

Efficient Polymer-Supported Sharpless Alkene Epoxidation Catalyst*

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Abstract: Homogeneous linear poly(tartrate ester) ligands provide high chemical yields and enantiomeric excesses in the epoxidation of *trans*-hex-2-en-1-ol using Ti(OPrⁱ)₄-*tert*-butyl hydroperoxide. Branched poly(tartrate ester) can be used as heterogeneous ligands in the epoxidation of *trans*-hex-2-en-1-ol using Ti(OPrⁱ)₄-*tert*-butyl hydroperoxide. Removal and recovery of the polymer catalyst is a simple filtration at the end of reactions.

Keywords: Asymmetric epoxidation, Sharpless epoxidation, polymer-supported catalyst

Introduction

Immobilization of reactive species on a polymer support could provide many important advantages over analogous homogeneous systems; for example separation of the support from the reaction mixture can be achieved by simple filtration aiding isolation and purification procedures, reactive species can become more active and/or more selective due to changes in the microenvironment of the active sites, excess of a polymeric reagent can be readily employed without incurring a penalty in work-up, transition metal complexes and optically active catalysts might be efficiently retained for re-use, and noxious or toxic species might be encapsulated when bound to a macromolecule, with obvious advantages in environmental terms [1]. Though the limited commercial availability and the initial extra costs do not

favour the use of polymer supports, the numerous advantages are well recognised [1]. 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 focused on polymer-supported asymmetric alkene oxidation catalysts [3]. Interestingly, there are no reports of the successful immobilisation of the Sharpless Ti-tartrate ester-based asymmetric alkene epoxidation catalyst, despite this being a relatively long-standing and well used methodology. Some approaches to the production of a heterogeneous Sharpless-type epoxidation catalyst have been reported, but the level of asymmetric induction achieved was generally only modest [4].

We have previously reported on the synthesis of a group of poly(tartrate ester) ligands and their use with

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titanium tetraisopropoxide and *tert*-butyl hydroperoxide (tBHP) as the oxidant in epoxidising *trans*-hex-2-en-1-ol in high chemical yield and with good enantioselectivity [5]. Although the enantiomeric 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]. We believe therefore that our results are important in methodological and potentially technological terms, and offer the prospect of new information regarding the structure of the active species and its mechanistic role.

We have also synthesized in common organic solvents insoluble branched and/or crosslinked poly(tartrate ester)s and have studied the use of both homogeneous and heterogeneous optically active poly(tartrate ester) ligands in asymmetric epoxidations of a number of *trans*-allylic alcohols with titanium tetraisopropoxide and tBHP [6]. We have investigated the effect of the ratio of polymer ligand to titanium on the enantioselectivity and the yields, and the influence of the polymer backbone molecular architecture on asymmetric induction.

Results and Discussions

In a recent communication we 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 polyesters having pendant functional groups such as hydroxyl groups on a mainchain by melt polycondensation since the pendant groups participate in the reaction leading to crosslinking [7].

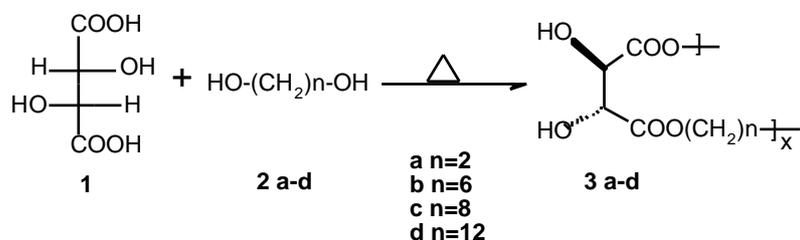
However, according to the ^1H NMR spectra of the products no branching/crosslinking was observed [8]. We therefore started our studies to evaluate the possibility of mimicking the Sharpless procedure using these linear soluble optically active polymers as ligands to achieve efficient and enantioselective catalysis. From the results obtained in a preliminary study of the epoxidation of *trans*-hex-2-en-1-ol, we hoped that the synthesis of similar but

heterogeneous polymer systems would be also possible. Accordingly we have now synthesized some branched/crosslinked optically active polyesters using elevated reaction temperature and prolonged reaction time [6].

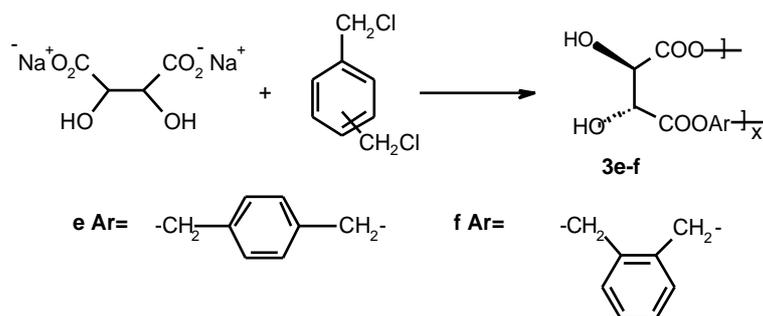
Optically active poly(tartrate ester)s

Poly(tartrate ester)s **3a-3d** were synthesized from L-(+)-tartaric acid **1**, diols **2** and **3** w-% *p*-toluene sulphonic acid as a catalyst using a standard polycondensation procedure, as shown in Scheme 1 [9]. Poly(tartrate ester)s **3e-3f** were synthesized from L-(+)-tartaric acid disodium salt dissolved in water and 1,2-dichloroethane dissolved in CHCl_3 by a phase transfer catalyzed procedure using tetrabutylammonium bromide hydrate (TBAB) as the catalyst as shown in Scheme 2 [10]. Polymers **3a-f** dissolved in some organic solvents, for example in Me_2SO and therefore the optical rotation could be measured. All the polymers display a positive optical rotation. Since the observed values are comparable to those reported for dimethyl-L-(+)-tartrate and for diethyl-L-(+)-tartrate [11], it seems that no significant racemization occurs during the various polymerization procedures. Solubility limitations have made molecular weight determination difficult, but two different batches of **3d** yielded $M_w = 4150$ and 4210 , with $M_w/M_n = 1.7$ by gel permeation chromatography using polystyrene standards in THF. Table 1 gives the relevant data for the synthesis and characterisation of polyesters **3a-f**.

The branched/crosslinked C_8 -alkyl group-containing poly(tartrate ester) gel **4** was synthesized from L-(+)-tartaric acid **1**, 20 mol-% excess of 1,8-octanediol **2c** and 3 w-% *p*-toluene sulphonic acid as a catalyst, as shown in Scheme 3 [9]. The conditions used were anaerobic and more forcing than with **3c**, and this seems to be the origin of the branching/crosslinking. Most of the polymer batches were soluble either in hot pyridine, hot THF or hot Me_2SO . All the polymers which were soluble in hot THF, displayed a positive optical rotation [12].



Scheme 1. Reagents and conditions: toluene-*p*-sulfonic acid (3 mass%), ca. 120 °C, 3days.



Scheme 2. Reagents and conditions: Bu_4NBr (20 mol%), H_2O , CHCl_3 , reflux, 7 days.

Table 1 Synthesis of polyesters **3**.

Polyester	Conversion (%)	$[\eta]_D^{25}$ ^a	$\nu_{\text{max}}/\text{cm}^{-1}$ (C=O, OH)	Elemental microanalysis (%)	
				Calculated	Found
3a	73	+13 ^b	1755, 3479	C, 40.92; H, 4.58	C, 39.2; H, 4.6
3b	68	+25	1755, 3479	C, 51.72; H, 6.94	C, 51.5; H, 6.5
3c ^c	95	+17	1747, 3469	C, 55.37; H, 7.74	C, 56.4; H, 7.8
3d ^d	55	+4 ^e	1755, 3470	C, 60.74; H, 8.92	C, 61.0; H, 9.2
3e	45	+18	1748, 3430	C, 57.14; H, 4.80	C, 52.3; H, 5.1
3f	48	+15	1747, 3420	C, 57.14; H, 4.80	C, 56.3; H, 5.1

^a Concentrations: 0.2 g per 100 ml Me_2SO , Perkin Elmer WM250.

^b Concentration: 0.4 g per 100 ml MeOH.

^c Washed with hexane.

^d $M_w = \text{ca. } 4200$, $M_w/M_n = \text{ca. } 1.7$, determined by GPC with polystyrene standards in THF.

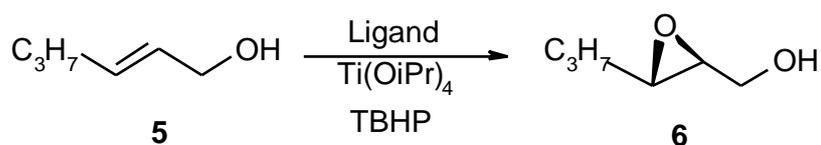
^e Concentration: 0.8 g per 100 ml in CHCl_3 .

Asymmetric epoxidation of *trans*-hex-2-en-1-ol using homogeneous poly(tartrate ester)s ligands

The results for epoxidation reactions of *trans*-hex-2-en-1-ol are summarized in Table 2. Poly(tartrate ester) ligands **3a-f** formed CH_2Cl_2 soluble complexes with titanium tetraisopropoxide and *tert*-butylhydroperoxide and thus could not be filtered off at the end of the reaction [13]. It was expected that these homogeneous systems would react like low molar mass dimethyl- and diethyltartrates since the reactants and the soluble catalysts are uniformly distributed throughout the reaction medium [14]. In practice reactions were somewhat slower with the polymer ligands than with the low molar mass esters, and so the

ligand/substrate ratios and Ti/substrate ratios used were somewhat higher.

Sharpless *et al.* [15] have shown that by adding molecular sieves in the epoxidation of *trans*-hex-2-en-1-ol, using 5/6 % Ti/diethyl-L-(+)-tartrate as the catalyst, reaction rates are roughly twice as fast as without sieves, the main function of the sieves being protection of the catalyst from adventitious water in the reaction medium [16]. All our reactions were therefore performed using molecular sieves. Conversions were monitored using GC, and the reactions were stopped when the conversions were over 60 %. In general, the conversion of this allylic alcohol to epoxide is good (up to 92 %) and comparable to the value obtained with dimethyl tartrate. The isolation procedure has not however been fully optimised and it was



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

Table 2. Epoxidation of *trans*-hex-2-en-1-ol **5** with tBHP by L-(+)-polyester **3a-f/4** and Ti(OiPr)_4 at -20°C (Scheme 4).

Ligand	Molar ratio 5:Ti:tartrate	Reaction time /h ^a	Epoxide yield (%), GC ^b	Isolated yield (%) ^c	Ee% ^e
3a Homogen.	100:17:20	3	51	50	8
3b Homogen.	100:17:20	3	63	63	55
3c Homogen.	100:5:10	3	22	59	79
3c Homogen.	100:17:20	7	92	58	79
4 Heterogen.	100:40:50	6	88	72 ^d	72 ^f
4 Heterogen.	100:25:50	6	87	53 ^d	87 ^f
3d Homogen.	100:10:30	3	80	61	77
3d Homogen.	100:17:20	3	75	61	64
3e Homogen.	100:17:20	3	73	42	47
3f Homogen.	100:17:20	3	74	80	68

^a From addition of **5**.

^b From GC analysis.

^c After additional 12 h in freezer, work-up and Kugelrohr-distillation.

^d After additional 12 h in freezer, work-up and Flash-chromatography.

^e ee% determined via chiral HPLC (Chiralcel OB, hexane-PrⁱOH).

^f ee% determined by ¹H NMR Shift analysis of the derived acetate with Eu(hfc)_3 in benzene-d₆.

Conclusion

The first successful polymer-supported Sharpless-type epoxidation catalyst has been developed. Several oligomeric linear poly(tartrate ester)s ligands have been used homogeneously in the epoxidation of *trans*-hex-2-en-1-ol with titanium tetraisopropoxide and *tert*-butyl hydroperoxide as the oxidant. These ligands provide high chemical yields and good enantioselectivities, comparable

to the monomeric catalytic system. The highest enantioselectivity (79 ee%) was attained using polymer **3c** having a flexible C₈-spacer between the functional hydroxyl groups. The nature of the complex with Ti (intramolecular vs. intermolecular) is now being studied by molecular modelling.

Preliminary results indicate that the branched poly(tartrate ester) **4** can be used successfully as a heterogeneous ligand in the epoxidation of *trans*-hex-2-en-

1-ol. Surprisingly the chemical yields and enantiomeric excesses were even higher than when using oligomeric polymer ligands (up to 87 ee%). Removal and recovery of the polymer catalyst is a simple filtration at the end of the reactions which remarkably facilitates the work-up procedure.

Experimental Section

General

The ^1H NMR and ^{13}C NMR spectra were obtained on a 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 Carlo Erba GCHR 5300 Mega Series employing a SGE BPX5 column or Perkin Elmer 8500 equipped with FID detector employing a 25-m packed with fused silica column (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 Perkin-Elmer WM250 or Perkin-Elmer 243 B polarimeters 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. 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. Absolute configurations were determined by comparison of the observed rotation by polarimetry with the literature value. General preparation and shift study analysis of acetates followed the procedure described in reference 15.

Materials

Pre-activated and powdered 4Å molecular sieves were available from Aldrich Chemical Co. and they were used as received. Cooling was accomplished through the use of the following bath: acetone/liquid nitrogen. The dichloromethane used did not contain methanol and therefore was not distilled but was stored over CaCl_2 . Aqueous 70 % *tert*-butyl hydroperoxide (TBHP) was obtained from the Aldrich Chemical Co. Preparation and molarity determination of anhydrous TBHP followed the procedure described in reference 21. Reagents handled by

syringe were measured by weight or by volume.

General work-up procedure

The work-up followed the literature procedure [15] with slight modifications. The work-up procedure is described for reactions utilizing 0.1 mol of substrate, 3.0 g of sieves, 5 mmol of $\text{Ti}(\text{O}-i\text{-Pr})_4$, 6 mmol of tartrate and 0.2 mol of TBHP. The amounts were scaled proportionally.

The cold (–20 °C) reaction mixture was quenched with a 30 % aqueous solution of sodium hydroxide saturated with sodium chloride. After 10 w-% 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 of TBHP was removed by azeotropic distillation with toluene.

Linear Optically Active Polyesters 3d

An oven-dried 100 ml three-necked round-bottomed flask equipped with a magnetic stir-bar was charged with L-(+)-tartaric acid (5 g, 0.033 mol), 1,12-dodecanediol (6.74 g, 0.033 mol) and 3 w-% *p*-toluene sulphonic acid (0.3 g). The reaction mixture was stirred at 120 °C for 3 days. Water and unreacted diol were removed by distillation under high vacuum at the end of reaction. The resulting solid was crushed, washed with acetone/hexane in a Soxhlet apparatus for *ca.* 16-20 hours and dried in vacuum oven (50 °C) for *ca.* 15 hours to yield 5.70 g, 55 % C_{12} -poly(tartrate ester) **3d**.

FTIR (KBr) 3470, 3308, 2916, 2849, 1755, 1722, 1468, 1287, 1195, 1132, 1070, 971. ^1H NMR (400MHz, $\text{DMSO}-d_6$, 70 °C) 4.36 (s, 2H), 4.09 (t, $J = 6.6$ Hz, 4H), 1.59 (m, 4H), 1.30 (m, 16H). ^{13}C NMR (400MHz, $\text{DMSO}-d_6$, 70°C) 171.1, 72.5, 64.5, 60.8, 28.8, 28.5, 28.1, 25.2.

Polymers **3 a-c** were obtained analogously (Table 1).

Preparation of linear optically active polyesters containing aromatic spacer 3f

An oven-dried 100 ml three-necked round-bottomed flask equipped with a magnetic stir-bar and a reflux condenser was charged with 5g of L-(+)-tartaric acid disodium salt (0.022 mol) dissolved in 10 ml of water, 3.8 g of ,'-dichloro-*o*-xylene (0.022 mol) dissolved in 20 – 30 ml of chloroform and 20 mol-% tetrabutyl ammonium bromide hydrate (1.42 g, 0.0044 mol) as a phase transfer catalyst. The reaction mixture was reflux for 7 days. Solvents were evaporated to dryness and white solid was washed with hot water and diethyl ether and dried in a vacuum oven (+50 °C) for 2 days to yield 2.65 g, 48 %

poly(tartrate ester) **3f**. FTIR (KBr) 3545, 3394, 2967, 2873, 1747, 1445, 1421, 1374, 1290, 1266, 1225, 1128, 1089, 970, 818, 677. ¹H NMR (400MHz, DMSO-d₆, 70 °C) 7.39 (m, 4H), 5.21 (s, 4H), 4.56 (s, 2H). ¹³C NMR (400MHz, DMSO-d₆, 70 °C) 170.10, 128.82, 128.62, 127.86, 127.70, 72.21, 65.78.

Polymer **3e** was obtained analogously (Table 1).

Preparation of branched/crosslinked optically active polyester **4**

An oven-dried 100 ml three-necked round-bottomed flask equipped with a magnetic stirbar, 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, 0.07996 mol) and 3 w-% p-toluene sulphonic acid (0.6 g). Temperature was raised to 140-150 °C to get a homogeneous mixture and then stirred at 120-130 °C for 3-4 days under nitrogen. Water and unreacted diol were removed by distillation under high vacuum at the end of reaction. The resulting solid was swelled by refluxing in ethyl acetate and then poured in *n*-hexane. The solvents were decanted and the polymer dried in high vacuum at +40 °C for 6 hours and at room temperature for 2 days to yield 16.6 g, 95 % of C₈-poly(tartrate ester) **4**. [_D²⁵ + 9° (c 1.6, THF). FTIR (KBr) 3450, 2932, 2857, 1743, 1466, 1395, 1128, 1091, 1011, 956. Anal. Found: C, 55.26; H, 8.47. ¹H NMR (400MHz, DMSO-d₆, 70 °C) 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). ¹³C NMR (400MHz, DMSO-d₆, 70 °C) 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).

General procedure for the catalytic asymmetric epoxidation using homogeneous polymer-ligand

The literature procedure [15] 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, polymer-ligand **3** and dry CH₂Cl₂. The flask was cooled to -20 °C and Ti(O-*i*-Pr)₄ (via syringe) was added sequentially with stirring. The reaction mixture was stirred at -20 °C and after about one hour 2 equiv. of TBHP in *iso*-Octane was added with a syringe at a moderate rate. The resulting mixture was stirred at -20 °C at least for hour. Substrate (dissolved in dry CH₂Cl₂) 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 3-7 hours at -15 °C to -20 °C and the yield was determined using gas chromatographic analysis. The reaction mixture was stored

in a freezer overnight, the GC yield was then determined and work-up was performed. The crude product was purified by Kugelrohr-distillation and the enantiomeric purity of the epoxide was measured by chiral HPLC analysis.

(2*S*-trans)-3-Propyloxiranemethanol (**6**)

The epoxidation was performed as described above. C₈-poly(tartrate ester) **3c** (0.52 g, 0.002 mol) was swelled in 30 ml of CH₂Cl₂ containing 0.6 g of powdered, activated 4 Å molecular sieves. Ti(OPr^{*i*})₄ (0.28 g, 0.001 mol), 10.1 ml of a 3.97 M solution of TBHP in *iso*-Octane and 2 g (0.020 mol) of *trans*-hex-2-en-1-ol (dissolved in 10 ml CH₂Cl₂) were added. The reaction mixture was stirred at -20 °C for 3 h. The reaction mixture was stored at -20 °C over the weekend. Workup was then performed and crude product was purified by Kugelrohr-distillation to give a colourless oil **5** (1.36 g, 59 % yield, 91 % purity, 79 % ee by HPLC, Chiralcel OB column): [_D²⁵ - 32° (c 1.95, CHCl₃), GC analysis after 3 h: 22 % epoxide, GC analysis before work-up: 61 % epoxide. FTIR (CHCl₃) 3030, 3013, 2977, 2952, 2883, 2856, 1237, 1196, 1083, 1029, 938, 879. ¹H NMR (200 MHz, CDCl₃) 3.82 (dd, *J* = 2, 13 Hz, 1H), 3.53 (dd, *J* = 2, 13 Hz, 1H), 2.91-2.83 (m, 2H), 2.68 (s, 1H), 1.55-1.43 (m, 4H), 0.90 (t, *J* = 7 Hz, 3H). MS (EI, *m/z*, relative intensity) 99 (2, M-17)⁺, 81 (13), 73 (48), 55 (100), 43 (36). HRMS (EI) Calcd for C₆H₁₂O₂ 116.0837, found 116.0832.

General procedure for the catalytic asymmetric epoxidation using heterogeneous polymer-ligand

The literature procedure [15] for the epoxidation of allylic alcohols was followed with modifications. An oven-dried three-necked round-bottomed flask equipped with a magnetic stirbar, nitrogen inlet, septum and bubbler was charged with 4 Å powdered, activated molecular sieves, polymer-ligand **4** and dry CH₂Cl₂. The flask was cooled to -20 °C and Ti(O-*i*-Pr)₄ (via syringe) was added sequentially with stirring. The reaction mixture was stirred at -20 °C and after about one hour 2 equiv. of TBHP in *iso*-Octane was added with syringe at a moderate rate. The resulting mixture was stirred at -20 °C at least for one hour. Substrate (dissolved in dry CH₂Cl₂) 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 at -15 °C to -20 °C. The reaction mixture was stored in a freezer up to weeks. 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 dichloromethane. Workup was then performed. The crude product was purified by flash-chromatography (eluent: petrol ether (40 °C-60 °C):diethyl ether, 50 %) and enantioselectivity of epoxide was

measured by 400 MHz NMR using chiral Eu(hfc)₃-reagent (as acetates).

(2*S*-*trans*)-3-Propyloxiranemethanol (6)

The epoxidation was performed as described above. C₈-poly(tartrate ester) **4** (2.6 g, 0.01 mol) was swelled in 40 ml of CH₂Cl₂ containing 0.3g of powdered, activated 4Å molecular sieves. Ti(OPrⁱ)₄ (1.42 g, 0.005 mol), 12.5 ml of a 3.2 M solution of TBHP in *iso*-Octane and 2 g (0.02 mol) of *trans*-hex-2-en-1-ol (dissolved in 10 ml CH₂Cl₂) were added. The reaction mixture was stirred at -20 °C for 6 h and stored at -20 °C overnight. Polymer was filtered off and washed throughly with CH₂Cl₂. Workup was then performed and crude product was purified by flash-chromatography (eluent: petrol ether (40°C - 60°C):diethyl ether, 50 %) to give colourless oil (1.22 g, 53 % yield, 100 % purity, 87 %ee by ¹H NMR analysis of the derived acetate with Eu(hfc)₃): [²⁵D -38° (c 2.01, CHCl₃), GC analysis before work-up: 78 % epoxide. FTIR (CHCl₃) 2977, 2952, 1717, 1457, 1237, 1196, 933, 881, 806, 796. ¹H NMR (200 MHz, C₆D₆) 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 C₆H₁₂O₂ 116.0837, found 116.0882.

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Sample Availability: available from the authors.