

# Preparation and Characterization of Magnetic Amphiphilic Polymer Microspheres

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**ABSTRACT:** Magnetic amphiphilic polymer microspheres were prepared by copolymerization of styrene with poly(ethylene oxide) macromonomer (MPEO) in the presence of Fe<sub>3</sub>O<sub>4</sub> magnetic fluid in ethanol/water medium. Magnetic microsphere size, size distribution, and surface morphology were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The structure of copolymer was determined by infrared spectroscopy. With increasing MPEO used in the polymerization, the resulting microsphere size decreased. Magnetic amphiphilic polymer microspheres containing 0.02–0.2 mmol/g hydroxyl groups could be prepared by using different MPEO concentration. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1847–1851, 2001

**Key words:** amphiphilic; magnetic; microsphere; polymer

## INTRODUCTION

Magnetic polymer microspheres have been widely used in biomedical and bioengineering, such as cell separation, enzyme immunoassay, target drug, etc., in the past 20 years, because of their relatively rapid and easy magnetic separation.<sup>1</sup> Recently, polymer-supported catalysts have attracted much interest due to the recyclability of the catalysts by filtration or precipitated from the reaction media by adding precipitating agents<sup>2–4</sup>, but these methods are time-consuming and energy-consuming also. Magnetic polymer micro-

sphere-supported catalysts are considered to remedy this drawback, due to their easy separation. To avoid reducing the efficiency of catalysts, magnetic amphiphilic polymer microsphere-supported catalysts system, which combined the advantages of homogeneous catalysis with easy separation, were designed by us. In this work, magnetic amphiphilic polymer microspheres, which could be used as support for some activities, such as catalysts, enzyme, etc., have been prepared by copolymerization of styrene (St) and poly(ethylene oxide) macromonomer in the presence of Fe<sub>3</sub>O<sub>4</sub> magnetic fluid.

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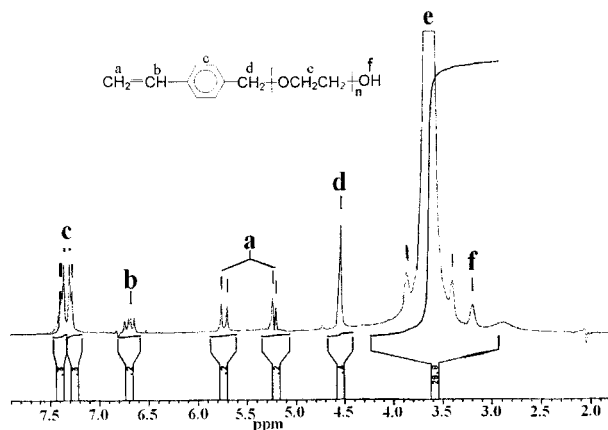
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## EXPERIMENTAL

### Materials

Styrene was treated with 10% sodium hydroxide solution to remove the inhibitor. Pyridine (AR), acetic anhydride (AR), tetrahydrofuran (THF,

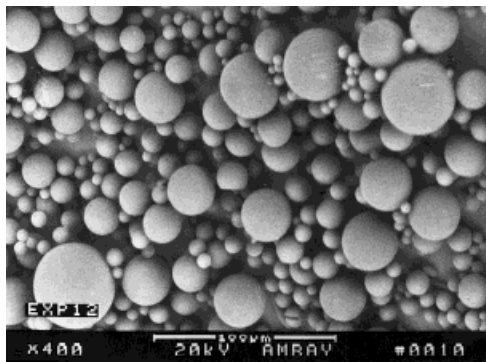


**Figure 1**  $^1\text{H-NMR}$  spectra of PEO macromonomer in  $\text{CDCl}_3$ .

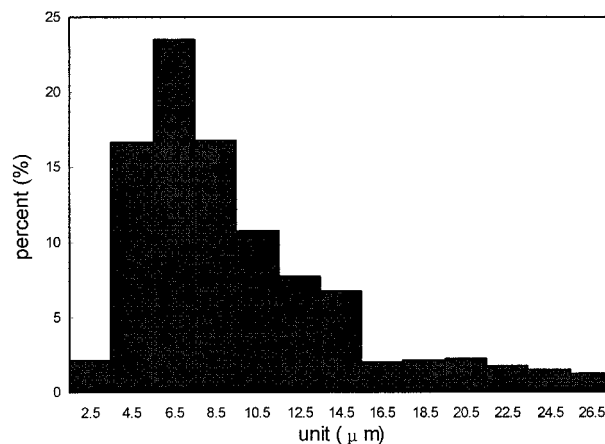
AR), and methylene chloride ( $\text{CH}_2\text{Cl}_2$ , AR) were used after being purified by distillation. NaH (55–65% in oil, Fluka), poly(ethylene glycol) (PEG,  $M_n = 2000$ ,  $M_n = 4000$ ), *p*-vinylbenzyl chloride (90%, Acros), potassium persulfate (KPS, AR), and ethanol (AR) were used without further purification. Water was two-times distilled.

#### Synthesis of Poly(ethylene oxide) Macromonomer (MPEO)

Fifty-five grams of PEG, dried for 24 h under vacuum at  $90^\circ\text{C}$ , was dissolved in 60 mL of fresh-distilled THF; 1.96 g sodium hydride was added to this mixture and stirred for 6 h at  $40^\circ\text{C}$ . *p*-Vinylbenzyl chloride (4.66 mL) was added to the reaction mixture at  $40^\circ\text{C}$  and stirred for another 16 h. The products were precipitated from the filtrate by adding ethyl ether, then dissolved in



**Figure 2** SEM photograph of  $\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$  magnetic microspheres. Polymerization conditions: 4.0 g PEG, 15.0 g St, 0.45 g KPS, 39.0 g  $\text{H}_2\text{O}$ , 10.0 g magnetic fluid, 52.0 g ethanol, 1.5 g MPEO.

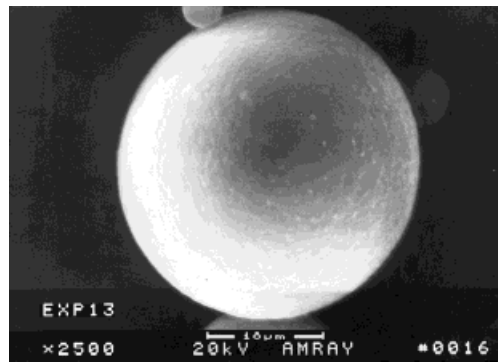


**Figure 3** Histogram of  $\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$  magnetic microspheres. Polymerization conditions: 4.0 g PEG, 15.0 g St, 0.45 g KPS, 39.0 g  $\text{H}_2\text{O}$ , 10.0 g magnetic fluid, 52.0 g ethanol, 1.5 g MPEO.

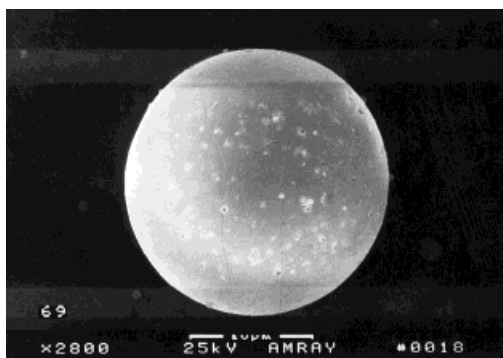
$\text{CH}_2\text{Cl}_2$ . Insoluble impurities were removed by filtration. Solid products were obtained by adding cold ethyl ether in the mother liquid. The purification procedure mentioned above was repeated at least 3 times. Pure products were obtained by drying under vacuum at room temperature.

#### Preparation of $\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$ Magnetic Amphiphilic Polymer Microspheres

$\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$  magnetic amphiphilic polymer microspheres were prepared by copolymerization of St with MPEO by using KPS as initiator in ethanol/water medium together with  $\text{Fe}_3\text{O}_4$  magnetic fluid, which was prepared in the same manner as described in our previous work.<sup>5</sup> PEG ( $M_n = 4000$ ) was used as stabilizer in the poly-



**Figure 4** SEM photograph of  $\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$  magnetic microspheres. Polymerization conditions: 4.0 g PEG, 15.0 g St, 0.45 g KPS, 39.0 g  $\text{H}_2\text{O}$ , 10.0 g magnetic fluid, 52.0 g ethanol, 2.0 g MPEO.

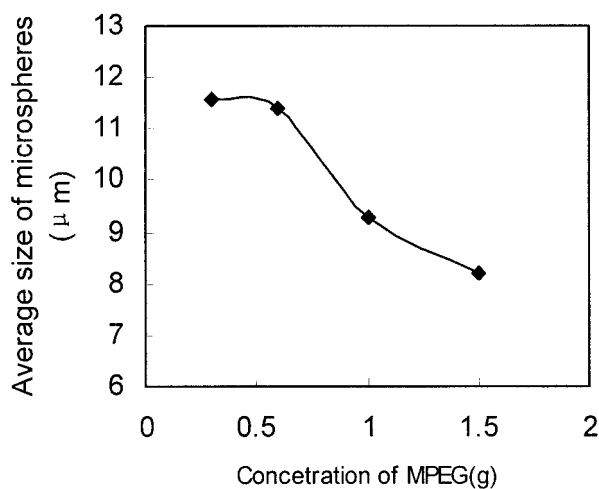


**Figure 5** SEM photograph of  $\text{Fe}_3\text{O}_4/\text{PSt}$  magnetic microspheres. Polymerization conditions: 4.0 g PEG, 15.0 g St, 0.45 g KPS, 39.0 g  $\text{H}_2\text{O}$ , 10.0 g magnetic fluid, 52.0 g ethanol.

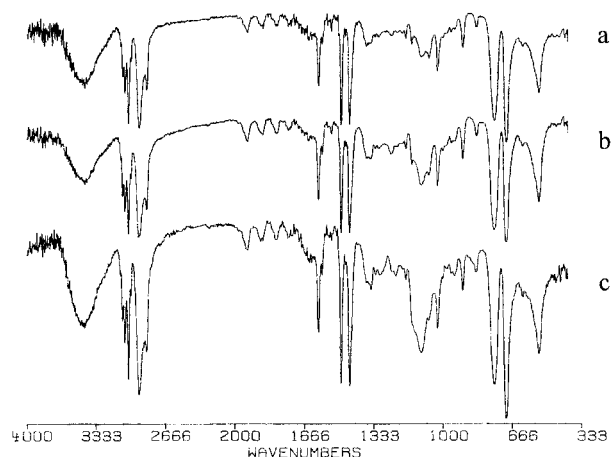
merization. A required amount of ingredients was added into a 250-mL four-necked flask; reaction was allowed to proceed for 12 h in nitrogen atmosphere at  $70^\circ\text{C}$  under stirring. The resulting microspheres were purified by repeated magnetic separation, and this purification procedure was repeated after the microspheres had been immersed into 1M HCl solution for 48 h to remove the  $\text{Fe}_3\text{O}_4$  powder nonencapsulated by the polymer.

### Characterization

The structure of poly(ethylene oxide) macromonomer was confirmed by  $^1\text{H-NMR}$  Spectra (AC-P,



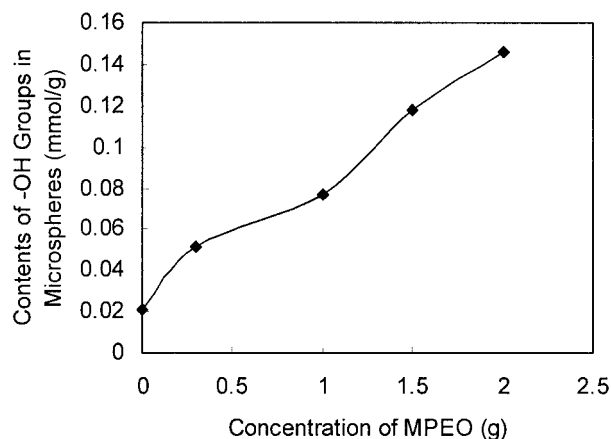
**Figure 6** Effect of MPEO concentration on  $\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$  magnetic microspheres diameter. Polymerization conditions: 4.0 g PEG, 15.0 g St, 0.45 g KPS, 39.0 g  $\text{H}_2\text{O}$ , 10.0 g magnetic fluid, 52.0 g ethanol.



**Figure 7** IR spectra of  $\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$  magnetic microspheres. a: 0.3 g MPEO; b: 1.0 g MPEO; c: 2.0 g MPEO. Polymerization conditions: 4.0 g PEG, 15.0 g St, 0.45 g KPS, 39.0 g  $\text{H}_2\text{O}$ , 10.0 g magnetic fluid, 52.0 g ethanol.

300 MHz, Bruker) in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard. The copolymer structure was confirmed by infrared spectroscopy (MX-IE, PE) by using KBr pellet.

The average size, size distribution, and surface morphology of  $\text{Fe}_3\text{O}_4/\text{Poly}(\text{St-MPEO})$  microspheres were obtained by using a scanning electron microscope (AMRAY-1000) and atomic force microscopy (AFM, Dimension 3000, Digital Instruments). To obtain the average size and size distribution from five SEM photographs, more than 800 microspheres were collected by com-



**Figure 8** Contents of  $-\text{OH}$  groups localized in magnetic microspheres prepared by using different MPEO concentration. Polymerization conditions: 4.0 g PEG, 15.0 g St, 0.45 g KPS, 39.0 g  $\text{H}_2\text{O}$ , 10.0 g magnetic fluid, 52.0 g ethanol.

puter linked with the SEM and followed by statistical treatment with computer software. For SEM studies, samples were coated under vacuum with a thin layer of gold.

The content of hydroxyl groups localized in the microspheres was determined by titration as follows: 0.7 g microspheres was dissolved in 15 mL fresh distilled pyridine at 110°C for 40 min. The solution was filtrated to remove Fe<sub>3</sub>O<sub>4</sub> powder entrapped by copolymers, and an excess amount of 10 mL mixture of pyridine (100 mL) and acetic anhydride (5 mL) was added to the filtrate and refluxed for another 30 min. An amount of 10 mL distilled water was added to the solution, after cooling to room temperature. The solution was titrated by 0.3N aqueous NaOH by using phenolphthalein/ethanol solution as indicator. The final content of —OH could be calculated by:

$$\text{—OH (mmol/g)} = (V_0 - V)N/W$$

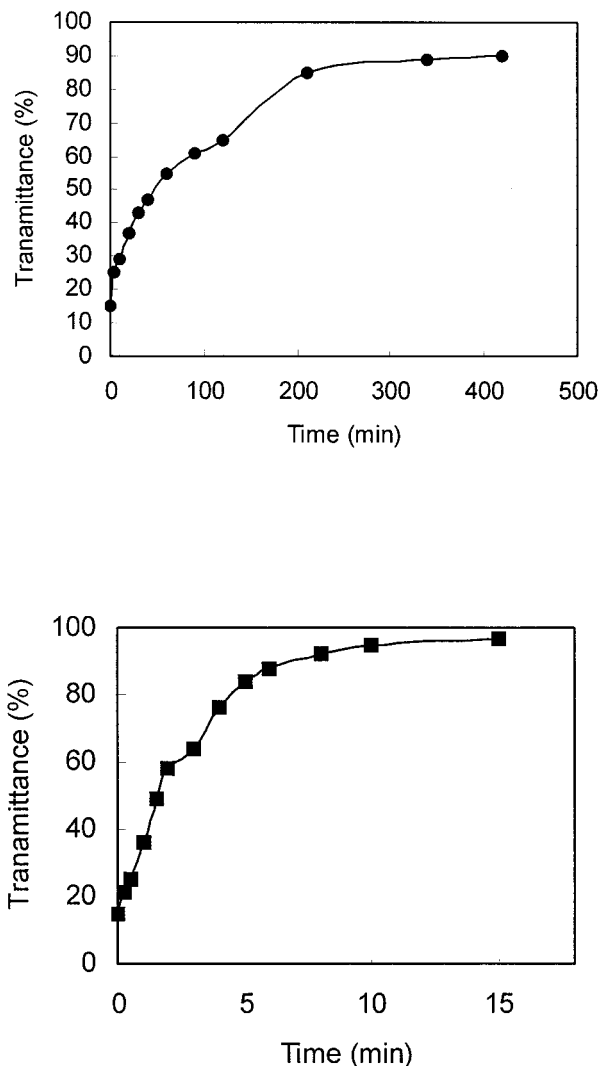
where  $V_0$ ,  $V$  are the volume of NaOH consumed by blank and sample, respectively,  $N$  is the equivalent concentration of aqueous NaOH, and  $W$  is the weight of microspheres.

The magnetic responsiveness of Fe<sub>3</sub>O<sub>4</sub>/Poly(St-MPEO) microspheres was determined as follows: about 0.5 g Fe<sub>3</sub>O<sub>4</sub>/Poly(St-MPEO) microspheres were suspended in 20 mL water. The transmittance of the suspension was determined with a spectrometer (721) at 580 nm after the mixture had been separated by an additional magnetic field (0.42 T) for a certain time.

## RESULTS AND DISCUSSION

MPEO was prepared from poly(ethylene glycol) ( $M_n = 2000$ ) by alkoxidation with sodium hydride, followed by reaction with *p*-vinylbenzyl chloride. The structure of MPEO was confirmed by <sup>1</sup>H-NMR; the result is shown in Figure 1.

The morphology, average size, and size distribution of magnetic microspheres were determined by SEM. Figures 2 and 3 show the photograph and histogram of magnetic microspheres, respectively. The results showed that the average size was about 11 μm, and the microsphere sizes are polydisperse, with more than 80% magnetic microspheres in the 5–15 μm range. The detailed surface morphology of magnetic microspheres was studied on SEM photography taken with higher magnifications. Coarse structure could be



**Figure 9** Transmittance of suspension of magnetic microspheres after being separated by external magnetic field (0.42 T) for a certain time.

observed in the surface of Fe<sub>3</sub>O<sub>4</sub>/P(St-MPEO) magnetic microspheres, whereas the surface of Fe<sub>3</sub>O<sub>4</sub>/PSt was smooth, as shown in Figures 4 and 5, respectively. The average value of roughness of Fe<sub>3</sub>O<sub>4</sub>/P(St-MPEO) and Fe<sub>3</sub>O<sub>4</sub>/PSt obtained by AFM was 33.15 and 6.13, respectively, which confirmed that Fe<sub>3</sub>O<sub>4</sub>/P(St-MPEO) had a remarkably coarse structure on its surface. This result indicated that a hydrophilic layer was generated on the surface of microspheres during the polymerization because of the water solubility of PEO chains.

The average size of Fe<sub>3</sub>O<sub>4</sub>/P(St-MPEO) magnetic microspheres ranging from 5–100 μm could be prepared by changing the polymerization con-

dition. Several kinds of amphiphilic magnetic microspheres were prepared by using different concentrations of MPEO. The results showed that the average size of magnetic microspheres decreased with the increase of concentration of MPEO (Fig. 6). The reason for this phenomena is that MPEG acted as a costabilizer in the course of polymerization. However, when the concentration of MPEO was further increased to 3.0 g, non-spherical magnetic microspheres were obtained. The reason will be examined in further studies.

The structures of  $\text{Fe}_3\text{O}_4/\text{P}(\text{St-MPEO})$  magnetic microspheres prepared by using different MPEO concentration was characterized by IR spectroscopy, as shown in Figure 7. The adsorption bands in the region  $2000\text{--}1668\text{ cm}^{-1}$  and the double peak of  $760$  and  $690\text{ cm}^{-1}$  are the characteristic band of polystyrene. A band at  $1090\text{ cm}^{-1}$  appears due to the C—O groups of PEO, which implied the existence of PEO in the magnetic microspheres. The intensity of this adsorption band is appreciably stronger with the higher concentration of MPEO used in the copolymerization. The results confirm that St undergoes copolymerization with MPEO.

The content of hydroxyl group (—OH) localized in the magnetic microspheres was determined by titration. The results showed that the content of —OH groups in magnetic microspheres was increased with the increase of MPEO to St ratio (as shown in Fig. 8). It was found that there is about  $0.02\text{ mmol/g}$  —OH group localized in the magnetic microspheres prepared without using MPEO. This may be explained as follows: (1) PEG used as stabilizer in the copolymerization could be absorbed by the microspheres during their formation; (2) PEG chains could be grafted on the poly(St-MPEO) chains by the hydrogen abstraction of PEG chains.<sup>6</sup> Our experimental results

showed that magnetic microspheres containing  $0.05\text{--}0.2\text{ mmol/g}$  hydroxyl groups could be prepared by changing MPEO concentration used in the copolymerization.

Figure 9 shows the magnetic separation property of the particles, which was determined through transmittance of the microsphere suspension after being separated by  $0.42\text{ T}$  magnetic field for a certain time. Experimental results showed that magnetic separation using  $\text{Fe}_3\text{O}_4/\text{Poly}(\text{St-MPEO})$  microspheres is rapid and easy. The transmittance of the suspension reached about 98% within 15 min by magnetic separation, whereas separation by deposition required at least 7 h to reach up to 90% transmittance.

Magnetic amphiphilic polymer microspheres containing —OH groups mentioned above used as support for chiral catalysts will be investigated in our further work.

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## REFERENCES

1. Ugelstad, J.; Berge, A.; Ellingsen, T.; Nilsen, T. N.; Mørk, P. C.; Stenstad, P.; Hornes, E.; Olsvik, Ø. *Prog Polym Sci* 1992, 17, 87.
2. Han, H.; Janda, H. *J Am Chem Soc* 1996, 118, 7632.
3. Uozumi, Y.; Danjo, H.; Hayashi, T. *Tetrahedron Lett* 1997, 38(2), 3557.
4. Renil, M.; Meldal, M. *Tetrahedron Lett* 1996, 37(34), 6185.
5. Ding, X. B.; Sun, Z. H.; Wan, G. X.; Jiang, Y. Y. *React Funct Polym* 1998, 38, 11.
6. Shen, S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci, Part A: Polym Chem* 1994, 32, 1087.