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Styrene–hydroxyethyl methacrylate copolymer microsphere immobilized porphyrinatomanganese(III) as a mild, reusable and highly efficient catalyst for epoxidation of cyclohexene with molecular oxygen

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ABSTRACT

On the basis of synthesis of styrene–hydroxyethyl methacrylate copolymer microspheres with a functionalized hydroxyl, we have prepared a new type of copolymer microspheres immobilized porphyrinatomanganese(III), P(St-co-HEMA)MnP, by a condensation reaction between a hydroxyl in copolymer microspheres surface and a carboxyl in porphyrin ring. The obtained copolymer catalyst (P(St-co-HMEA)MnP) was characterized by SEM, UV–vis, IR, ICP and TG–DTG. The SEM image shows that the morphology of the copolymer catalyst is spheriform with *ca.* 4 μm diameter. The catalytic activity of P(St-co-HMEA)MnP to epoxidize cyclohexene in the presence of molecular oxygen and isobutylaldehyde has been studied. The catalytic efficiency of P(St-co-HMEA)MnP is comparable to that of non-supported MnCMPTTP. It is a mild, reusable and highly efficient heterogeneous catalyst for the epoxidation of cyclohexene.

1. Introduction

Over the past few decades, several reports on metalloporphyrins as catalysts for epoxidation of olefins have appeared [1–5]. A variety of oxidants, such as PhIO [6], H_2O_2 [7], MMPP (magnesium monoperoxyphthalate) [8], TBAO (tetrabutylammonium monosulfate) [9], n-Bu_4NIO_4 (tetrabutylammonium periodate) [10] and molecular oxygen [11,12], in combination with different metalloporphyrin catalysts have been employed as oxygen atom donors. However, solid-supported metalloporphyrins are attracting more interests because of their increased stability, easy recovery from reaction media and recycling, as discussed recently in some reviews [13–17]. Among the supports that can be used to immobilize metalloporphyrins, polystyrene derivatives are often employed for their cheapness, ready availability, mechanical robustness, chemical inertness and facile functionalization. And there are several reports dealing with polystyrene derivatives bearing metalloporphyrins for epoxidation of olefins [16–27]. However, there are few reports about the epoxidation of olefins using polystyrene derivatives supported metalloporphyrins as catalysts and molecular oxygen as oxidant [28]. We have investigated epoxidation of alkenes catalyzed by very small amount of Mn(TPP)Cl with dioxygen [12,29]. This catalyst proved to be an effective catalyst in epoxidation systems with extremely high turnover number in the presence of molecular oxygen and isobutylaldehyde, which is comparable to most enzyme catalysis. On the bases of the preparation of several polystyrene-based supports immobilizing metalloporphyrins and the researches for their catalysis in hydrocarbon hydroxylation with molecular oxygen [30–34], in this work, a new polystyrene-based support, namely styrene–hydroxyethyl methacrylate copolymer microspheres with hydroxy groups on the surface, was prepared and Mn(III) complex of 5-(4-(carboxymethoxy)phenyl)-10,15,20-tri(*p*-tolyl) porphyrin was immobilized on it. The catalytic activity of this supported porphyrinatomanganese(III) to catalyze epoxidation of cyclohexene with oxygen molecules in the presence of reducing agent has been investigated.

2. Experimental

2.1. Materials

5-(4-(Hydroxyl)phenyl)-10,15,20-tri(p-tolyl) porphyrin (HPTTP) was synthesized in our laboratory [35]. Styrene (St) was washed with 5% NaOH several times to remove inhibitor and then distilled under reduced pressure. 2-Hydroxyethyl methacry-

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late (HEMA) supplied from Alfa Aesar was purified by passing through active alumina. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Other reagents were commercially available and used without further purification.

2.2. Physical measurements

Elemental analysis (C, H and N) was carried out on a PerkinElmer 240 Q elemental analyzer. ESI-MS was measured on a Thermo Finnigan LCQ DECA XP spectrometer. UV–vis and IR spectra were recorded on a Shimadzu UV-3150 spectrophotometer and an Equinox 55 Fourier transformation infra-red spectrometer, respectively. The scanning electron microscopy (SEM) analyze was performed with a JSM-6330F field emission scanning electron microscope. An Iris (HR) inductively coupled plasma (ICP)-atomic emission spectrometer was used to determine the content of porphyrinatomanganese(III). Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer was used to determine the surface area. Thermal analysis was performed with a Netzsch TG-209 thermogravimetric analyzer.

2.3. Preparation of styrene–hydroxyethyl methacrylate copolymer microspheres immobilized porphyrinatomanganese(III)

The strategy to prepare styrene–hydroxyethyl methacrylate copolymer microspheres immobilized porphyrinatomanganese(III) is shown in Scheme 1. On the basis of synthesis of Mn(III) porphyrin with a functionalized carboxyl and styrene–hydroxyethyl methacrylate copolymer microspheres with a functionalized hydroxyl, Mn(III) porphyrin is immobilized to copolymer microspheres by a condensation reaction between a carboxyl in porphyrin ring and a hydroxyl in copolymer microsphere surface.

2.3.1. Synthesis of 5-(4-(carboxymethoxy)phenyl)-10,15,20-tri(p-tolyl) porphyrin (CMPTTP)

A mixture of 0.3091 g HPTTP, 1.8 g K_2CO_3 and 50 ml DMF was stirred at 100 °C. 2 ml ethyl bromoacetate dissolved in 5 ml DMF was added dropwise. After 9 h, the mixture was washed with H_2O several times. After washing to neutrality with H_2O, it is concentrated via rotary evaporation. Then the crude product was dissolved in 15 ml $CHCl_3$, and 15 ml 10% KOH was added dropwise. The mixture was stirred for 0.5 h at room temperature. The mixture was washed with H_2O several times. After washing to neutrality with H_2O, drying over anhydrous Na_2SO_4 and concentrating via rotary evaporation, the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. Evaporation of solvent afforded CMPTTP. Yield: 0.3021 g (90.1%) (Found: C, 78.61; H, 5.41; N, 7.45%. Calc. for $C_{49}H_{38}N_4O_3{\cdot}H_2O$: C, 78.59; H, 5.38; N, 7.48%). ESI-MS [$CHCl_3$, m/z]: 731 ([CMPTTP]$^+$). ^{1}H NMR ($CDCl_3$, 300 MHz): δ −2.46 (s, 2H, pyrrole N–H), 2.66 (s, 9H, phenyl CH_3) 4.90 (s, 2H, –O–CH_2–CO), 7.25–7.55 (8H, phenyl m-H), 7.95–8.16 (8H phenyl o-H), 8.60–8.77 (s, 8H, pyrrole C–H).

2.3.2. Synthesis of 5-(4-(carboxymethoxy)phenyl)-10,15,20-tri(p-tolyl) porphyrin Mn(III) (MnCMPTTP)

0.5 g $Mn(Ac)_2$ and 1 g NaCl dissolved in 40 ml HAc were mixed with 20 ml $CHCl_3$ solution of CMPTTP (0.2990 g). The mixture was stirred at 65 °C for 8 h. Then, the reaction mixture was washed with H_2O several times. After washing to neutrality with H_2O, drying over anhydrous Na_2SO_4 and concentrating *via* rotary evaporation, the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. Evaporation of solvent afforded MnCMPTTP as a green powder. Yield: 0.3202 g (95.6%) (Found: C, 70.27; H, 4.60; N, 6.72%. Calc. for $C_{49}H_{36}N_4O_3MnCl{\cdot}H_2O$: C, 70.29; H, 4.57; N, 6.69%). ESI-MS [$CHCl_3$, m/z]: 783 ([MnCMPTTP]$^+$).

2.3.3. Synthesis of styrene–hydroxyethyl methacrylate copolymer microspheres P(St-co-HEMA)

Styrene–hydroxyethyl methacrylate copolymer microspheres, P(St-co-HEMA), were synthesized by dispersion copolymerization in a ethanol–water media using polyvinylpyrrolidone (PVP) as a dispersant and 2,2′-azobisisobutyronitrile (AIBN) as an initiator [33,34].

A total of 14.0 ml styrene, 2.0 ml HEMA, 0.5 ml divinylbenzene (DVB), 0.5 g polyvinylpyrrolidone (K-30) (PVP K-30), 0.12 g AIBN, 95 ml C_2H_5OH and 5 ml H_2O were mixed in a 250 ml three-neck reaction flask equipped with an anchor-shaped stirrer and a condenser. After stirring at 400 rpm, the mixtures were heated to 70 °C for 12 h under a N_2 atmosphere.

After completion of the polymerization period, the reactor content was cooled down to room temperature and centrifuged at 5000 rpm for 10 min for the removal of dispersion medium. The microspheres were redispersed within 30 ml of ethanol and centrifuged again under similar condition. The ethanol washing was repeated three times for complete removal of unconverted monomers and other components. The final product was dried for 24 h at 60 °C in vacuum.

2.3.4. Preparation of styrene–hydroxyethyl methacrylate copolymer microspheres immobilized MnCMPTTP (P(St-co-HEMA)MnP)

0.05 g MnCMPTTP was suspended in thionyl chloride (20 ml) and the mixture was refluxed for 7 h, after which the excess of thionyl chloride was distilled off. The residue was dissolved in 30 ml 1,2-dichloroethane. 3 g P(St-co-HEMA) and several drops of pyridine were added. The suspension was stirred at 80 °C for 12 h, after which the crude product was obtained. The polymer particles were filtered off and washed with 1,2-dichloroethane, acetone and ethanol respectively. The final product was dried for 24 h at 60 °C in vacuum.

2.4. Epoxidation of cyclohexene

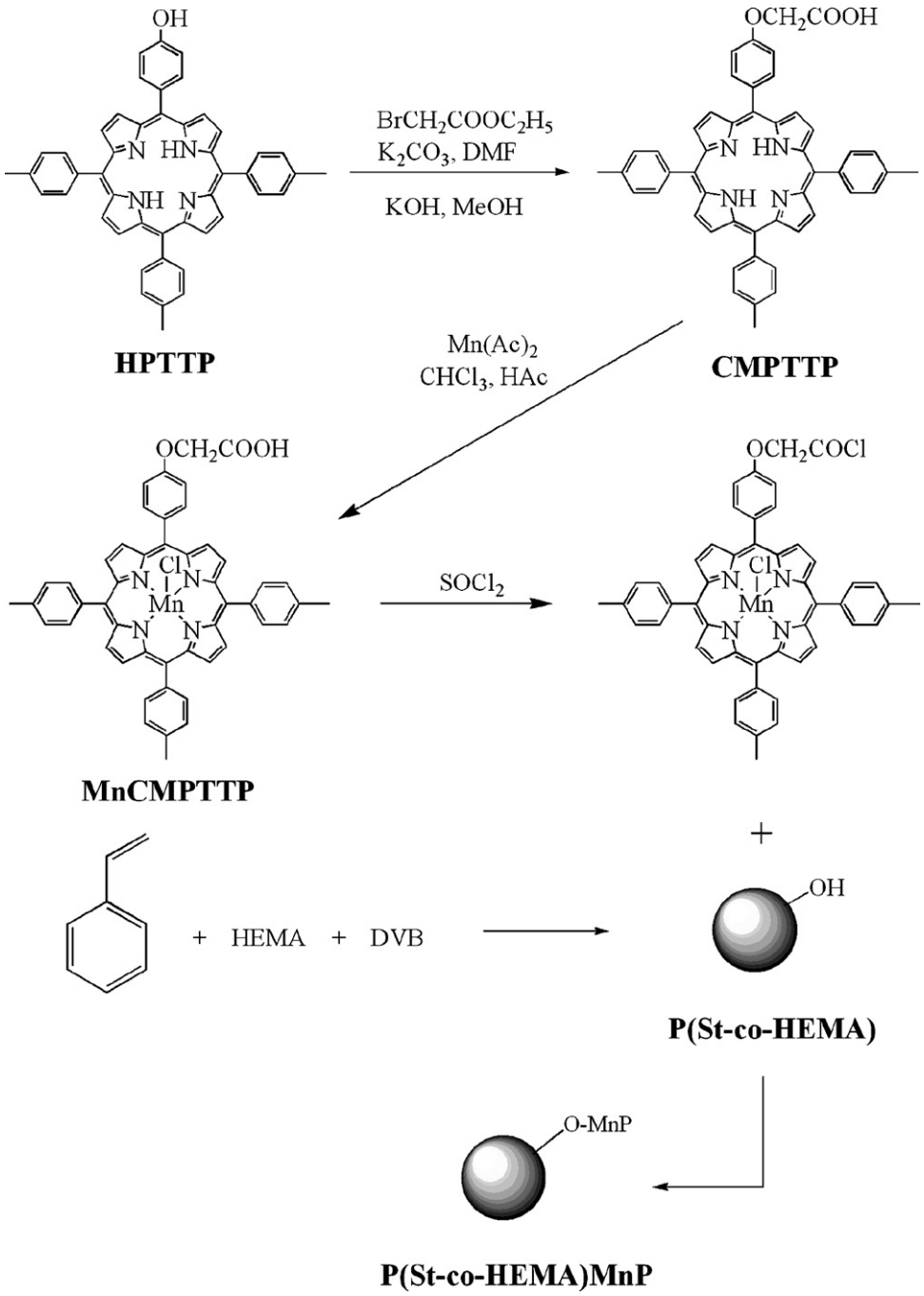
The epoxidation of cyclohexene using P(St-co-HEMA)MnP was carried out in a specially constructed reaction vessel at room temperature [12]. The catalytic system consisted of P(St-co-HEMA)MnP, substrate (2 mmol cyclohexene), 6 mmol isobutylaldehyde and 10 ml acetone. Dioxygen was bubbled through the solution. The products were detected and analyzed by gas chromatography (GC-7890II) and bromobenzene was used as internal standard. P(St-co-HEMA)MnP was recovered from the catalytic system by centrifugal separation after reaction for 4 h and then reused under identical conditions.

3. Results and discussion

3.1. Characterization of P(St-co-HEMA)MnP

The morphologies of P(St-co-HEMA) and P(St-co-HEMA)MnP were obtained by SEM as shown in Fig. 1(a) and (b). The SEM images of P(St-co-HEMA) and P(St-co-HEMA)MnP show smooth surfaces and spherical morphologies with an average diameter of *ca.* 4 μm.

The presence of MnCMPTTP in the copolymer can be confirmed by the solid state UV–vis spectrum. Typical absorption spectrum of MnCMPTTP with Soret band centred at *ca.* 490 nm, was observed in the solid state UV–vis spectrum of P(St-co-HEMA)MnP (Fig. 2). Comparing the spectrum with that of the corresponding non-supported MnCMPTTP, the Soret band is red-shifted by about 15 nm



Scheme 1. Synthesis scheme of P(St-co-HEMA) and P(St-co-HEMA)MnP.

(Fig. 2, insert). Red-shifted of Soret band usually can be observed when metalloporphyrins are immobilized on solid supports, which can be attributed to the distortion of the porphyrin rings [36–39].

IR spectra of P(St-co-HEMA) and P(St-co-HEMA)MnP are very similar to each other. Characteristic bands of styrene and hydroxyethyl methacrylate are shown in the IR spectra of P(St-co-HEMA) and P(St-co-HEMA)MnP. For example, four peaks at 1600, 1583, 1493 and 1452 cm^{-1}, and double peaks at 758 and 700 cm^{-1} are clearly observed and can be attributed to the benzene rings in styrene. Two bands at 1182 and 1726 cm^{-1} are also clearly observed and can be attributed to the ester group in hydroxyethyl methacrylate. A broad band in the region of 3450–3550 cm^{-1} attributed to the hydroxy group in styrene–hydroxyethyl methacrylate copolymer is observed in the IR spectrum of P(St-co-HEMA). As we had expected, same band is also observed in the IR spectrum of P(St-co-HEMA)MnP, which is due to only part of the hydroxy group in styrene–hydroxyethyl methacrylate copolymer reacting with functionalized carboxyl in Mn(III) porphyrin.

The MnCMPTTP content of the catalyst was determined by the method reported in the literature [32–34] and the porphyrinatomanganese(III) content of P(St-co-HEMA)MnP was 0.39%. The surface area of P(St-co-HEMA)MnP has been determined by BET surface area measurement, which is approximately 5.3 m^2/g.

Thermostability of P(St-co-HEMA)MnP has been determined by using thermogravimetric analysis (TGA). TG–DTG curves of P(St-co-HEMA)MnP are shown in Fig. 3. It can be seen that P(St-co-HEMA)MnP degrades at 312 °C. This demonstrates that the catalyst is thermally stable up to almost 310 °C. And when the temperature

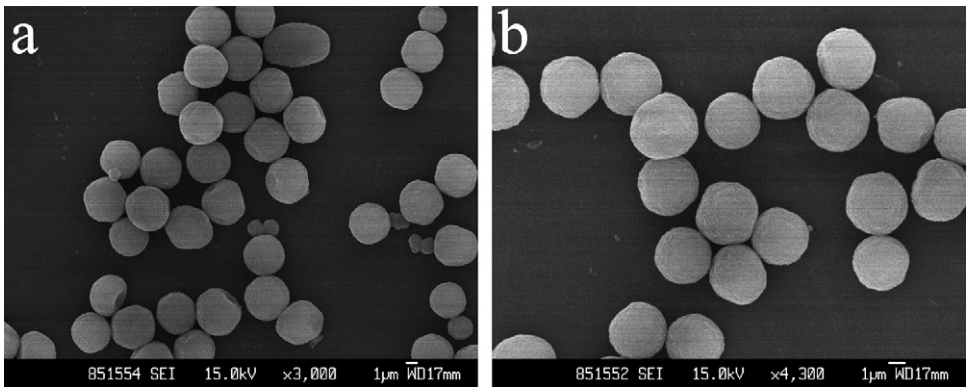


Fig. 1. SEM images of P(St-co-HEMA) (a) and P(St-co-HEMA)MnP (b).

rises at 545 °C, the organic parts of P(St-co-HEMA)MnP decompose completely.

3.2. Catalysis of P(St-co-HEMA)MnP for cyclohexene epoxidation

The epoxidation of cyclohexene catalyzed by P(St-co-HEMA)MnP was investigated in catalyst–O_2–isobutyraldehyde system. It is found that the main product was 1,2-epoxycyclohexane. Since isobutyraldehyde concentration has a great influence on epoxide yield [40], the epoxidation with various molar ratios of isobutyraldehyde to substrate was examined in P(St-co-HEMA)MnP–O_2–isobutyraldehyde system. The results are shown in Table 1. It displayed that when isobutyraldehyde was absent, the epoxidation of cyclohexene was not observed. When the molar ratio of isobutyraldehyde and substrate was 3 mol/mol, the highest value of epoxide yield was obtained, and the increase of isobutyraldehyde concentration cannot increase the epoxide yield considerably. So, the isobutyraldehyde/substrate molar ratio as 3 mol/mol is used in catalytic experiments.

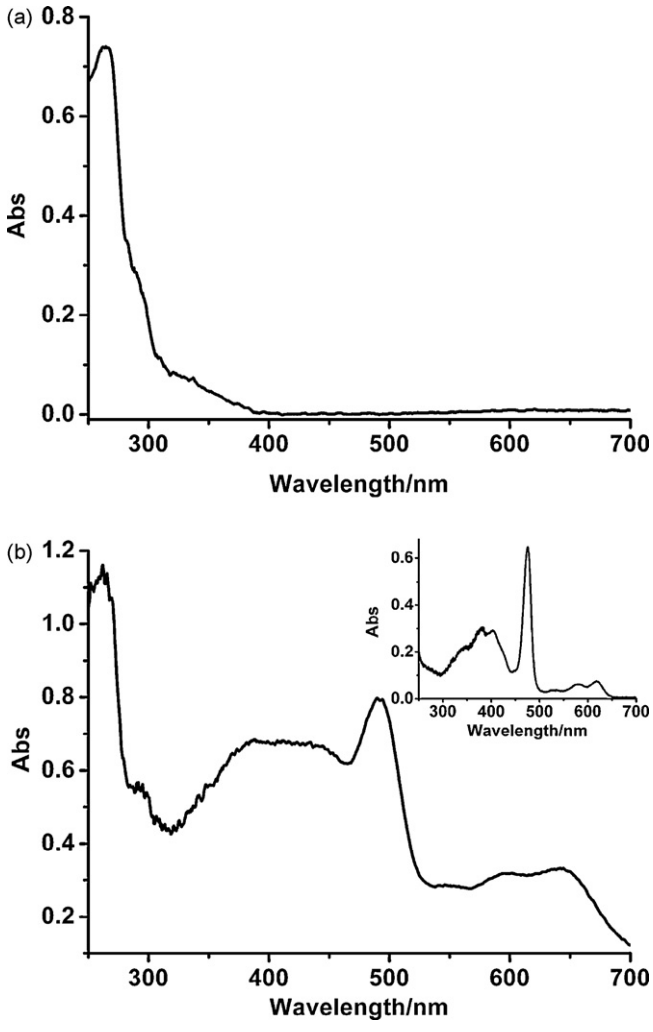


Fig. 2. Solid state UV–vis absorption spectra of P(St-co-HEMA) (a) and P(St-co-HEMA)MnP (b). Inset: absorption spectrum of MnCMPTTP in CH_2Cl_2.

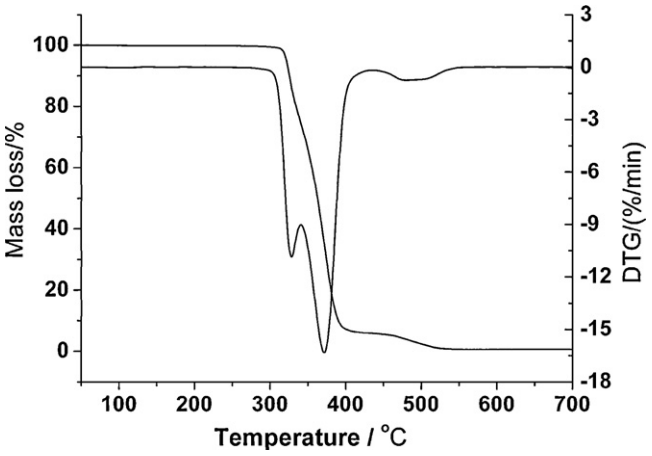


Fig. 3. TG–DTG curves of P(St-co-HEMA)MnP.

The relationship between the yield of 1,2-epoxycyclohexane and reaction time in the epoxidation of cyclohexene catalyzed by P(St-co-HEMA)MnP is shown in Fig. 4. It can be seen that the yield of 1,2-epoxycyclohexane was enhanced rapidly after about 1 h, and reached maximum value after about 4 h. The yield of 1,2-

Table 1
Variation of product yield with isobutyraldehyde to substrate molar ratios [a].

Isobutylaldehyde/cyclohexene (molar ratio)	Conv. (%)	Yield (%)
0:1	0.0	0.0
1:1	47.2	42.0
2:1	95.7	89.6
3:1	>99	93.0
4:1	98.0	93.5
5:1	98.5	95.0

[a] 13 mg P(St-co-HEMA)MnP (containing 0.06 μmol MnCMPTTP), cyclohexene (2 mmol), acetone (10 ml), and 1 atm of oxygen, rt. 4 h

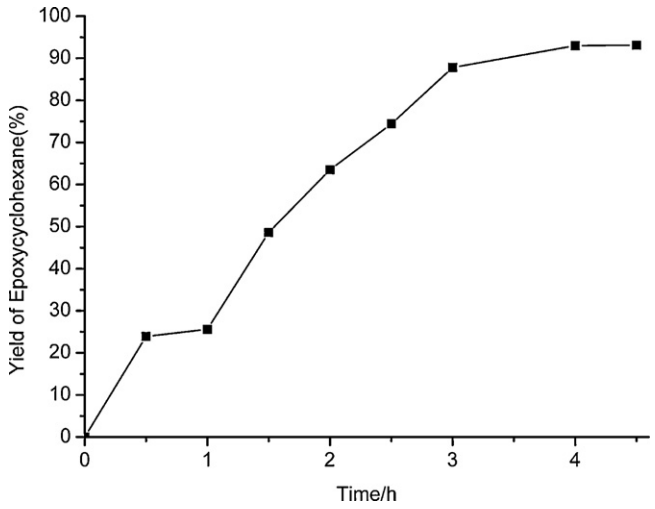


Fig. 4. Changes of the yield of epoxycyclyohexane with catalytic time in the epoxidation of cyclohexene catalyzed by P(St-co-HEMA)MnP. Reaction conditions: catalysts (0.013 g P(St-co-HEMA)MnP, containing 0.06 μmol porphyrinatomanganese(III)), substrate (2 mmol), isobutylaldehyde (6 mmol), acetone (10 ml), 1 atm of oxygen, rt.

epoxycyclohexane is almost unchanged with a further increase in the reaction time. The results suggest that 4 h may be the optimum reaction time in this experiment system.

The results of cyclohexene epoxidation catalyzed by P(St-co-HEMA)MnP (fresh and recovered) and non-supported MnCMPTTP are summarized in Table 2. Controlled experiment using P(St-co-HEMA) as catalyst was carried out and only 12% cyclohexene could be converted, indicating that the metalloporphyrin is crucial for the epoxidation. From Table 2, we can find that the yield of cyclohexene epoxide catalyzed by P(St-co-HEMA)MnP is 93.3% and TON of P(St-co-HEMA)MnP is 24,049 in the presence of molecular oxygen and isobutylaldehyde after 4 h. It is obvious that P(St-co-HEMA)MnP is a highly efficient heterogeneous catalyst for the epoxidation of cyclohexene and its catalytic activity is comparable to that of non-supported MnCMPTTP.

It is notable that P(St-co-HEMA)MnP can be completely recovered and effectively reused. After the epoxidation of cyclohexene, P(St-co-HEMA)MnP was recycled by simple filtration and subsequent washing of the solid remnants with acetone. A fresh solution of substrate was then introduced to the catalytic material, and the catalyzed reaction was restarted. As shown in Table 2, P(St-co-HEMA)MnP retains its high yield of cyclohexene epoxide and high turnover numbers after being reused four times. All reaction solutions analyzed after catalytic reactions did not show the characteristic Soret band of MnCMPTTP, which demonstrated that no MnCMPTTP was leaching into the reaction solution. Thus, our results reveal the stable catalytic capability of this catalyst as well as the success of this new synthetic route.

Table 2
Catalytic performances of P(St-co-HEMA)MnP and non-supported MnCMPTTP.

Catalysts	Run	Conv. (%)	Yield (%)	TON[c]
P(St-co-HEMA)MnP[a]	1	99.6	93.3	24,049
	2	99.0	93.0	23,968
	3	96.0	90.7	23,379
	4	90.4	83.6	21,545
MnCMPTTP[b]	1	99.1	95.0	24,356
P(St-co-HEMA)	1	12.0	10.0	

[a] 13 mg P(St-co-HEMA)MnP (containing 0.06 μmol MnCMPTTP).
[b] 0.06 μmol MnCMPTTP.
[c] Turnover number = product (mol)/catalyst (mol).

4. Conclusion

On the basis of synthesis of styrene–hydroxyethyl methacrylate copolymer microspheres with a functionalized hydroxyl and Mn(III) porphyrin with a functionalized carboxyl, we have prepared a new type of copolymer microspheres immobilized porphyrinatomanganese(III), P(St-co-HEMA)MnP, by a condensation reaction between a carboxyl in porphyrin ring and a hydroxyl in copolymer microsphere surface. The copolymer microspheres have smooth surface and spherical morphology with *ca.* 4 μm diameter. The catalysis of P(St-co-HEMA)MnP to epoxide cyclohexene in the presence of molecular oxygen and isobutylaldehyde have been investigated in the presence of molecular oxygen and isobutylaldehyde. It is found that P(St-co-HEMA)MnP has high catalytic activity, to be comparable to that of non-supported MnCMPTTP, and retains its high catalytic activity after being reused four times. It seems that P(St-co-HEMA)MnP is a mild, reusable and highly efficient heterogeneous catalyst for the epoxidation of cyclohexene.

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