

# Synthesis of Amphiphilic Microspheres by Suspension Copolymerization of Styrene and Poly(ethylene oxide) Macromonomer

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**ABSTRACT:** Amphiphilic microspheres, ranging in size from 3 to 35  $\mu\text{m}$ , were prepared by suspension copolymerization of styrene with poly(ethylene oxide) vinylbenzyl (PEO-VB) macromonomer by changing polymerization conditions. It was found that an increase in the amount of dispersant and the PEO-VB concentration resulted in decreases of the size and size distribution of amphiphilic microspheres. The morphology, size, and size distribution of amphiphilic microspheres were characterized by scanning electron microscopy. The structure of copolymer was confirmed by infrared spectroscopy, differential scanning calorimetry, elemental analysis, and X-ray photoelectron spectroscopy. The content of the hydroxyl groups localized in the microspheres ranged from 0.05 to 0.2 mmol/g. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 333–339, 2001

**Key words:** amphiphilic polymer; microspheres; suspension copolymerization; poly(ethylene oxide)

## INTRODUCTION

Although homogeneous catalysis has received increasing attention in the past 20 years, the recycling and reuse of the expensive catalysts remain a major problem. Different kinds of inorganic and organic polymers, including soluble and insoluble types, have been devised as supports for catalysts. The catalysts, supported by a traditional

polymer that is insoluble, usually have reduced reactivities and selectivities. The catalysts bonded to soluble supports, such as PEG and PAA, exhibit excellent reactivities, but the separation of the polymers from the solution requires special treatments such as adding a nonsolvent.

With the development of solid-phase synthesis, especially combinatorial synthesis, amphiphilic polymers have become the focus of even greater attention. As a novel material of functional polymer, amphiphilic polymer microspheres have been applied in many fields, such as solid-phase organic synthesis, polymeric catalysis, analytical chemistry, and biomedicine.<sup>1–3</sup> Polystyrene-*g*-poly(ethylene oxide) (PSt-*g*-PEO) amphiphilic microspheres are one of the most useful types of amphiphilic polymer microspheres, and because

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of their excellent swelling capability in both polar and nonpolar solvents, the catalysts bonded to them have high reactivity and selectivity in various solvent media. In a previous study,<sup>4</sup> PSt-*g*-PEO amphiphilic microspheres were synthesized by the modification of functional polystyrene microspheres through grafting of poly(ethylene glycol) (PEG) in the presence of NaH or NaOH in high concentration. One shortcoming of this method is that, because it is a heterogeneous reaction, the yield would be low when the molecular weight (MW) of PEG used is greater than 1000 Da,<sup>5</sup> whereas amphiphilic microspheres with PEO chains that are greater than 1000 Da have proved to be optimal.<sup>1</sup> To synthesize amphiphilic microspheres with PEO chains longer than 1000 Da, Bayer et al.<sup>6</sup> grafted PEO chains on crosslinked PSt microspheres by means of anionic polymerization of ethylene oxide, although the whole process seems too complicated and difficult to carry out. Ottewill and Satguranathan<sup>7</sup> synthesized PEO amphiphilic polymer microspheres containing PEO chains using methoxy polyethylene glycol methacrylate as comonomer; however, the diameter of amphiphilic microspheres, ranging in size from 0.1 to 0.6  $\mu\text{m}$ , is too small to be easily separated by filtration, which hinders its application in the field of catalysis.

In this study, PSt-*g*-PEO amphiphilic polymer microspheres, ranging in size from 3 to 35  $\mu\text{m}$ , were prepared with suspension copolymerization of poly(ethylene oxide) vinylbenzyl (PEO-VB) macromonomer by changing the suspension polymerization conditions.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA, Acros, Belgium) and styrene (St, Acros) were distilled under reduced pressure to remove the inhibitor. Benzoyl peroxide (BPO, Acros) was purified by recrystallization in ethanol/chloroform. THF was refluxed with Na to remove water. PEG (MW = 2000, Acros) was dehydrated under vacuum at 90°C for 24 h. NaH (55–65% in oil; Fluka, Milwaukee, WI), *p*-vinylbenzyl chloride (>90%; Acros), sodium nitrite, ethyl ether, chloroform, NaOH, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were used as received without further purification. (Materials without company name are supplied by Chengdu Factory of Chemical Reagents, China.)

**Table I** Typical Recipe of Suspension Copolymerization

Material	Weight (g)
Styrene	13.5
PEO-VB	3.0
PSMA	0.5
NaNO <sub>2</sub>	0.05
Water	100.0
BPO	0.1

### Synthesis of PEO Macromonomer

The synthesis of PEO-VB macromonomer was carried out as previously described.<sup>8</sup>

### Synthesis of Poly(sodium methacrylate)

A 150-mL aliquot of NaOH (6 mol/L) was added to a three-neck flask fitted with a mechanical beater, and then heated to 45°C. MMA (125 mL) was added dropwise to the solution and the temperature of solution was kept below 50°C; the methanol produced was removed by distillation. The entire process lasted for 3 h. The solution was cooled to 30°C, and the initiator [0.43 g Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and 0.63 g (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 2.5 mL H<sub>2</sub>O] was added to the solution. After heating 10 min, the whole solution was poured into a tray and kept at room temperature for 7 days to yield the final product with MW of 2,500,000.

### Preparation of Amphiphilic Polymer Microspheres

Amphiphilic microspheres were prepared by suspension copolymerization of styrene with PEO-VB using BPO as the initiator. Suspension copolymerizations were carried out in a 250-mL three-neck reactor fitted with a condenser and a mechanical stirrer (300 rpm) under nitrogen atmosphere. A typical recipe and conditions of copolymerization are shown in Table I, and the reaction proceeded for 8 h. The final microspheres were purified by centrifugation and dialysis.

### Characterization

The structure of PEO macromonomer was confirmed by <sup>1</sup>H-NMR spectra (AC-P, 300 MHz; Bruker Instruments, Billerica, MA) in CDCl<sub>3</sub> with tetramethylsilane as an internal standard.

The copolymer structure was confirmed by infrared spectroscopy (MX-IE; Perkin-Elmer, Foster City, CA) using KBr pellet. Surface character-

**Table II** Effect of PSMA Concentration on Amphiphilic Microspheres<sup>a</sup>

Concentration of PSMA (wt %) <sup>b</sup>	Size Range of Amphiphilic Microspheres ( $\mu\text{m}$ )
0.1	3–35 (extensive agglomeration)
0.3	3–30 (some agglomeration)
0.5	3–17 (no agglomeration, $D_{av} = 10.6 \mu\text{m}$ )
1.0	4–12 (no agglomeration, $D_{av} = 8.8 \mu\text{m}$ )

<sup>a</sup> Polymerization conditions: St = 13.5 g, BPO = 0.1 g, PEO–VB = 3.0 g, H<sub>2</sub>O = 100.0 g, NaNO<sub>2</sub> = 0.05 g, 80°C for 8 h.

<sup>b</sup> Based on H<sub>2</sub>O.

istics of the microspheres were determined by X-ray photoelectron spectroscopy (XPS, NP-1, Shengyang Factory of Science Instruments, China).

The glass-transition temperature ( $T_g$ ) of the particles was obtained by differential scanning calorimetry (DSC 2010; TA Instruments) with a scanning rate of 20°C/min, in a nitrogen atmosphere.

The oxygen content in the amphiphilic microspheres was measured by an elemental analyzer (model 1106, Carlo Erba), and the PEO content was calculated from the oxygen content.

The average size, size distribution, and surface morphology of microspheres were obtained by SEM (AMRAY-1000, Amray, USA). To obtain the average size and size distribution, five SEM photographs and more than 800 microspheres were collected by computer, which linked with the SEM, followed by statistical analysis of data by computer. 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: a 0.7-g sample of microspheres was dissolved in a 10-mL mixture of pyridine (100 mL) and acetic anhydride (5 mL), by refluxing for 30 min. Distilled water (10 mL) was added to the solution, which had been cooled to room temperature. The solution was titrated by 0.3N aqueous NaOH using phenolphthalein/ethanol solution as indicator. The final content of –OH was calculated by the following equation:

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

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

## RESULTS AND DISCUSSION

### Effect of Dispersant Concentration on Amphiphilic Microspheres

Table II shows the results of the effect of PSMA concentration on the size characteristics of amphiphilic microspheres. It indicates that, when the dispersant concentration used in the polymerization was less than 0.5 wt %, agglomeration of microspheres occurred during the course of polymerization. In addition, the size and size distribution of microspheres were found to decrease with the increase of dispersant concentration.

### Effect of PEO–VB Concentration on Amphiphilic Microspheres

Figure 1 shows the <sup>1</sup>H–NMR of the PEO–VB used in our experiment. The ratio of bifunctional PEO macromonomer (VB–PEO–VB) can be determined by probability analysis, according to the following equation<sup>9</sup>:

$$\text{VB–PEO–VB} = (1 - p)^2$$

where  $p$  is the probability of the hydroxyl group to be substituted.

By analyzing the squares of different peaks, we can calculate the composition of the PEO macromonomer: PEG : PEO–VB : VB–PEO–VB = 0.16 : 0.48 : 0.36.

To investigate the effects of PEO–VB concentration on the diameter of microspheres, several different macromonomer concentrations were used in our experiments, the results of which are shown in Figure 2. The results indicate that an increase of PEO–VB concentration in copolymerization leads to a decrease in the size of amphiphilic microspheres. The reason for this phenomenon is that MPEG acted as costabilizer during the

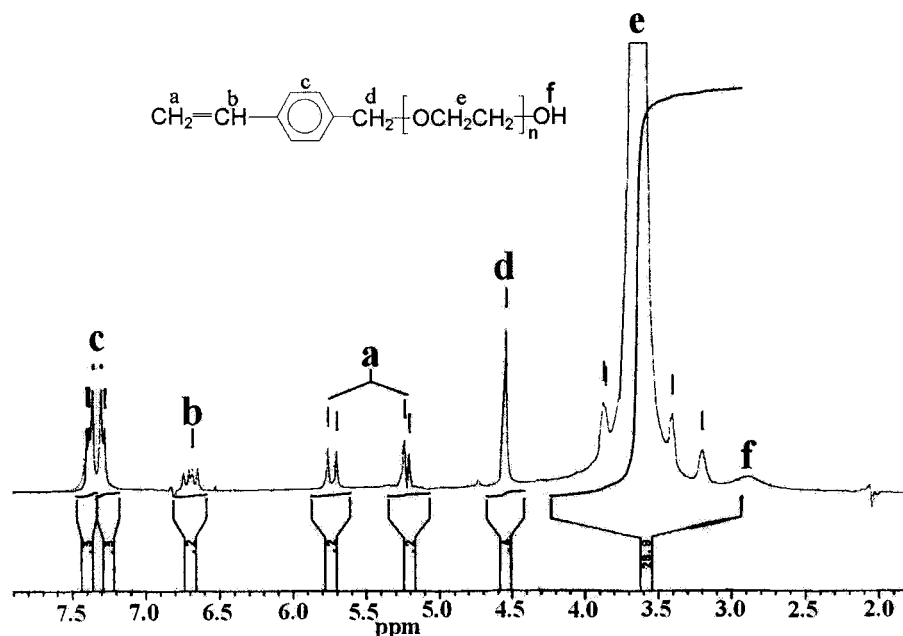


Figure 1  $^1\text{H-NMR}$  spectrum of PEO-VB in  $\text{CHCl}_3$ .

course of polymerization because of the hydrophilic PEO chains.

#### Characterization of Amphiphilic Microspheres

The SEM photograph and the size distribution histogram of amphiphilic microspheres are shown in Figures 3 and 4, respectively. It was observed that the microspheres are polydisperse.

Amphiphilic microspheres were swollen only in benzene (Fig. 5), whereas polystyrene micro-

spheres were completely dissolved. The swelling behaviors of amphiphilic microspheres in solvents of differing polarities will be discussed in detail in an upcoming study.

Figure 6 shows the FTIR spectra of five sample amphiphilic microspheres, prepared using different concentrations of PEO-VB. The adsorption bands in the region  $2000\text{--}1668\text{ cm}^{-1}$  and the double peaks at  $760$  and  $690\text{ cm}^{-1}$  are the characteristic bands of polystyrene. The peak at  $1090\text{ cm}^{-1}$  is the adsorption C—O group of PEO, which con-

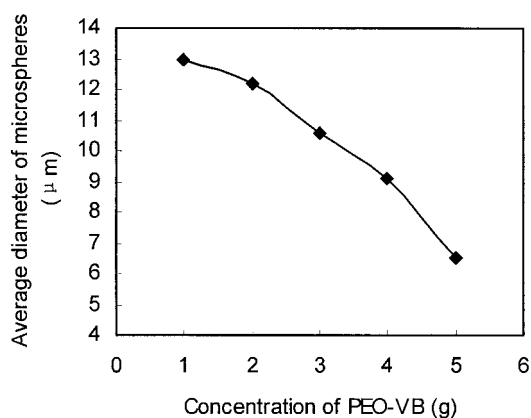


Figure 2 Effect of PEO-VB on the size of amphiphilic microspheres. Polymerization conditions: St = 15 ml, PSMA = 0.5 g, BPO = 0.1 g, water = 100 ml,  $\text{NaNO}_2$  = 0.05 g,  $80^\circ\text{C}$  for 8 h.

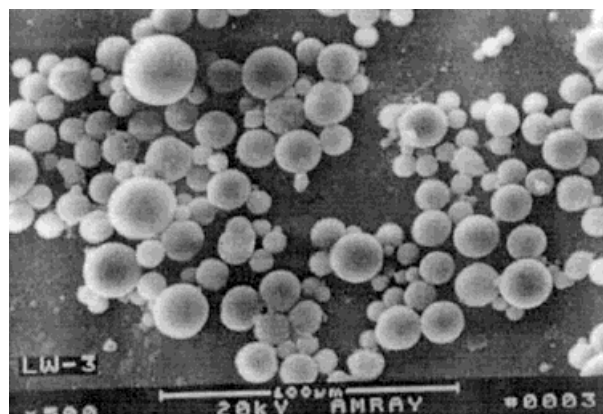
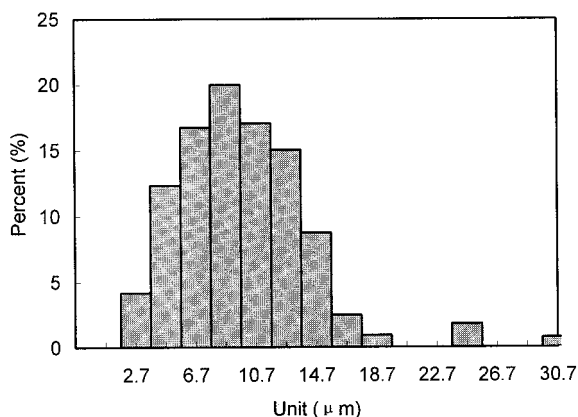


Figure 3 SEM photograph of amphiphilic microspheres. Polymerization conditions: PEO-VB = 4.0 g, St = 15 ml, PSMA = 0.5 g, water = 100 ml, BPO = 0.1 g,  $\text{NaNO}_2$  = 0.05 g,  $80^\circ\text{C}$  for 8 h.

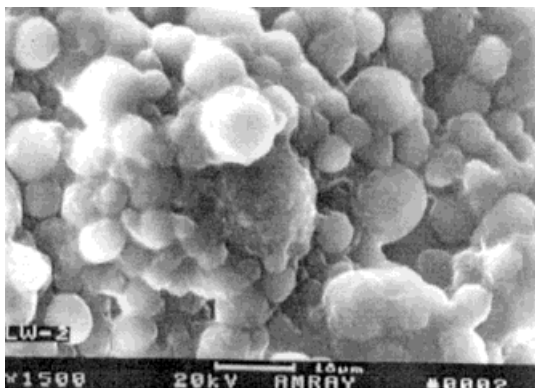


**Figure 4** Size distribution of amphiphilic microspheres. Polymerization conditions: PEO-VB = 4.0 g, St = 15 ml, PSMA = 0.5 g, water = 100 ml, BPO = 0.1 g,  $\text{NaNO}_2$  = 0.05 g,  $80^\circ\text{C}$  for 8 h.

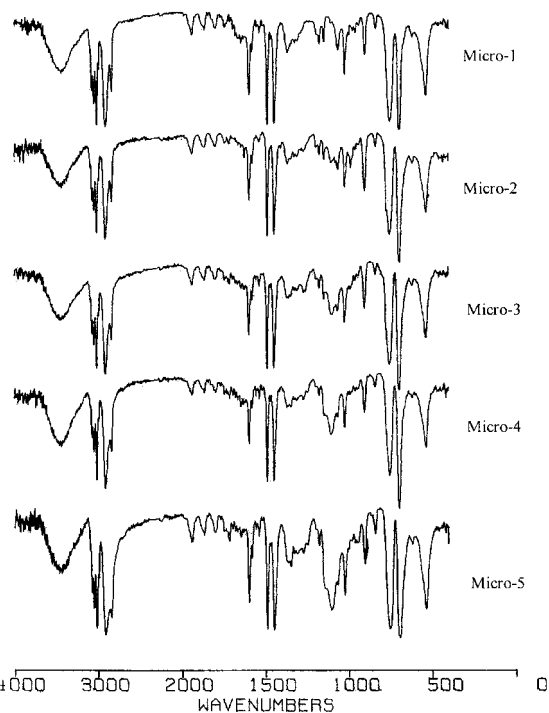
firmed the existence of PEO in the microspheres. When the proportion of PEO-VB in the total monomer increased, the intensity of the peaks at  $1090\text{ cm}^{-1}$  also increased.

Several DSC curves of final microspheres containing various contents of PEO-VB are shown in Figure 7, where each curve exhibits two adsorption peaks, indicating the existence of phase separation in amphiphilic microspheres. The  $T_g$  data obtained from DSC are listed in Table III.  $T_{g1}$  and  $T_{g2}$  are attributed to PEO chains and polystyrene chains, respectively, and the depression in the  $T_{g2}$  value suggests the polystyrene chains in the microspheres are plasticized by PEO chains.

The oxygen content in amphiphilic microspheres was measured by elemental analysis, and

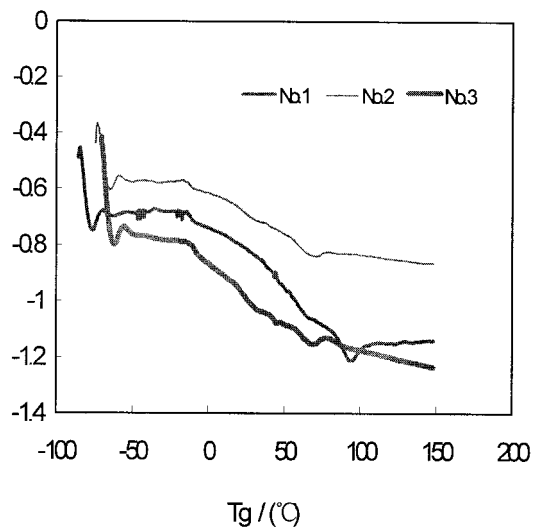


**Figure 5** SEM photograph of amphiphilic microspheres in benzene for 48 h. Polymerization conditions: PEO-VB = 5.0 g, St = 13.5 g, PSMA = 0.5 g, AIBN = 0.1 g, water = 100 ml,  $\text{NaNO}_2$  = 0.05 g,  $80^\circ\text{C}$  for 8 h.



**Figure 6** FTIR spectrum of microspheres. PEO-VB: Micro-1 = 0.5 g, Micro-2 = 1.0 g, Micro-3 = 2.0 g, Micro-4 = 3.0 g, Micro-5 = 4.0 g; St = 15 ml, PSMA = 0.5 g, water = 100 ml, BPO = 0.1 g,  $\text{NaNO}_2$  = 0.05 g,  $80^\circ\text{C}$  for 8 h.

the content of PEO was calculated from the oxygen data, as shown in Figure 8. The results indicate that the content of PEO in the microspheres



**Figure 7** DSC curves of amphiphilic microspheres. Polymerization conditions: PSMA = 0.5 g, BPO = 0.1 g, St = 13.5 g,  $\text{H}_2\text{O}$  = 100.0 g,  $\text{NaNO}_2$  = 0.05 g, PEO-VB (No. 1 = 3 g, No. 2 = 4 g, No. 3 = 5 g),  $80^\circ\text{C}$  for 8 h.



**Table III**  $T_g$  Values of Amphiphilic Microspheres<sup>a</sup>

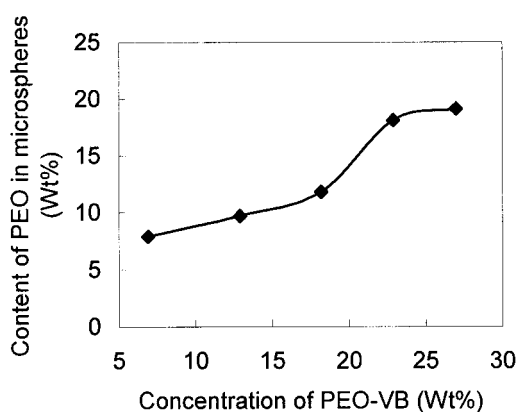
Microspheres	PEO-VB (g)	Styrene (g)	$T_{g1}$ (°C)	$T_{g2}$ (°C)
No.1	3.0	13.5	-9.5	95.6
No.2	4.0	13.5	-9.5	69.6
No.3	5.0	13.5	-7.9	70.2

<sup>a</sup> Polymerization conditions: PSMA = 0.5 g, BPO = 0.1 g, St = 13.5 g, H<sub>2</sub>O = 100.0 g, NaNO<sub>2</sub> = 0.05 g, 80°C for 8 h.

increases with increasing concentration of PEO-VB used in the polymerization. The final content of PEO in the microspheres is not equal to the content of PEO used in the polymerization, the reason for which is that some PEO-VB homopolymer would be formed during the polymerization and remain in the medium.

The surface chemical composition of microspheres was also determined by XPS. The PEO content in different layers of final microspheres was calculated from the oxygen data obtained by XPS, the results of which are shown in Table IV. It was observed that the PEO content in the surface of microspheres is greater than that inside. This phenomenon is attributed to the existence of a rich PEO hydrophilic layer on the surface of microspheres.

The content of the hydroxyl group (-OH) localized in the microspheres was determined by titration. The results show that the content of -OH groups in microspheres increased with increasing PEO-VB-to-styrene ratio (as shown in Fig. 9). Our experimental results showed that microspheres



**Figure 8** Variation of content of PEO in amphiphilic microspheres with the concentration of PEO-VB. Polymerization conditions: [PSMA] = 0.5 wt %, BPO = 0.1 g, St = 13.5 g, H<sub>2</sub>O = 100.0 g, 80°C for 8 h.

**Table IV** Content of PEO in Different Layers in Microspheres<sup>a</sup>

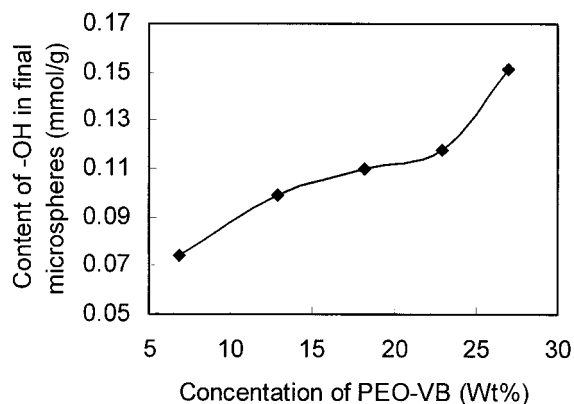
	PEO (wt %)
Amphiphilic microspheres	19.1
Surface	
Without etching	48.4
Etching 1 min	40.9

<sup>a</sup> Polymerization conditions: PSMA = 0.5 g, BPO = 0.1 g, PEO-VB = 5.0 g, St = 13.5 g, H<sub>2</sub>O = 100.0 g, NaNO<sub>2</sub> = 0.05 g, 80°C for 8 h.

containing 0.05–0.2 mmol/g hydroxyl groups could be prepared by changing the PEO-VB concentration used in the copolymerization.

## CONCLUSIONS

1. Polystyrene-*g*-poly(ethylene oxide) amphiphilic microspheres, ranging in size from 3 to 35  $\mu\text{m}$ , were prepared by changing suspension polymerization conditions.
2. Increasing the dispersant concentration resulted in a decrease of both the size and the extent of agglomeration of amphiphilic microspheres. Little agglomeration was observed when the dispersant concentration was greater than 0.5 wt %. The size and size distribution of microspheres decreased with increasing content of PEO-VB in copolymerization.
3. Amphiphilic microspheres, containing 0.05–



**Figure 9** Variation of content of -OH group in amphiphilic microspheres with concentration of PEO-VB. Polymerization conditions: PSMA = 0.5 g, BPO = 0.1 g, St = 13.5 g, H<sub>2</sub>O = 100.0 g, NaNO<sub>2</sub> = 0.05 g, 80°C for 8 h.

0.2 mmol/g hydroxyl groups, could be prepared by changing the concentration of PEO-VB, and richer PEO chains exist on the surface of amphiphilic microspheres.

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