

Preparation and Catalytic Application of Poly 4-Vinylpyridine Microspheres

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ABSTRACT: Poly 4-vinylpyridine (P4VP) microspheres between 170 and 728 nm were synthesized by Emulsifier-Free Emulsion Polymerization. The monomer concentration, ionic strength, and initiator concentration affected the microsphere size and size distribution. The increasing monomer concentration led to the increase of microsphere size, whereas the size distribution of the resultant P4VP microspheres increased with the increasing ionic strength of the reaction systems. Mo(O₂)₂O·2DMF was successfully anchored onto the P4VP microspheres

by ligand exchange, and the heterogeneous catalyst showed high-catalytic activity for epoxidation of *cis*-cyclooctene with environmentally friendly hydrogen peroxide. The size and morphology of the supported microspheres has important influence on the catalytic activity. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3178–3183, 2010

Key words: 4-vinylpyridine; microspheres; emulsifier-free emulsion polymerization; epoxidation; supported catalyst

INTRODUCTION

Polymer microspheres have recently attracted great interest for their potential applications in the field of catalysis, optical nanosensor, and drug delivery.^{1–4} While their size, dispersity, surface functional groups affect their applications.⁵ Therefore, polymer microspheres with different size and functional surface have received remarkable attention.⁶

Poly 4-vinylpyridine (P4VP) has reactive pyridine group for coordinative with transition metals, which can be widely used in the field of catalysis,^{7–10} humidity sensitive material.¹¹ The microspheres could be synthesized by different methods: emulsion polymerization, disperse polymerization, and suspension polymerization. Ma and Fukutomi¹² prepared P4VP microspheres of 100 to 700 nm in diameter using a polymeric emulsifier in methanol by emulsion polymerization. P4VP microspheres with diameters between 710 and 4530 nm were prepared by disperse polymerization using polystyrene-block-polybutadiene as stabilizer in a mixture

solvent of *N, N*-dimethylformamide and toluene.¹³ These microspheres were synthesized in organic solvent, and the emulsifier or stabilizer generally influence their further application. While monodisperse microspheres with high purity are obtained by emulsifier-free emulsion polymerization, which uses very small amount of emulsifier or no emulsifier in the polymerization systems.¹⁴ 4-Vinylpyridine (4VP) was generally used as stabilizer to copolymer with other monomer in the emulsifier-free emulsion polymerization system.^{15,16} Less literature reported the synthesis and size control of homopolymer microspheres with emulsifier-free emulsion polymerization technology.¹⁷

Poly (styrene-*co*-4-vinylpyridine) has been used as support to immobilize molybdenum compounds by some groups,^{7,18} and these heterogeneous catalysts show outstanding catalytic activity in olefin epoxidation in the presence of tert-butyl hydroperoxide.¹⁹ Tert-butyl hydroperoxide usually produces by-product, while hydrogen peroxide is an attractive oxidant based on environmental and economic account.

In this study, P4VP microspheres have been prepared by emulsifier-free emulsion polymerization, and the influences of initiator concentration, monomer concentration, as well as ionic strength on microsphere size and size distribution have been systematically studied. Molybdenum complexes were immobilized onto the surface of the P4VP microspheres. The activity and selectivity of the heterogeneous catalyst were examined under epoxidation of *cis*-cyclooctene with hydrogen peroxide.

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EXPERIMENTAL

Materials

The monomer 4-vinylpyridine (4VP) and cross-linker divinylbenzene (DVB) were purchased from Alfa Aesar (John Matthey company, Lancashire, England). 4VP was purified by washing with 10% NaOH solution, and then being distilled under reduced pressure. DVB was distilled under vacuum to remove the inhibitor. The initiator potassium persulfate (KPS) and inorganic salt sodium chloride (NaCl) were purchased from Beijing Chemical Reagent Company (Beijing, China) and used without being further purified.

Preparation of P4VP microspheres

P4VP microspheres were synthesized by emulsifier-free emulsion polymerization. It was conducted under N₂ atmosphere in a 500-mL round bottom four-neck flask fitted with a mechanical stirrer and reflux condenser. Deionized water (70 mL) was first added into the flask. The reactor was immersed in a thermostated oil bath to maintain constant temperature at 80°C and the stir speed was kept at 300 rpm. After 30 min, 4VP and DVB were added into the reactor. The polymerization was initiated by adding certain amount of KPS into the flask. The reaction proceeded for 4 h, and then the reaction vessel was cooled to room temperature. The product was centrifuged, washed with deionized water and ethanol three times, respectively.

Preparation of P4VP·Mo catalyst

Mo(O₂)₂O·2DMF was prepared according to the procedure reported previously.²⁰ Mo(O₂)₂O·2DMF (0.30 g) was suspended in 50-mL ethanol at room temperature, and 0.25 g powdered P4VP microspheres were added into the above solution. The mixture was stirred for 2 days at room temperature, and the color of mixture changed from white to bright yellow during this period. The obtained mixture was centrifuged and the solid residue was washed with ethanol several times until the filtrate was colorless.

General procedure for epoxidation of *cis*-cyclooctene

An exact weight of supported Mo catalyst (100 mg) and *cis*-cyclooctene (0.46 mL, 3.5 mmol) in acetonitrile (5 mL) was added H₂O₂ (2.5 mL, 22 mmol) under stirring at 60°C for 6 h. After centrifugation, the filtrate was used to measure the catalytic activity by Gas Chromatography-Mass Spectrum, and nitrobenzene was employed as internal standard.

Characterization methods

The microsphere size and size distribution were calculated from SEM morphologies with SUPRA55 Field emission scanning electron microscopy. SEM samples were prepared by placing a drop of sample (diluted with ethanol) on silicon wafer and left to dry. Fourier transform infrared (FTIR) spectroscopic studies were carried out using VECTOR 22. Gas chromatography-mass spectrum was recorded using Thermo DSQ, AB-5MS column was used in GC, the injection temperature is 50°C, and Helium gas was employed as carrier gas.

RESULTS AND DISCUSSION

Preparation of P4VP

P4VP microspheres were prepared by emulsifier-free emulsion polymerization. The influencing factors such as monomer concentration, initiator concentration, as well as ionic strength were investigated with all detail.

Monomer concentration

The monomer concentration was changed from 0.27 to 1.00M, whereas the cross-linker concentration and initiator concentration were fixed at 8 mol % and 3 mol % based on the amount of monomer. Figure 1 showed clearly that all obtained microspheres have narrow size distribution. The size of prepared microspheres increased with increasing 4VP concentration. When the concentration of 4VP changed from 0.40 to 0.55M, 0.65M, and 0.80M, the size of obtained microspheres increased from 260 to 444 nm, 556 and 728 nm (Fig. 1). When the concentration increased to 1.00M, microspheres were easily to coagulate. While the concentration of monomer decreased to 0.27M, P4VP microspheres with 170 nm in diameter were obtained. Furthermore, if the concentration of 4VP is under 0.27M, the preliminary particles could not be obtained from aqueous phase because of the short polymer chain.

In emulsifier-free emulsion polymerization systems, particle nucleation and oligoradical formation occur simultaneously. The radicals grow up to a critical chain length and generate precursor particles. These particles are unstable and prone to coagulate to form the stable primary particles. Then polymerization continues by monomers swelling into the primary particles, and the size increases with more monomers swelling into the primary particles.²¹ Therefore, the size of microspheres increases with the increasing concentration of 4VP.

FTIR spectrum of P4VP microspheres was performed as shown in Figure 2. All characteristic bands of P4VP could be observed. The absorption

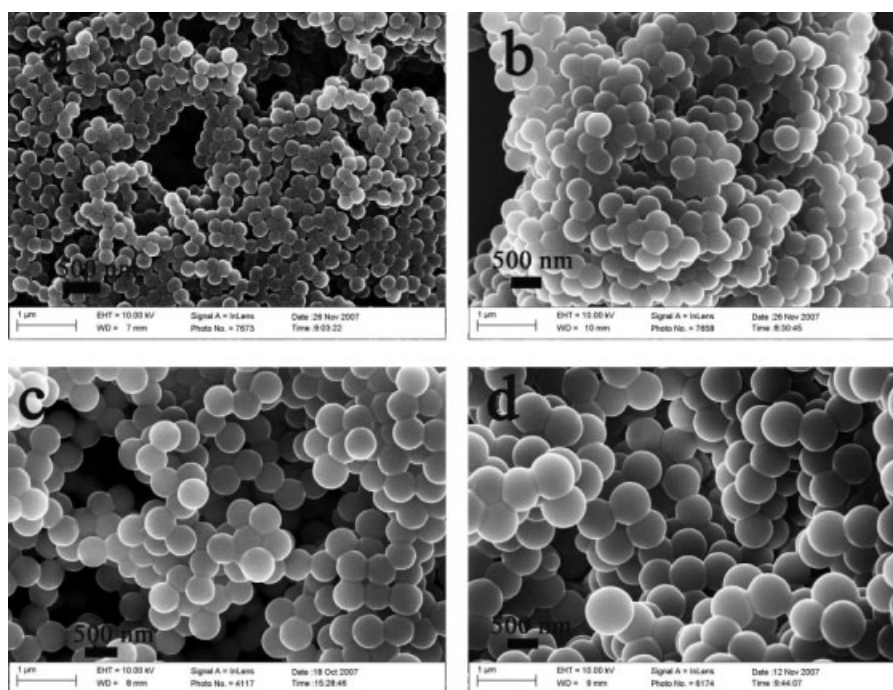


Figure 1 SEM micrographs of poly 4-vinylpyridine microspheres with different monomer concentration: (a) 0.40M, (b) 0.55M, (c) 0.65M, and (d) 0.80M. Synthesis conditions: DVB = 8 mol %, KPS = 3 mol %. The amount of DVB and KPS were based on the amount of 4-VP monomer. Polymerizations were carried out at 80°C for 4 h.

bands at 1597 cm^{-1} , 1553 cm^{-1} are attributed to aromatic quadrant $\text{C}=\text{C}$ stretching, 1450 cm^{-1} is ascribed to CH_2 deformation, and 1412 cm^{-1} is attributed to aromatic semicircle $\text{C}=\text{N}$ stretching.^{22,23}

Initiator concentration

Figure 3 illustrates the morphologies of prepared microspheres with KPS concentration varied from 2.40 to 5.30 mM. When KPS concentration was as low as 2.40 mM [Fig. 3(a)], microspheres with diameter in 593 nm and broader size distribution were produced. As the initiator concentration increased to 3.20 mM, the diameter of microspheres increases to 728 nm [Fig. 3(b)]. However, further increasing the initiator concentration from 4.20 to 5.30 mM, the size of microspheres decreased to 658 nm and 611 nm, and the size distribution widened [Fig. 3(c,d)].

In emulsifier-free emulsion polymerization system, stabilization of the microspheres is depend on electrostatic force which is related to surface charge density of the microspheres and ionic strength of the aqueous phase.⁶ When KPS concentration is low (2.40 mM), the microspheres with low-surface charge were obtained. The preliminary particles are highly unstable and prone to coagulation; therefore, smaller microspheres with broader size distribution were obtained. As the concentration of KPS increased to

3.20 mM, the prepared microspheres are well dispersed and have a narrow size distribution. When the concentration of KPS is higher, the initiator has two effects on the morphology of resultant microsphere. In one way, the increasing initiator concentration increases the number of sulfate ions which involved in microspheres stabilization and produces smaller primary particles.²⁴ In another way, large amount of initiator increases ionic strength of the aqueous phase which would destroy the emulsion system and lead to coagulation.¹⁴

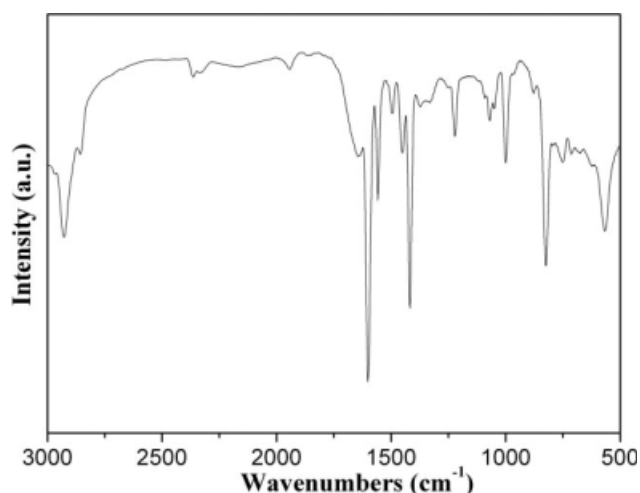


Figure 2 FTIR spectrum of poly 4-vinylpyridine microspheres [sample of Fig. 1(d)].

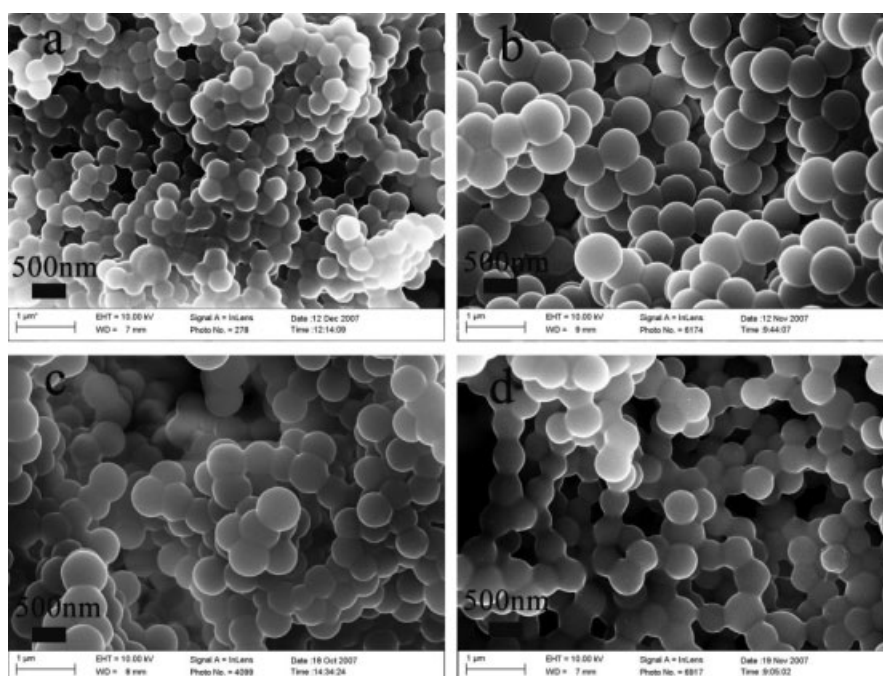


Figure 3 SEM micrographs of poly 4-vinylpyridine microspheres with different KPS concentrations: (a) 2.40 mM, (b) 3.20 mM, (c) 4.20 mM, and (d) 5.30 mM. Synthesis conditions: $[4\text{-VP}] = 0.80\text{M}$, $\text{DVB} = 0.08$ mol. Polymerizations were carried out at 80°C for 4 h.

Ionic strength

The morphological effect of ionic strength on P4VP microspheres were shown in Figure 4 and Table I. The size distribution of the P4VP microspheres

became broader with the increase of ionic strength in aqueous phase. When the concentration of NaCl is 15 mM, the microsphere varies between 590 and 896 nm as shown in Figure 4(d).

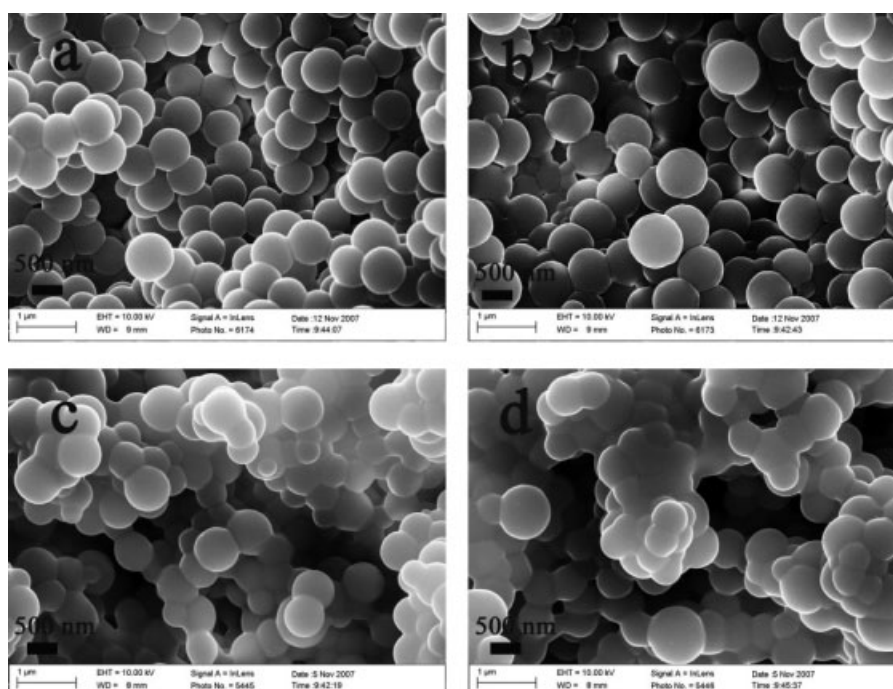


Figure 4 SEM micrographs of poly 4-vinylpyridine microspheres with different concentrations of NaCl: (a) 0 mM, (b) 5 mM, (c) 10 mM, and (d) 15 mM.

TABLE I
The Influence of Ionic Strength on Size and Size Distribution of Microspheres^{a,b}

NaCl (mM)	Ionic strength $\times 10^{-3}$ (mol kg ⁻¹)	Diameter (nm)
0	6	728 \pm 20
5	11	722 \pm 56
10	16	703 \pm 74
15	21	743 \pm 153

^a Polymerizations were carried out at 80°C for 4 h. [4-VP] = 0.80M, DVB = 0.08M, [KPS] = 3.20 mM.

^b Average microsphere diameters were obtained from electron micrographs.

The ionic strength of aqueous phase is one of the most important parameters on size distribution of the prepared microspheres as expressed in Table I. The ionic strength comes from initiator and adding strong electrolytes such as NaCl.¹² Increasing the ionic strength of aqueous phase would depress the electrical double layer, which makes the microspheres undergo seriously agglomeration and widen size distribution.²⁵

Catalytic performance of P4VP supported catalysts

Mo(O₂)₂O·2DMF was successfully anchored onto the P4VP microspheres by ligand exchange, and the content of molybdenum is 4.90 mmol g⁻¹. P4VP microspheres supported Mo catalysts were applied to the epoxidation of *cis*-cyclooctene with 30 wt % hydrogen peroxide (H₂O₂) as oxidant. The obtained products were analyzed by GC-MS and the results were summarized in Table II.

A good yield of epoxide was achieved with P4VP supported catalysts in the presence of hydrogen peroxide as green oxygen source at 60°C for 6 h. The results also indicated that the size of P4VP microspheres influenced the activity of the heterogeneous catalyst. P4VP with irregular morphology showed a lower catalytic activity and selectivity for epoxidation because of lower surface area. Smaller microspheres provided larger specific surface area, therefore they had higher catalytic activity.²⁶ Furthermore, polymeric microsphere catalyst has advantages including the high dispersion, ease of separation, and recycling.⁷ More detailed research on P4VP supported molybdenum complexes are still being conducted by our laboratory.

CONCLUSIONS

P4VP microspheres with diameter ranging from 170 to 728 nm were prepared by emulsifier-free emulsion polymerization. The monomer concentration, initiator concentration, and ionic strength were found to influence the microsphere size and size dis-

TABLE II
Epoxidation of *Cis*-Cyclooctene Catalyzed by P4VP Microspheres Supported Mo Catalyst^{a,b}

	Diameter (nm)	Specific surface area (m ² g ⁻¹)	Conversion (%)	Selectivity (%)
1	260	52.68	78	98
2	444	36.45	72	99
3	728	23.65	64	99
4	Irregular morphology	0.87	54	98

^a Reaction conditions: the substrate (3.5 mmol), catalyst (100 mg), 30% aqueous H₂O₂ (22 mmol) dissolved in acetonitrile (5 mL) at 60°C for 6 h.

^b Determined by GC-MS by using an internal standard technique.

tribution. The monomer concentration is the dominant parameter in microsphere size, and the size increased from 170 to 728 nm as increasing the monomer concentration from 0.27 to 0.80M. The size distribution of the microspheres increased as ionic strength increased from 6×10^{-3} to 21×10^{-3} mol kg⁻¹. The increasing concentration of initiator also showed effect on final size distribution of microspheres. Mo(O₂)₂O·2DMF was successfully anchored onto the P4VP microspheres. When using these P4VP microspheres supported catalyst for epoxidation in the presence of hydrogen peroxide, the heterogeneous catalyst with regular spherical morphology showed higher activity, and the activity of the catalyst increased with the decrease of microsphere size.

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