



# A novel layered organic polymer-inorganic hybrid zinc poly (styrene-phenylvinylphosphonate)-phosphate immobilized chiral salen Mn(III) catalyst large-scale asymmetric epoxidation of unfunctionalized olefins

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## ABSTRACT

A novel layered organic polymer-inorganic hybrid zinc poly (styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPA) has been synthesized under mild conditions and diphenol-modified ZnPS-PVPA was used to successfully immobilize the chiral salen Mn(III) by axial coordination. The obtained heterogeneous chiral catalysts exhibited excellent activities and enantioselectivities using sodium periodate as an oxidant for asymmetric epoxidation of unfunctionalized olefins, especially for the epoxidation of  $\alpha$ -methylstyrene (conversion: up to 97%; *ee*: exceed 99%). Moreover, these synthesized catalysts were relatively stable and could be expediently separated from the reaction system, and could be recycled at least ten times without obvious loss of activity and enantioselectivity. These novel catalysts could be efficiently used in large-scale reactions with the enantioselectivity being maintained at the same level, which offer a great possibility for application in industry.

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## 1. Introduction

The asymmetric epoxidation of unfunctionalized olefins takes a great importance in synthesis of chiral epoxides, which are widely used in the manufacture of drugs, vitamins, fragrances and other optical materials [1–3]. Chiral Jacobsen-type salen Mn(III) complexes as homogeneous catalysts have emerged extremely efficient systems for the asymmetric epoxidation of the unfunctionalized olefins [4] in the presence of terminal oxidants such as iodosylbenzene, sodium hypochlorite, *m*-Chloroperbenzoic acid, hydrogen peroxide and so on [5–8]. However, the recycle of the expensive homogeneous catalysts is so difficult that limit the practical applications of chiral salen Mn(III) catalysts in both synthetic chemistry and industrial processes [9]. Consequently, the last decades have witnessed an intense research effort to Jacobsen-type salen Mn(III) complexes on supports to make them recyclable and enhance their stability, activity, and selectivity [10,11]. For

example, salen Mn(III) complexes have been immobilized onto inorganic supports such as clays [12], SBA-15 [13], MCM-41 [14]; organic poly-systems such as PS [15], *p*-divinylbenzene [16]; and organic polymer-inorganic hybrid solids as zirconium phosphate-phosphonate materials reported in our group: ZPS-IPPA [17]; ZPS-PVPA [18] and ZSPP [19]. By contrast, the inorganic materials and organic polymers which were employed for the immobilization of homogeneous catalysts generally exhibited higher or lower catalytic activities than their corresponding homogeneous counterparts, whereas the organic polymer-inorganic hybrid materials as very promising support which were used to immobilize chiral salen Mn(III) complexes and obtained heterogeneous catalysts displayed comparable or even higher conversions and enantioselectivities than those reported in the relevant literatures [17–20].

To the best of our knowledge, there are no reports on hybrid zinc phosphate-phosphonate materials immobilized chiral salen Mn(III) catalysts for the asymmetric epoxidation reaction. Meanwhile, there are relatively few reports using sodium periodate as an oxidant in the system of asymmetric epoxidation. Hence, we have designed and synthesized a novel layered organic polymer-inorganic hybrid-zinc poly (styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPA) based on our previous work. This layered compound was prepared under mild conditions in the absence of

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organic template. Noteworthy features of this new compound as support for immobilization of chiral salen Mn(III) complexes are: (1) the hybrid material possesses adjustable of functional organic groups, which allows us to tailor their density, chemical reactivity, and thermal stability [18]; (2) this compound with abundant framework as well as the layers of the phosphates [21–24] are separated on either side by the pendent organic moieties of the phosphonate groups; (3) the compound can be prepared easily and economically from commercially available sources. Founded on these advantages, the chiral salen Mn(III) complexes were immobilized onto the diphenol-modified layered ZnPS-PVPA through axial coordination for the first time and showed significantly higher enantioselectivities with  $\text{NaIO}_4$  as an oxidant system at room temperature for asymmetric epoxidation of unfunctionalized olefins, furthermore, the catalysts could be recycled at least ten times without significant loss of activity and enantioselectivity. Such excellent catalytic effect is likely to attribute to the specific frameworks of ZnPS-PVPA which could provide the advantaged reaction microenvironment for the asymmetric epoxidation. In addition, these novel heterogeneous catalysts could be efficiently used in large-scale reactions with the enantioselectivity being maintained at the same level. As far as our information goes, there are scarcely any reports about large-scale reactions in the asymmetric epoxidation of unfunctionalized olefins, which offer a great possibility for application in industry.

## 2. Experimental

### 2.1. Material and instruments

(1*R*, 2*R*)-1, 2-diaminocyclohexane, chloromethyl methyl ether (toxic compound), 1-octene, styrene,  $\alpha$ -methylstyrene, 4-chlorostyrene, indene, *n*-nonane and sodium periodate were supplied by Alfa Aesar. Other commercially available chemicals were laboratory-grade reagents from local suppliers. Styrene was passed through a pad of neutral alumina before use.

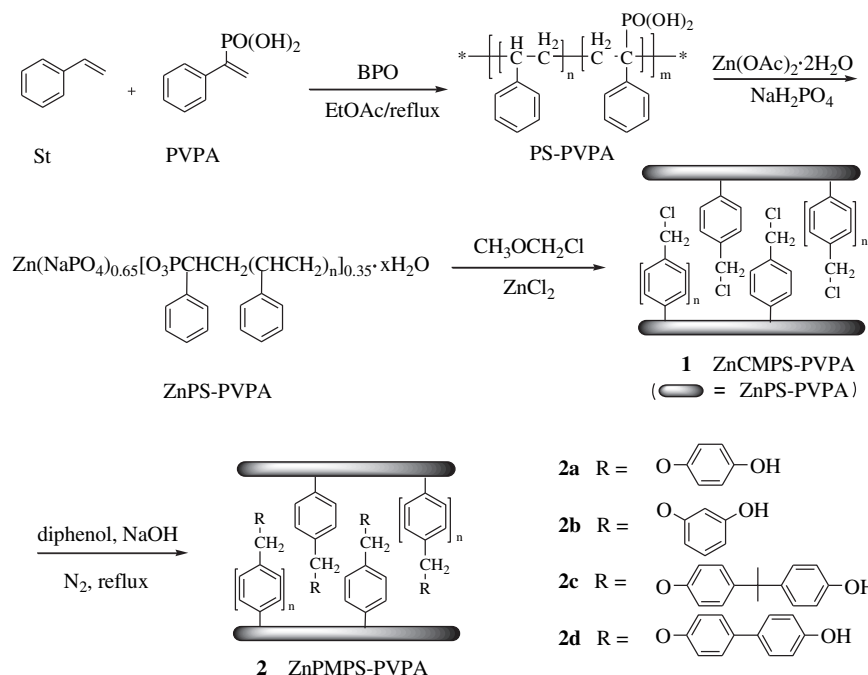
FT-IR spectra was recorded from KBr pellets using a Bruker RFS100/S spectrophotometer (USA), and diffuse-reflectance UV–vis

spectra of the solid samples were recorded in the spectrophotometer with an integrating sphere using  $\text{BaSO}_4$  as standard. TG analysis was performed on a SBTQ600 thermal analyzer (USA) with the heating rate of  $15\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  from 25 to  $1000\text{ }^\circ\text{C}$ . The Mn content of the catalysts was determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy (AAS). XRD powder pattern was collected on D/MAX-3C diffractometer using graphite-monochromatic Cu  $K\alpha$  radiation in the angular range  $2\theta = 2\text{--}50^\circ$  with a step size of  $0.02^\circ$ . Atomic Force Microscope (AFM) was performed on NanoScope Quadrex (USA). The BET surface area was determined with the use of  $\text{N}_2$  sorption data measured at 77 K (Quantachrome Autosorb-1). The conversion (with *n*-nonane as internal standard) and the *ee* value were analyzed by gas chromatography (GC) with Shimadzu GC2014 (Japan) instrument equipped using a chiral column (HP 19091G–B213,  $30\text{ m} \times 30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$ ) or high performance liquid chromatography (HPLC) with Agilent 1200 instrument using Chiralcel OD-H ( $4.6\text{ mm} \times 250\text{ mm}$ ) columns.

### 2.2. Synthesis of zinc poly (styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPA)

The synthesis and characterization of PS-PVPA were accorded to the literature [18] (Scheme 1).

PS-PVPA (6.0 g, 8.5 mmol) was dissolved in 100 ml THF. Hydrated sodium orthophosphate (2.66 g, 17 mmol) dissolved with deionized water was slowly added and vigorously stirred for 1 h. The ratio of polystyrene-phenylvinyl phosphonate parts to inorganic phosphate parts is 0.35:0.65 in mol stoichiometric. Afterward, this solution of  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$  (5.61 g, 25.6 mmol) was slowly added to the reactants with vigorously stirring, accompanied with a step by step temperature rise to  $65\text{ }^\circ\text{C}$ . The reaction mixture was kept at  $65\text{ }^\circ\text{C}$  for 72 h. After cooling down to room temperature, the pH of the reaction mixture was adjusted to neutral by addition of triethylamine and then washed with distilled water and ethanol and subsequently dried under vacuum. Primrose yellow solid ZnPS-PVPA was obtained in 90% yield.



Scheme 1. Synthesis of the support.

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