Copolymers of Polystyrene—New Polymer Supports for Asymmetric Epoxidation of Allylic Alcohols

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ABSTRACT: Tartrate-functionalized polystyrene copolymers were prepared with divinyl benzene, tetraethylene glycol diacrylate, and diallyl tartrate as the crosslinking agents. These insoluble materials possessed the unique advantages of heterogeneous reagents. These resins were used to support the asymmetric epoxidation of allylic alcohols along with titanium tetraisopropoxide and tert-butyl hydroperoxide with reasonably good yields and a high enantiomeric excess. The swelling behavior and molecular architecture of the polymer backbone significantly influenced the effectiveness of the catalyst.

INTRODUCTION

Many reports1–3 have been published on the use of polymer-based heterogeneous supports as catalysts or reagents. By heterogenizing catalysts or reagents, one can eliminate certain practical limitations of homogeneous catalysis. The discovery by Katsuki and Sharpless4 of a procedure for the asymmetric epoxidation of allylic alcohols with diethyl tartrate, titanium tetraisopropoxide, and tert-butyl hydroperoxide was an important milestone in asymmetric synthesis. Because the methodology4–7 involves a rather elaborate workup procedure, the development of a solid-phase analogue of the reaction would be a worthwhile improvement. If the tartrate ester is heterogenized, the crucial saponification step in the workup can be avoided. Attempts already have been made with considerable success to develop polymer-supported systems.8–10 Farrall et al.’s8 employment of a single tartrate ester unit bound to a polystyrene resin for the asymmetric epoxidation of allylic alcohol resulted in a very low asymmetric induction. Karjalainen et al.9 introduced soluble polytartrate esters for use as ligands in asymmetric epoxidation with significant success. Enantiomeric excess up to 98% was achieved with heterogeneous ligands containing branched/crosslinked poly(tartrate ester)s.10 Longer reaction times were needed to epoxidize cis-allylic alcohols with branched/crosslinked poly(tartrate ester)s.10 Recently, we synthesized a new set of tartrate crosslinked resins based on polystyrene that were used efficiently as reagents in the epoxidation of trans-olefinic alcohols, replacing diethyl tartrate in the conventional Sharpless epoxidation methodology. We report here the development and uses of the new polymeric supports.

RESULTS AND DISCUSSION

A chloromethyl group attached to styrene can be functionalized by a nucleophilic substitution that involves reactive anions. Ester functions have been introduced through triethylamine11,12 with chloromethylated groups. The use of triethylamine for esterification is a known reaction.13 Tartrate esters of polystyrene crosslinked with...
divinyl benzene (DVB) and tetraethylene glycol diacrylate (TTEGDA) were prepared from chloromethylated resins by the nucleophilic displacement of chlorine in the presence of triethylamine under acetone reflux. These tartrate resins were prepared to study the performance of a solid-phase reagent in the asymmetric epoxidation of allylic alcohols.

The performance of any polymer-supported reaction is decided largely by the microenvironment of the solid support, such as the nature of the polymer backbone and the nature and extent of the crosslinking and separation of the functional group from the three-dimensional macromolecular matrix. To study the influence and interdependence of these factors we decided to choose the polymers discussed next.

Tartrate-functionalized polystyrene resins containing 1 mol % DVB (P1), 2 mol % DVB (P2), 1 mol % TTEGDA (P3), and 2 mol % TTEGDA (P4) as the crosslinking agents were employed as polymer supports. The resin containing TTEGDA was expected to perform better than the resins containing DVB crosslinks because of the greater swelling of the resin. The variation of the nature of the crosslinking agent and its concentration also were expected to give an idea about the interdependence of the crosslinking density and hydrophobicity of the polymeric material toward the epoxidation process. Locational alteration of the tartrate group was provided by the preparation of a new terpolymeric polystyrene resin copolymerized with diallyl tartrate (DAT) and DVB, in which the tartrate group was attached to the main polymer backbone (P5).

The suspension polymerization of styrene with DVB and TTEGDA as the crosslinking agents was carried out. The polymer beads formed were insoluble in common solvents and were sieved to obtain particle sizes in the range of 180 to 850 μm. The IR spectrum (KBr) of the DVB crosslinked resins showed intense absorption bands characteristic of phenyl groups. In TTEGDA crosslinked polystyrenes, the presence of carbonyl stretching in the IR spectrum (KBr pellet) at 1728 cm⁻¹ and a broad band at 1150 cm⁻¹ characteristic of ether linkages of the crosslinking agent confirmed the copolymer formation.

The crosslinked resins were subjected to chloromethylation with chloromethyl methyl ether (CMME) according to the reported procedure with modifications. The TTEGDA crosslinked resins were chloromethylated with Lewis acid (ZnCl₂). Some degradation likely took place but did not affect adversely the performance of the resin, as seen in the literature. The ester group of the crosslinker in the TTEGDA crosslinked resins was not affected significantly under the reaction conditions employed for chloromethylation. This was confirmed by IR with the presence of absorption bands at 1728 cm⁻¹ characteristic of ester carbonyl and at 1150 cm⁻¹ corresponding to ether linkages.

Because the polymer was insoluble in all types of solvents, UV and NMR by solution techniques were not possible. However, IR spectroscopy was very useful. IR spectra were run with a fine powder of polymer beads pelletized with KBr. In the DVB crosslinked resins after tartrate incorporation (P1 and P2), ester peaks appeared at 1728 cm⁻¹ in IR. Absorption due to free acid was not seen in the IR spectra of the functionalized resin. The tartrate-functionalized resins were analyzed quantitatively for the extent of esterification via infrared spectroscopy by a new technique developed in this study. The tartrate resin was transesterified by absolute ethanol in the presence of dry hydrogen bromide, and the diethyl tartrate formed was separated quantitatively and was analyzed for its tartrate content by IR spectroscopy. The intense ester carbonyl peak at 1725–1745 cm⁻¹ was compared with a set of standards prepared from diethyl tartrate in CCl₄. Repeated analysis of the resin gave consistent results confirming the accuracy of the method. Analysis of tartrate-functionalized TTEGDA crosslinked resins also were carried out in a similar manner. Although some degradation of the resin could have taken place in these resins during transesterification with EtOH/HBr, it may not have been significant because the resin did not dissolve. The recovered resins were not examined. Such degradation, obviously, did not affect the accuracy of the estimation.

The remaining chlorine present in the tartrate-functionalized resin was estimated by Volhard’s method. If the only process leading to chlorine loss were displacement by tartrate, there should have been a correlation between these two. However, the chlorine content of the resins left unreacted after the reaction as estimated by titrimetry was much lower than that expected from the tartrate content (Table I) estimated by the IR method. The low chlorine content present in the functionalized resin may not have been due to tartrate formation alone. It also may have been due to the loss of chlorine as exchangeable chlo-
ride from the quaternary salt formed because of the reaction with triethylamine. The results are tabulated in Table I.

Suspension polymerization with styrene and DAT monomers was attempted. Even after 72 h, the polymer beads were not formed. Hence, we decided to bulk polymerize the monomers. Even the bulk polymer prepared was very soft and rubbery in nature, possibly because the polymer growth was lost by a degradative chain transfer due to the presence of an allyl group. Generally, the polymerization of allyl monomers will not proceed to high molecular weights in the usual free-radical polymerization techniques but instead will result in branched polymers at higher conversions. Ohata et al. studied the copolymerization of DAT with styrene and compared its reactivity ratios. When nonpolar solvents were used for bulk polymerization, DAT units increasingly were incorporated. In this study, the addition of DVB as an additional crosslinking agent was carried out in the bulk polymerization of styrene and DAT with benzene as the solvent. Suspension polymerization was attempted, but no beads were formed. The terpolymeric resin (P5) thus prepared was insoluble in CH₂Cl₂, the solvent used for epoxidation and also found to possess improved mechanical stability. The presence of tartrate functionality was confirmed by the strong absorption band at 1740 cm⁻¹. The estimation of tartrate function by hydrolysis was attempted by refluxing with dilute HCl, but the residue collected had unidentifiable impurities. Hence, the quantity of the tartrate group incorporated could not be determined.

Structure of the Polymer

In resins P1 to P4, the IR spectrum and transesterification by ethanol clearly showed the incorporation of tartaric acid. Whether the tartaric acid was present as a diester (i.e., crosslinked), a monoester (i.e., pendant group), or both could not be decided conclusively. The absence of an IR band at 1700 cm⁻¹ suggested the absence of a free COOH group. However, considering the low intensity of the carbonyl signals in the IR spectrum of the resins, we could not accept this as conclusive evidence. The tartrate contents (Table I) were on the higher side in comparison to the chloride equivalent of the parent resin. It is possible that both crosslinked tartrate (diester) and pendant tartrate (monoester) were present. The residue did show titerable acidity (Table I). If the acidity was due to free carboxyl groups, the acid equivalent of the resin corresponded to 3 to 7.8% of the tartaric acid monoester. Hence, crosslinking may not have been the only mode of the attachment of tartrate.

In resin P5, the DAT was copolymerized with styrene and DVB. The rate of polymerization of the allyl substrates was much lower than that of styrene. Hence, tartrate incorporation in the polymer was expected to be low. Because allyl groups could act as a chain-transfer agent, the molecular weight of the polymer also may be low. Although DAT potentially could be a crosslinking agent, due to its low reactivity, most of the tartrate incorporated may have remained pendant groups. This was demonstrated by styrene-DAT, in the absence of DVB, not yielding a rigid polymer. The presence of unreacted pendant allyl groups also was confirmed by the bromine number (2.06 g/100 g of resin; measured in accordance with ASTM D 1492). Hence, it was reasonable to expect that the terpolymer styrene-DAT-DVB was a styrene-DVB crosslinked polymer with occasional allyl tartrates in the chain.

Table I. Analysis of Tartrate Functionalized Resin

<table>
<thead>
<tr>
<th>Resin</th>
<th>Cl Content Before Functionalization (mmol/g)ᵃ</th>
<th>Tartrate Content (mmol/g)ᵇ</th>
<th>Free Acid (mmol/g)ᶜ</th>
<th>Cl Content (mmol/g)ᵃ</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>2.53</td>
<td>1.00</td>
<td>0.078</td>
<td>0.15</td>
</tr>
<tr>
<td>P2</td>
<td>2.39</td>
<td>0.90</td>
<td>0.052</td>
<td>0.13</td>
</tr>
<tr>
<td>P3</td>
<td>1.72</td>
<td>0.78</td>
<td>0.020</td>
<td>0.13</td>
</tr>
<tr>
<td>P4</td>
<td>1.78</td>
<td>0.74</td>
<td>0.023</td>
<td>0.16</td>
</tr>
</tbody>
</table>

ᵃ Chlorine content estimated by Volhard’s method.ᵇ Estimated by IR.ᶜ By titrimetry (estimated from alkali consumed by 5 g of resin kept soaked in 20 mL of 0.05 N KOH overnight).
Solvation and Swelling Characteristics of the Resin

The swelling of a crosslinked polymer is a measure of its solvation by a given solvent.\textsuperscript{20} For maximum accessibility of functional groups in a resin, there should be extensive swelling of the polymer. Swelling characteristics were measured as the volume of solvent absorbed in mL/g of the dry resin.\textsuperscript{14} The swelling of the resins (Table II) were in the order $P_5 > P_3 > P_4 > P_1 > P_2$. The resins made out of DAT had maximum swelling. As expected, the polystyrene resins crosslinked with TTEGDA were less hydrophobic compared to polystyrene crosslinked with DVB. Also, the less crosslinked resins had better swelling characteristics, perhaps because an increase in the crosslinking densities increased the rigidity of the resin.

Surface Analysis by Scanning Electron Microscopy (SEM)

Scanning electron micrographs were taken for polystyrenes crosslinked with DVB and TTEGDA. The electron micrographs furnished in Figure 1(a) reveal that the beads were porous, although they were gel-type resins. The polystyrene resin copolymerized with DAT and DVB also was examined by SEM. The granular particles had pores on the surface [Fig. 1(a)]. Recovered resins also were examined for surface defects [Fig.1(b)].

Application in Asymmetric Synthesis

These chiral resins were used as the tartrate component of the Sharpless asymmetric epoxidation of the allylic alcohols. The procedure for epoxidation essentially was based on the Sharpless procedure for the homogeneous reaction. A control reaction using a homogeneous catalyst was performed according to the Sharpless method\textsuperscript{7} with a substrate : Ti : tartrate ratio of 100 : 5 : 7.5. Preliminary studies on epoxidation were conducted with tartrate resins at the substrate : Ti : tartrate ratio employed for the homogeneous reaction. The asymmetric induction achieved was very low, 12 to 23\% enantiomeric excess. Hence, a series of experiments were conducted through variance of the substrate : Ti : tartrate ratio, and optimum results were obtained at the ratio 100 : 25 : 50. Previous studies\textsuperscript{10} using branched/crosslinked poly(tartrate ester)s also indicate that the optimum Ti : tartrate ratio is 1 : 2. The resin soaked in dichloromethane was dried with molecular sieves overnight. We performed the reaction by giving sufficient time for the reagents to equilibrate after each addition. For all the substrates reported, the reaction was carried out at $-20^\circ \text{C}$, and the residence time was more than what has been reported previously for homogeneous conditions. Workup by the addition of water regenerated the resin tartrate.

During the water workup, the hydrolyzed titanium compounds remained as a suspension in the aqueous phase. All that was required was the separation of the dichloromethane layer that contained, in addition to the epoxide, small quantities of unreacted allylic alcohol, t-butyl hydroperoxide, and possibly isopropyl alcohol. The product was isolated readily. In the original Sharpless reaction, the diethyl tartrate was present in the reaction mixture and had to be removed by either alkaline hydrolysis or chromatography. The advantage of using a polymer-supported reagent is

Table II. Swelling* Behavior of Crosslinked Polystyrene Resins

<table>
<thead>
<tr>
<th>Resin</th>
<th>DMF\textsuperscript{b} (ml)</th>
<th>DMSO\textsuperscript{c} (ml)</th>
<th>THF (ml)</th>
<th>Benzene (ml)</th>
<th>DCM\textsuperscript{d} (ml)</th>
<th>Acetone (ml)</th>
<th>IPA\textsuperscript{e} (ml)</th>
<th>Methanol (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.80</td>
<td>2.10</td>
<td>2.15</td>
<td>2.60</td>
<td>2.95</td>
<td>1.9</td>
<td>0.55</td>
<td>0.40</td>
</tr>
<tr>
<td>P2</td>
<td>1.70</td>
<td>1.95</td>
<td>2.00</td>
<td>2.55</td>
<td>2.65</td>
<td>1.9</td>
<td>0.43</td>
<td>0.21</td>
</tr>
<tr>
<td>P3</td>
<td>2.23</td>
<td>2.20</td>
<td>2.34</td>
<td>2.30</td>
<td>3.20</td>
<td>2.4</td>
<td>0.98</td>
<td>0.71</td>
</tr>
<tr>
<td>P4</td>
<td>2.20</td>
<td>2.20</td>
<td>2.15</td>
<td>2.10</td>
<td>2.95</td>
<td>2.2</td>
<td>0.90</td>
<td>0.72</td>
</tr>
<tr>
<td>P5</td>
<td>2.86</td>
<td>2.85</td>
<td>3.16</td>
<td>2.20</td>
<td>3.41</td>
<td>2.6</td>
<td>1.80</td>
<td>1.58</td>
</tr>
</tbody>
</table>

\* Measured as the volume of the solvent absorbed in mL/g of dry resin.\textsuperscript{14} 
\textsuperscript{b} dimethylformamide 
\textsuperscript{c} dimethyl sulfoxide 
\textsuperscript{d} dichloromethane 
\textsuperscript{e} isopropyl alcohol
mainly the ease of the workup. A summary of the results is listed in Table III. In terms of the yield on all the resins, the epoxidation of geraniol was less efficient than that of the other two substrates. The longer chain and greater branching in the molecule possibly made access to the polymer-bound reaction sites more difficult. The change in the mol % of the crosslinking agent in both the DVB and TTEGDA crosslinked resins did not affect the yield of the product formed but significantly influenced the asymmetric induction (Table III). The styrene-TTEGDA crosslinked systems (P3 and P4) were comparatively better in performance than styrene-DVB. These inferences could be attributed not only to the swelling behavior but also to the topography of the polymer, which was determined by the chemical nature and mol % of the crosslinking agent. The highest enantioselectivity achieved was 91% in the epoxidation of cinnamyl alcohol with P3 resin, which was much lower than that achieved by the conventional Sharpless method but higher than that reported8,10 with earlier polymer-supported catalytic systems. The styrene-diallyltartrate-DVB system gave comparatively smaller chemical yields and less enantioselectivity. This could be attributed to the difficulty of the polymer backbone to attain the required conformation for the formation of the polymer-titanium complex.10

The resins were tested for reuse after being dried in vacuo. We successfully used them three times without changing any reaction parameters.

Figure 1. (a) SEMs of tartrate resins and (b) SEMs of recovered tartrate resins after second recycle.
Isolation of the resin after the reaction was easier and without much weight loss if it was removed when the crude mixture was at a temperature below 0 °C. After a water and acetone wash, the dried recovered resin was free from TiO₂. The absence of TiO₂ was confirmed by an established procedure.²¹ An IR spectrum of the resin taken before and after the reaction indicated that there was no significant change in the tartrate function of the resin during the reaction that established the hydrolytic stability of the tartrate ester under the epoxidation conditions. However, the recovered resin, as shown by SEM [Fig. 1(b)], had surface damage.

### EXPERIMENTAL

### Reagents and Materials

All the reagents used in this study were of analar grade and were distilled before use. Methanol was refluxed over KOH pellets (15 g/L) for 6 h and then distilled (bp = 65 °C). Ethanol, diethyl ether, acetone, dichloromethane (CH₂Cl₂), and benzene were purified by standard methods.²² Titanium tetraisopropoxide, tert-butylhydroperoxide (TBHP), DVB 55% (technical grade), and TTEGDA were procured from Aldrich, USA. TBHP was purified²³ before use. Styrene (Merck, Germany) was washed with NaOH (1% aqueous solution) to remove the polymerization inhibitor and then was washed with water dried over anhydrous sodium sulfate. It then was deaerated with nitrogen for 30 min and distilled under reduced pressure. CMME and 1 M zinc chloride were prepared in our laboratory. DAT was prepared according to the reported procedure²⁴ and was distilled under reduced pressure before use (bp = 170–171 °C/10 mm Hg). DVB was destabilized just as the styrene and was distilled under reduced pressure. TTEGDA was used as obtained from Aldrich.

### Instrumental Methods

IR spectra were recorded on a Shimadzu (Japan) IR-470 or a Perkin–Elmer (USA) 983 spectrometer in the range of 4000 to 200 cm⁻¹. The gas chromatography (GC) analysis was carried out on a Chemito (India) GC equipped with a flame ionization detector using a SE 30 column. ¹H NMR spectra were recorded on a JEOL (Japan) JNM-GSX-400 FT NMR instrument operating at 400 MHz with tetramethylsilane as the internal standard. Optical rotations were measured on a JASCO (Japan) DIP 370 digital polarimeter. Scanning electron micrographs were taken with a JEOL JSM 5300 scanning microscope.

### Suspension Polymerization of Styrene with DVB as the Crosslinking Agent

The preparation of polystyrene crosslinked with 1% DVB (P1) was carried out according to the

### Table III. Epoxidation of Allylic Alcohols

<table>
<thead>
<tr>
<th>Resin</th>
<th>Residence Time (Min)</th>
<th>Yield (%)</th>
<th>ee (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>DET²⁵</td>
<td>180</td>
<td>90</td>
<td>150</td>
</tr>
<tr>
<td>P1</td>
<td>460</td>
<td>180</td>
<td>330</td>
</tr>
<tr>
<td>P2</td>
<td>465</td>
<td>190</td>
<td>330</td>
</tr>
<tr>
<td>P3</td>
<td>380</td>
<td>170</td>
<td>310</td>
</tr>
<tr>
<td>P4</td>
<td>390</td>
<td>175</td>
<td>300</td>
</tr>
<tr>
<td>P5</td>
<td>435</td>
<td>135</td>
<td>310</td>
</tr>
</tbody>
</table>

²¹ Reaction temperature, −20°C; substrate : Ti : tartrate ratio, 100 : 25 : 50.
²² Refers to the time required for the complete disappearance of the starting material by TLC. A = trans-cinnamyl alcohol; B = trans-geraniol; C = trans-2-hexen-1-ol.
²³ Configuration assigned by comparison with the literature.⁷
²⁴ (2S,3S)-3-phenyl oxiranemethanol. ee % was determined by ¹H NMR shift analysis of the ester derived from (+)-α-methoxy-α-(trifluoromethyl) phenylacetyl chloride (MTPA chloride).ⁱ⁰
²⁵ (2S,3S)-3-methyl-3-(4-methyl-3-pentenyl) oxiranemethanol. ee % was determined by ¹H NMR shift analysis⁷ of the derived acetate with Eu(hfc)₃.
²⁶ (2S,3S)-3-propyl oxiranemethanol. ee % was determined by ¹H NMR shift analysis⁷ of the derived acetate with Eu(hfc)₃.
²⁷ Control reaction with L(-)-diethyltartrate (homogeneous epoxidation) was carried out at the substrate : Ti : tartrate ratio 100 : 5 : 7.5.
reported procedure\textsuperscript{15} with modifications. A mixture of destabilized styrene (30.9 g, 297 mmol), DVB (0.71 g, 3 mmol), benzoyl peroxide (500 mg), and toluene (14 mL, \(\sim 40\) vol % of the monomers) was suspended into a solution of polyvinyl alcohol (PVA) (4 g in 400 mL of distilled water) by the stirring of the whole mixture at about 400 rpm. The reaction flask was flushed with nitrogen and maintained at 80 °C. A slight bleed of nitrogen was maintained throughout the polymerization reaction. Once the reaction was over, the beaded polymer was filtered and washed thoroughly with water and acetone. The beads then were soxhlet-extracted with acetone for about 6 h and were dried under vacuum (27.2 g; yield \(\sim 86\%\)).

Polystyrene crosslinked with 2\% DVB (P2) was prepared according to the aforementioned procedure. A mixture of styrene (30.6 g, 294 mmol), DVB (1.42 g, 6 mmol), benzoyl peroxide (500 mg), and toluene (14 mL, \(\sim 40\) vol % of the monomers) was suspended in a solution of PVA (4 g in 400 mL of distilled water). The polymerization was carried out as described previously in a nitrogen atmosphere, and the beads were collected. (27 g; yield = 85\%).

Suspension Polymerization\textsuperscript{14} of Styrene with TTEGDA as the Crosslinking Agent

Polystyrene crosslinked with 1\% TTEGDA (P3) was prepared by the suspension of a mixture of destabilized and freshly distilled styrene (30.9 g, 297 mmol), TTEGDA (0.907 g, 3 mmol), and benzoyl peroxide (500 mg) dissolved in toluene (14 mL, \(\sim 40\) vol % of the monomers) in a solution of polyvinyl alcohol (4 g in 400 mL of distilled water) containing calcium sulfate (5 mg) and calcium phosphate (10 mg) kept under stirring and maintained at 75 to 80 °C. After 24 h, the resin beads were filtered and washed with dichloromethane, methanol, and acetone. The beads again were soxhlet extracted with acetone for 6 h to remove low molecular weight impurities and were dried under vacuum (yield = 28.6 g, \(\sim 90\%\)).

The preparation of polystyrene crosslinked with 2\% TTEGDA (P4) was carried out with a mixture of destabilized and freshly distilled styrene (30.6 g, 294 mmol), TTEGDA (1.81 g, 6 mmol), and benzoyl peroxide (500 mg) in toluene (14 mL, \(\sim 40\) vol % of the monomers) suspended in a solution of polyvinyl alcohol (4 g in 400 mL of distilled water), calcium sulfate (5 mg), and calcium phosphate (10 mg) kept under stirring and maintained at 75 to 80 °C. The polymerization and product isolation were carried out exactly as described previously (yield = 29.8 g, \(\sim 92\%\)).

Preparation of the Chloromethylated Resins of P1, P2, P3, and P4

The chloromethylation of crosslinked polystyrene was carried out by the reported procedure\textsuperscript{14,16} with modifications and CMME (Caution: CMME is a highly toxic carcinogen, and any transfer or use of this chemical should be carried out only in an efficient fume hood).

The resins P1, P2, P3, and P4 were sieved and collected with particle sizes ranging from 180 to 850 \(\mu\)m (20–80 mesh). They were chloromethylated according to the procedure described next.

In a typical reaction, the resin P1 (4 g) was allowed to swell in 40 mL of CH\(_2\)Cl\(_2\) overnight. To the swollen resin, 24 mL of CMME was added and stirred for 1 h at room temperature. To the mixture, 0.6 mL of ZnCl\(_2\) (1 M) was added dropwise with constant stirring. The whole mixture was refluxed at 50 °C for 12 h. The resin was filtered off through a sintered glass funnel, washed with tetrahydrofuran (THF; 30 mL) four times, water-filtered, washed with a dioxane-3 N HCl (1 : 1) mixture, a dioxane-water mixture (1 : 1), dioxane, and methanol and finally soxhlet-extracted with THF and methanol. The beads were dried at 40 °C under vacuum for 10 h. In the chloromethylation of resins P3 and P4, the reaction was stopped by the addition of water after 5 h. The chloride equivalent for all the chloromethylated resins (Table I) were estimated by Volhard’s method.\textsuperscript{17}

Preparation of Tartrate Diester (P1–P4)

Chloromethylated DVB crosslinked polystyrene (2.39–2.53 mmol of Cl/g resin) and TTEGDA crosslinked polystyrene resins (1.72–1.78 mmol of Cl/g resin) with 1\% and 2\% crosslinking densities were functionalized as a tartrate diester as follows: A solution of 1.5 g of (+)-tartaric acid (10 mmol; EMerck, (India); \([\alpha]_{D}^{25} = 12.8\) (c 20, H\(_2\)O)) and 2.1 g of triethylamine (20 mmol) in acetone was added to the chloromethylated crosslinked resin (5 g), and the mixture was stirred and refluxed. After 48 h, the product was filtered, washed with a 1 : 1 mixture of methanol and water several times, and finally washed with acetone and dried under vacuum. IR spectrum of the resin (KBr pellet) showed the characteristic ester carbonyl band at 1740 cm\(^{-1}\), confirming the incorporation of tartrate.
Estimation of the Tartrate Function in the Resin by IR Spectroscopy

The tartrate resin (1 g) was taken in a round-bottom flask fitted with a condenser, and 50 mL of dry ethanol was added. Dry HBr gas was bubbled through the contents of the flask at a rate of about 10 mL/min. After about 1 h, the contents of the flask were cooled to room temperature. Then the flask was connected to a rotary evaporator, and the ethanol was distilled at reduced pressure. Once the ethanol was removed completely, the contents of the flask were transferred quantitatively to a 50-mL volumetric flask with CCl₄ and diluted up to the mark with CCl₄. With a pipette, 2.0 mL was transferred to a 50-mL volumetric flask and made up to the mark with CCl₄. This solution was taken in an IR liquid sampler, and absorbance at 1728 to 1747 cm⁻¹ was measured with an IR spectrophotometer in quant mode in which a working curve was plotted with a diethyltartrate standard (Aldrich). From the working curve, the tartrate content was estimated.

Preparation of the DAT Crosslinked Polystyrene (P5)

A mixture of destabilized and freshly distilled styrene (29.3 g, 281 mmol), DAT (3.45 g, 15 mmol), and DVB (0.71 g, 3 mmol) was placed in a round-bottom flask fitted with a reflux condenser, and the contents of the flask were bulk polymerized with benzene as the solvent in the presence of benzoyl peroxide (500 mg) as the catalyst for 8 h at 60 °C. The terpolymeric resin was recovered by distillation of the solvent. The resin obtained was powdered with a mortar and pestle, washed with methanol and acetone to remove low molecular weight impurities, and dried under vacuum (yield = 26.1 g). The terpolymer was characterized by the presence of an ester carbonyl peak in IR at 1728 to 1740 cm⁻¹ (KBr pellet). Polystyrene crosslinked with DAT in the absence of DVB resulted in a semisolid polymer.

Procedure for the Epoxidation

The epoxidations of trans-cinnamyl alcohol, trans-geraniol, and trans-2-hexen-l-ol were carried out according to the Sharpless methodology with minor modifications as outlined next. The reactions were carried out with all the tartrate resins, P1 to P5, under identical conditions and the same substrate : Ti : tartrate ratio. A control reaction was carried out with the same substrates for comparison following the Sharpless procedure.

A flame-dried 250-mL round-bottom flask fitted with a rubber septum was flushed with dry nitrogen and charged with tartrate resin (1 mmol of tartrate) and 200 mL of CH₂Cl₂ predried with molecular sieves (4 Å). The resin soaked in CH₂Cl₂ was dried with molecular sieves (4 Å) overnight. The mixture was cooled to −20 °C in a cryobath. Titanium tetraisopropoxide (0.7 g, 2.5 mmol) was added with a syringe dropwise and with continuous stirring and was allowed to remain at −20 °C for about 60 min. TBHP (6 mL, 3.67 M in CH₂Cl₂, ~20 mmol) was added slowly by the maintenance of the temperature at −20 °C with constant stirring and, after 30 min, allylic alcohol (50 mmol) was added with a dry syringe. The progress of the reaction was monitored by thin-layer chromatography (TLC). Once the reaction was over, the reaction mixture was warmed to 0 °C and the tartrate resin settled at the bottom was separated by the careful pouring of the contents into a flask containing cold water at <2 °C. The resin was washed with CH₂Cl₂, and the washings were added to the crude mixture. The whole mixture was allowed to warm to room temperature. The lower organic layer was separated, and the aqueous phase along with the solids was washed several times with water to remove TBHP. The product was isolated by drying with anhydrous sodium sulfate and Kugelrohr distillation or flash chromatography. The results of the epoxidation are furnished in Table III.

Estimation of the TiO₂ Content in the Recovered Resin

The recovered resins P1 to P4 were analyzed for TiO₂ content by the following procedure. The resin (1 g), placed in a Kjeldahl flask, was heated for 15 min on a mantle in the presence of 20 mL of H₂SO₄ (d. 1.82) to destroy the organic matter. To the contents, 20 mL of hydrogen peroxide (30%) was added inside a fume hood and digested until the solution became clear. After cooling, the contents were transferred into a measuring flask containing 5 mL of 3% H₂O₂. The solution was made up to 100 mL in a measuring flask and maintained at 20 °C. The resulting titanium peroxide sulfate was measured with a spectrophotometer, and the absorption at 408 nm was compared to a
calibration chart drawn with titanium standard solutions prepared from Fixanal RdH 38578 (Riedel-de Haen AG, Seelze) (1 ampoule was equivalent to 1 g of Ti).

CONCLUSION

Styrene crosslinked with DVB and TTEGDA was functionalized as tartrate esters. A new terpolymer of styrene-DAT-DVB also was synthesized. These polymeric materials possessed the unique advantages of heterogeneous reagents and were used as polymer supports in the asymmetric epoxidation of allylic alcohols along with titanium tetraisopropoxide and TBHP. The product isolation was easy and involved minimum workup. The swelling characteristics of the resin and molecular architecture of the polymer backbone significantly influenced the effectiveness of the catalyst.

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REFERENCES AND NOTES