaction. The resulting solid was swelled in ethyl acetate by refluxing and then it was poured into *n*-hexane. The solvents were decanted and the polymer obtained was dried under high vacuum at +40°C for 6 hours and at room temperature for 2 days to yield 16.6 g, 95% of C_8-poly(tartrate ester) **3**. $[\alpha]_D^{25}$=+9 (*c* 1.6, THF). FTIR (KBr) 3450, 2932, 2857, 1743, 1466, 1395, 1128, 1091, 1011, 956. Anal. found: C, 55.3; H, 8.5. ^{1}H NMR (400 MHz, DMSO-d_6, 70°C) δ 5.75 (br s), 5.41 (d, *J*=3.15 Hz), 4.62 (d, *J*=2.83 Hz), 4.37 (s, 2H), 4.09 (t, *J*=6.49 Hz, 4H), 1.58 (m, 4-5H), 1.30 (m, 9H). ^{13}C NMR (400 MHz, DMSO-d_6, 70°C) δ 172.42 (s), 171.28 (s), 171.03 (s), 80.41 (d, J^{CH}=142.04 Hz), 73.45, 72.45, 72.19 (d, J^{CH}=146.24 Hz), 64.47 (t, J^{CH}=147.2 Hz), 28.32 (t, J^{CH}=125.64 Hz), 28.04 (t, J^{CH}=125.92 Hz), 25.07 (t, J=125.66 Hz). Note: different batches of **3** analysed (^{1}H NMR) to show different levels of branching/crosslinking.

3.10. General procedure for the catalytic asymmetric epoxidation using heterogeneous polymer-ligand[12]

The literature procedure for the epoxidation of allylic alcohols was followed with modifications. An oven-dried three-necked round-bottomed flask equipped with a magnetic stir bar, nitrogen inlet, septum and bubbler was charged with 4 Å powdered, activated molecular sieves (3 g), polymer-ligand **3** (see Tables 1–4 for substrate:Ti:ligand ratios) and dry CH_2Cl_2. The flask was cooled to −20°C and Ti(O-*i*-Pr)$_4$ (5 mmol, via syringe) was added sequentially with stirring. The reaction mixture was stirred at −20°C and after about one hour *t*BHP (0.2 mmol in *iso*-octane) was added with syringe at a moderate rate. The resulting mixture was stirred at −20°C for at least 1 hour. Substrate (0.1 mol, dissolved in dry CH_2Cl_2) was added dropwise with a syringe, being careful to maintain the reaction temperature between −15°C and −20°C. The mixture was stirred for an additional 3–12 hours between −15°C and −20°C. The reaction mixture was stored in a freezer for various periods before work-up. The reaction was monitored by gas chromatography (GC) using dodecane as a GC internal standard. The polymer was filtered off the reaction mixture and washed thoroughly with CH_2Cl_2. The recovered solution was then quenched with a 30% aqueous solution of sodium hydroxide saturated with sodium chloride. After 10 wt% of diethyl ether was added, the cold bath was removed and the stirred mixture was allowed to warm to 10°C. Stirring was maintained for an additional 10 min at 10°C, whereupon $MgSO_4$ and Celite were added. After a final 15 min of stirring, the mixture was allowed to settle and the solution was filtered through a pad of Celite and washed with diethyl ether. Excess *t*BHP was removed by azeotropic distillation with toluene. The crude product was purified by flash-chromatography (eluent: petrol ether (40°C–60°C):diethyl ether, 50%) or by Kugelrohr-distillation and the enantioselectivity of the epoxide was calculated from the 400 MHz NMR spectrum using chiral Eu(hfc)$_3$-reagent (as acetates) or as Mosher esters.

*3.11. (2*S-trans*)-3-Propyloxiranemethanol (**4**) from heterogeneous catalyses*

The epoxidation was performed as described in the general procedure, in this case 40 ml of CH_2Cl_2 with 0.3 g of powdered, activated 4 Å molecular sieves, 2.6 g (0.01 mol) of the hetereogeneous C_8-poly(tartrate ester) **3**, 1.42 g (0.005 mol) of Ti(OPr^i)$_4$, 12.5 ml of a 3.2 M solution of *t*BHP in *iso*-octane and 2 g (0.02 mol) of *trans*-hex-2-en-1-ol (dissolved in 10 ml CH_2Cl_2). The reaction mixture was stirred at −20°C for 6 h and placed in a freezer overnight. The polymer-ligand was filtered off and washed throughly with CH_2Cl_2. The work-up was then performed and crude the product was purified by flash-chromatography (eluent: petrol ether (40°C–60°C):diethyl ether, 50%) to give a colourless oil (**4**) (1.22 g, 53% yield, ~100% purity, 87% ee by ^{1}H NMR analysis of the derived acetate with Eu(hfc)$_3$): $[\alpha]^{25}{}_D = -38$ (*c* 2.01, $CHCl_3$), GC analysis before work-up: 78% epoxide. FTIR ($CHCl_3$) 2977, 2952, 1717, 1457, 1237, 1196, 933, 881, 806, 796. ^{1}H NMR (200 MHz, C_6D_6) δ 3.72 (ddd, *J*=3, 6, 12 Hz, 1H), 3.46 (ddd, *J*=5, 7, 12 Hz, 1H), 2.79–2.85 (m, 1H), 2.70–2.74 (m, 1H), 2.33 (t, *J*=6 Hz, 1H), 1.34–1.45 (m, 4H), 0.93 (t, *J*=7 Hz, 3H). MS (EI, *m/z*, relative intensity) 99 (0.8, $M-17)^+$, 81 (7), 73 (20), 61 (8), 55 (100), 43 (86). HRMS (EI) calcd for $C_6H_{12}O_2$ 116.0837, found 116.0882.

*3.12. (2*S-trans*)-3-Octyloxiranemethanol (**5**) from heterogeneous catalyses*

The epoxidation was performed as described in the general procedure using in this case 35 ml of CH_2Cl_2 with 0.3 g of powdered, activated 4 Å molecular sieves, 1.56 g (0.0059 mol) of the heterogeneous C_8-poly(tartrate ester) **3**, 0.85 g (0.003 mol) of Ti(OPr^i)$_4$, 7.5 ml of 3.2 M solution of *t*BHP in *iso*-octane and 1 g (0.0059 mol) of *trans*-undec-2-en-1-ol (dissolved in 5 ml CH_2Cl_2). The reaction mixture was stirred at −20°C for 6 h and placed in a freezer overnight. The polymer-ligand was filtered off and washed throughly with CH_2Cl_2. The work-up was then performed and the crude product was purified by crystallization from petrol ether to yield 0.55 g of a white solid (**5**) (50% yield, 88% ee, by ^{1}H NMR analysis of the Mosher ester, GC analysis after 6 h: 87% epoxide). $[\alpha]^{25}{}_D = -22$ (*c* 1.33, $CHCl_3$). FTIR ($CHCl_3$) 2975, 2949, 2879, 2867, 2844, 1701, 1653, 1559, 1507, 1237, 1196, 933, 879, 836, 817. ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.88 (dd, *J*=2, 13 Hz, 1H), 3.59 (ddd, *J*=5, 7, 10 Hz, 1H), 2.87–2.96 (m, 2H), 2.68 (br s), 1.24–1.55 (m, 14H), 0.85 (t, *J*=3 Hz). MS (EI, *m/z*, relative intensity) 109 (1, $M-77)^+$, 95 (14), 83 (51), 69 (100), 55 (94), 41 (99), 29 (28). HRMS (EI) calcd for $C_{11}H_{22}O_2$ 186.162, found (M+1) 187.1700.

*3.13. (2*S-trans*)-3-Phenyloxiranemethanol (**6**) from heterogeneous catalyses*

The epoxidation was performed as described in the general procedure using in this case 40 ml of CH_2Cl_2 with 0.3 g of powdered, activated 4 Å molecular sieves, 1.95 g (0.0075 mol) of the hetereogeneous C_8-poly(tartrate ester) **3**, 1.07 g (0.00375 mol) of Ti(OPr^i)$_4$, 9.4 ml of 3.2 M solution of *t*BHP in *iso*-octane and 2 g (0.015 mol) of *trans*-2-cinnamyl alcohol (dissolved in 10 ml CH_2Cl_2) at −20°C for 6 h and the reaction mixture was placed in a freezer overnight. The polymer-ligand was filtered off and washed throughly with CH_2Cl_2. The work-up was then performed and the crude product was purified by Kugelrohr-distillation to yield a light yellow solid 0.85 g (**6**) (38% yield, 89% ee ^{1}H NMR analysis of the Mosher ester): $[\alpha]^{25}{}_D = -36$ (*c* 2.37, $CHCl_3$). FTIR ($CHCl_3$) 3035, 3007, 2976, 2399, 1734, 1717, 1684, 1616, 1489, 1457, 1296, 1237, 1196, 1093, 1074, 1057, 977, 938, 879. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26–7.34 (m, 5H), 4.06 (ddd, *J*=2, 5, 13 Hz, 1H), 3.94 (d, *J*=2 Hz, 1H), 3.81 (ddd, J=4, 8, 12 Hz, 1H), 3.21–3.26 (m, 1H), 1.97 (dd, *J*=5, 6 Hz, 1H). MS (EI, *m/z*, relative intensity) 149 (2, $M-1)^+$, 132 (17), 121 (28), 107 (78), 91 (100), 79 (56), 63 (27), 51 (31), 43 (15). HRMS (EI) calcd for $C_9H_{10}O_2$ 150.0681, found 150.0697.

*3.14. (2*S-trans*)-3-Methyl-3-(4-methyl-3-pentenyl)oxiranemethanol (**8**) from heterogeneous catalyses*

The epoxidation was performed as described in the general procedure using in this case 30 ml of CH_2Cl_2 with 0.3 g of powdered, activated 4 Å molecular sieves, 1.69 g (0.0065 mol) of heterogeneous C_8-poly(tartrate ester) **3**, 0.46 g (0.00163 mol) of Ti(OPr^i)$_4$, 8.1 ml of 3.2 M solution of *t*BHP in *iso*-octane and of *trans*-geraniol **7** (dissolved in 10 ml CH_2Cl_2) at −20°C for 7.5 h and the reaction mixture was placed in a freezer overnight. The polymer-ligand was filtered off and washed throughly with CH_2Cl_2. The work-up was then performed and the crude product was purified by flash-chromatography (eluent: petrol ether (40°C–60°C):diethyl ether, 50%) to give a colourless oil 1.48 g (**8**) (66% yield, 72% ee ^1H NMR analysis of the derived acetate with Eu(hfc)$_3$): $[\alpha]^{25}_D=-4$ (*c* 3.6, $CHCl_3$). FTIR ($CHCl_3$) 3035, 3007, 2896, 1701, 1684, 1653, 1237, 1196, 938, 879, 835, 816. ^1H NMR (200 MHz, C_6D_6) δ 5.23 (tt, *J*=1.4, 7 Hz, 1H), 3.61–3.69 (m, 2H), 2.98 (dd, *J*=5, 6 Hz, 1H), 2.16 (q, *J*=7 Hz, 2H), 1.98 (t, *J*=6 Hz, 1H), 1.77 (s, 3H), 1.64 (s, 3H), 1.49–1.72 (m, 2-3H), 1.19 (s, 3H). MS (EI, *m/z*, relative intensity) 149 (1, $M-21)^+$, 121 (4), 109 (70), 95 (25), 82 (46), 69 (100), 61 (36), 55 (45), 41 (97). Found HRMS (EI) calcd for $C_{10}H_{18}O_2$ 170.1307, found 170.1331.

4. Conclusions

Branched or crosslinked poly(tartrate ester)s have been prepared by *p*-toluene sulfonic acid catalysed condensation of L-(+)-tartaric acid with 1,8-octanediol. Different batches of the polymer have been shown by ^1H NMR analysis to have different levels of branching (3% to $\gg$15%). In the range 3–11% the polymers can be solubilised in hot solvents and so are branched, whereas polymers with apparent branching ($\gg$15%) are insoluble, cannot be analysed quantitatively, and are probably crosslinked rather than branched. All of the species can be employed as heterogeneous ligands for the complexation of $Ti(O^iPr)_4$ and the insoluble complexes formed have been used as catalysts in the asymmetric epoxidation of *trans*-hex-2-en-1-ol, *trans*-2-undecen-1-ol, *trans*-cinnamyl alcohol and *trans*-geraniol. Polymer catalysts can be removed by simple filtration at the end of reactions, and epoxide isolated yields up to 80% and enantiomeric excesses up to 98% have been achieved. The ratio of polymer-ligand:Ti and the molecular architecture of the polymer backbone influence the effectiveness of the catalysts. Optimum results are obtained typically with a polymer-ligand:Ti ratio of 2:1, and with polymers having a branching ratio of between 3 and 11%.

Currently the effectiveness of recycling of recovered polymer-ligands is being assessed, in combination with a molecular modelling study aimed at providing a structural basis for our observed results.

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17. $[\alpha]_D^{25}=+9$ (*c* 1.6, THF). Optical rotation did not depend on the degree of branching/crosslinking. Some polymer batches were not soluble in hot THF and thus it was assumed that these polymers had degrees of branching/crosslinking $\gg 15\%$ i.e. very much higher than THF soluble polymers (3–15%).
18. Polymer samples were dissolved in hot Me_2SO. The ^1H NMR spectra were obtained on a 400 MHz NMR spectrometer at 343 K. An example of the calculation of the branching/crosslinking degree by integration is as follows. ^1H NMR spectrum of poly(tartrate ester) **4**: δ 5.41 (d, intensity=0.185H) +4.61 (d, 0.164H) [–OOC–C*H*(OCO–)–CH(OH)COO–, –OOC–CH(OCO–)–C*H*(OH)COO–, Scheme 1, unit y]/ 4.37 (s, 2.001H) [–OOC–C*H*(OH)–C*H*(OH)–COO–, Scheme 1, unit x]+y*100%=14.8%.
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23. See Ref. 20. The metal alkoxide and metal alkyl catalysts are generally much more reactive in the presence of water or alcohols both of which are formed during the epoxidation reaction.
24. Enantioselectivity of geraniol oxide was 91% using L-(+)-diethyl tartrate as a ligand. See Ref. 12.
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