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# EFFICIENT POLYMER-SUPPORTED SHARPLESS ALKENE EPOXIDATION CATALYST

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# 1. INTRODUCTION

Over the past years a great deal of interest has been focused on organic reactions performed in the presence of functional polymers acting either as reagents or catalysts. The effective immobilisation of asymmetric catalysts, reagents and auxiliares is a particularly important methodological target, especially for metal complex-based catalysts.

Immobilisation of a reactive species on a support might provide a number of important advantages

- aids separation, isolation and purification procedures
- excess of a polymeric reagent can be readily employed without incurring a penalty in work-up

•corrosive, noxious or toxic species might be encapsulated, with obvious advantage in environmental terms
•transition metal complexes and optically active catalysts might be efficiently retained for re-use
The two obvious disadvantages are initial extra costs of such species which are also not yet available "off-the-shelf" [1].

In 1980 Sharpless described a method to produce chiral epoxides from a large range of allyllic alcohols in high yield (70-90 %) and with very efficient enantioselectivity (ee>90%) [2].

Now we have shown that linear poly(tartrate ester) ligands provide high chemical yields and enantiomeric excesses in the epoxidation of *trans*-hexen-1-ol using $Ti(OPr^{i})_4$-*tert*-butyl hydroperoxide [3].

## 2. EXPERIMENTAL

Poly(tartrate ester)s 1a-d were synthesised from L-(+)-tartaric acid and diols using a standard polycondensation procedure (Scheme 1).

Poly(tartrate ester)s 1e-f were synthesised from L-(+)-tartaric acid disodium salt dihydrate dissolved in water and α,α'-dichloroxylene dissolved in $CHCl_3$ by a phase transfer catalysed procedure (Scheme 2).

Polyesters 1a-f were used as ligands in the epoxidation of 2 with $Ti(OPr^i)_4$-tBHP as shown in Scheme 3 . The results are summarised in Table 1 . The heterogeneous polymer-ligand 1c could be filtered off the reaction mixture quantitatively. Effect of the reaction temperature and ligand:titanium-ratio was investigated.

## 3. SUMMARY

The recovery of epoxy alcohol would be greatly facilitated if a heterogeneous catalyst could be used in Sharpless asymmetric epoxidation.

Poly(tartrate ester)s can be used in the asymmetric epoxidation of *trans*-hex-2-en-1-ol. Preliminary investigations have shown that the polymeric catalyst 1c can be filtered off the reaction mixture quantitatively which helps the work-up procedure.

Further research to produce highly practical re-usable heterogeneous Sharpless epoxidation catalysts is in progress.

Factors such as the molecular weight of the poly(tartrate ester) and the nature of the complex with Ti are being studied by solid state NMR and Maldi-TOF technigues.

## 4. ACKNOWLEDGEMENTS

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## 5. REFERENCES

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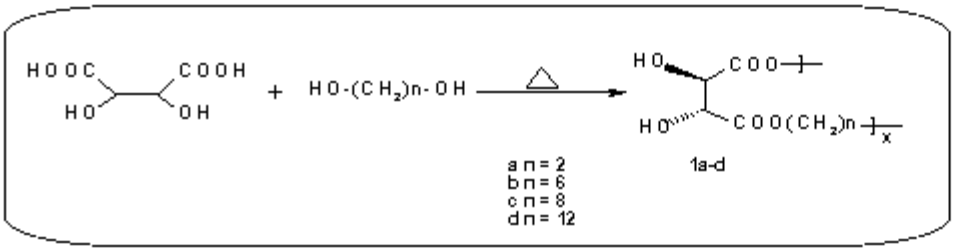
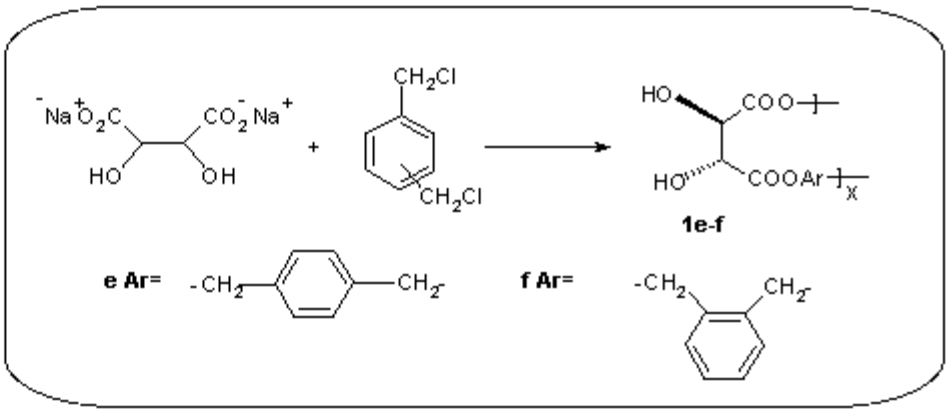
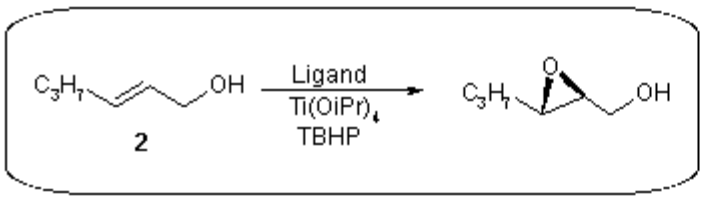



Scheme 1.




Scheme 2.




Scheme 3.

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

| Ligand | Molar ratio **2**:Ti:tartrate**1** | T/C | Reaction time /h[a] | Epoxide yield (%), GC[b] | Isolated yield (%)[c] | Ee%[e] |
|---|---|---|---|---|---|---|
| **1a** Homogen. | 100:17:20 | -20 | 3 | 51 | 50 | 8 |
| **1b** Homogen. | 100:17:20 | -20 | 3 | 63 | 63 | 55 |
| **1c** Homogen. | 100:5:10 | -20 | 3 | 22 | 59 | 79 |
| **1c** Homogen. | 100:17:20 | -20 | 7 | 92 | 58 | 79 |
| **1c** Heterogen. | 100:40:50 | -20 | 6 | 88 | 72[d] | 72[f*] |
| **1c** Heterogen. | 100:25:50 | -20 | 6 | 87 | 53[d] | 87[f*] |

| | | | | | | |
|---|---|---|---|---|---|---|
| **1d** Homogen. | 100:10:30 | -20 | 3 | 80 | 61 | 77 |
| **1d** Homogen. | 100:17:20 | -20 | 3 | 75 | 61 | 64 |
| **1e** Homogen. | 100:17:20 | -20 | 3 | 73 | 42 | 47 |
| **1f** Homogen. | 100:17:20 | -20 | 3 | 74 | 80 | 68 |

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