DOI: 10.15952/j.cnki.cjsc.2000.03.001
合成化学 (HECHENG HUAXUE) 第 8卷第 3期 (2000)

Preparation and Characterization of Amphiphilic Polymer Microspheres[20]

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Abstract Amphiphilic microspheres ranging from 0.5μm~ 1.5μm were prepared by dispersion copolymerization of poly(ethylene oxide) macromonomer with styrene in the media of ethanol/water. Increasing the concentration of poly(ethylene oxide) macromonomer used in the polymerization, the resulting microspheres size decreased. Amphiphilic polymer microspheres were characterized by scanning electronic microscope, IR etc.

Keywords Amphiphilic polymer, Styrene, Poly(ethylene oxide), Copolymerization, Microspheres, Dispersion polymerization, Macromonomer.

As a novel functional polymer material, amphiphilic polymer microspheres have been applied in a lot of fields such as solid phase organic synthesis, polymeric catalysis, analytic chemistry, biomedicine[1, 2]. Poly[styrene-co-poly(ethylene oxide)] amphiphilic microspheres are one of the most useful amphiphilic polymer microspheres and the reactant bonded to them have high reactivity and selectivity in different media because of their excellent swelling capability in polar or non-polar solvents. In the previous work poly[styrene-co-poly(ethylene oxide)] amphiphilic microspheres were synthesized by the reaction of functioned polystyrene microspheres and poly(ethylene glycol) in the present of NaH or NaOH in high concentration. Because the reaction is a heterogeneous, the yield was low when the molecular weight of poly(ethylene glycol) was beyond 1000[1]. In this papers, poly[styrene-co-poly(ethylene oxide)] monodispersed amphiphilic polymer microspheres ranging from 0.5μm to 1.5μm were prepared through the dispersion copolymeriztion of poly(ethylene oxide) macromonomer(Mw = 2000) and styrene.

Experiment

Materials

Styrene(St) was distilled in reduced pressure to remove the inhibitor. AIBN was purified

[20] Received January 21, 2000.

by recrystallization in the media of ethanol/chloroform, THF was refluxed with Na to remove water, NaH (55% ~ 65% in oil, Fluka), poly(ethylene glycol) (PEG, Mw = 2000), *p*-vinylbenzyl chloride(> 90%, Acros), sodium dodecyl sulfonate(A. R), Poly(*N*-vinylpyrolidone) (BDH, Mw = 44, 000), anhydrous ethanol(A. R), ethyl ether(A. R) and chloroform(A. R) were used without further treating.

Synthesis of PEO macromonomer(PEO- VB)[3]

55. 0g PEG dehydrated for 24h under vacuum at 90℃ was dissolved in 60mL THF, to the solution 1. 96g sodium hydride was added. After stirring for 6h at 40℃ 4. 66mL *p*-vinylbenyl chloride was added and the reaction mixture was stirred for another 16h at the same temperature. The product was precipitated by adding cool ethyl ether and then dissolved in CH_2Cl_2 to remove insoluble impurities by filtration. The purification procedure mentioned above was repeated 3 times. At last the precipitated products was dehydrated under vacuum at room temperature to get pure one.

Preparation of amphiphilic polymer microspheres

Amphiphilc microspheres were prepared by dispersion copolymerizations of styrene with PEO- VB using AIBN as initiator in a solvent of Ethanol/water. Dispersion copolymerizations were carried out with a 250mL three-neck reactor fitted with a condenser and a mechanical stirrer(200rpm) under nitrogen. The solvent composition was V_{EtOH} : V_{H_2O} = 90: 10. The weight of St was 15. 8% based on the total weight of reactants. The concentration of PEO- VB in total monomers varied from 2. 7(Wt)% ~ 12. 2(Wt)%. The resulting microspheres were purified by repeated centrifugation and washing.

Results and Discussion

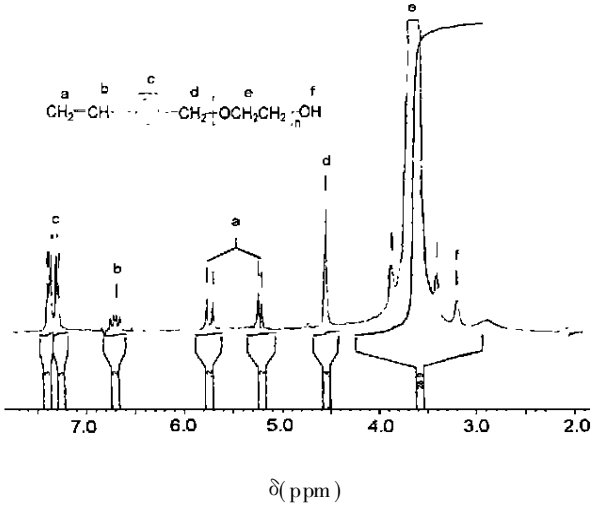
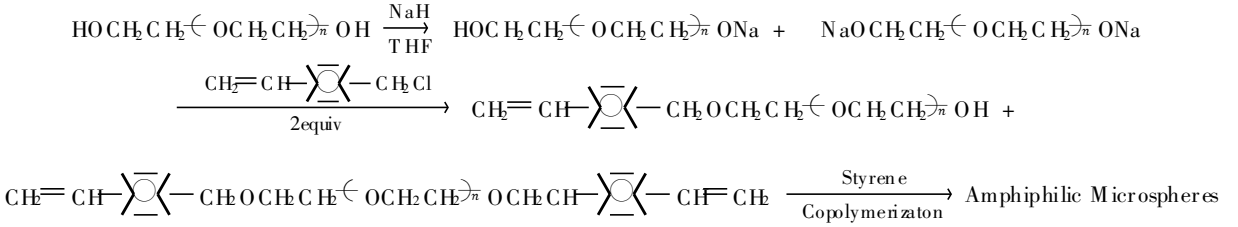


Fig. 1　^{1}H NMR Spectra of PEO- VB

The product PEO- VB was characterized by ^{1}H NMR in $CDCl_3$ and the result was shown in Fig. 1. The synthetic route was shown in Schem 1.

Amphiphilic microspheres and PSt microspheres prepared in the same condition as amphiphilic microspheres were placed in the media of benzene for 48h, the amphiphilic microspheres were only swollen while the polystyrene microspheres were completely dissolved, proving the structure of amphiphilic microspheres were crosslinked. Because part of PEO- VB was bifunctional monomer(Scheme 1), which acted as linking agent in copolymerization, the resulting amphiphilic microspheres were crosslinked. This is essential for amphiphilic microspheres

to apply in different media.



Scheme 1 Synthesis of Amphiphilic Microspheres

The morphology, average size and size distribution of amphiphilic microspheres were characterized by scanning electronic microscope (SEM) as shown in Fig. 2 and Fig. 3. The results indicated the resulting microspheres were nearly monodispersed.

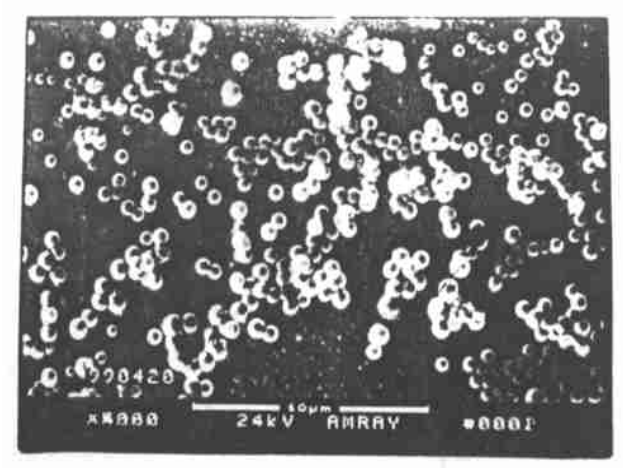


Fig. 2 SEM Photograph of Amphiphilic Microspheres

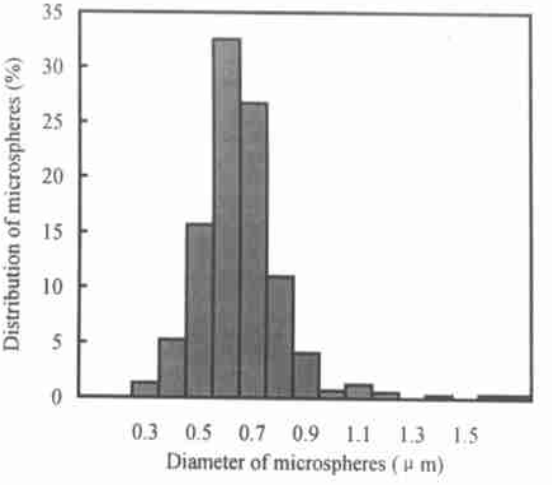


Fig. 3 Size Distribution Histogram of Amphiphilic Microspheres.

([St]= 16Wt%, [PVP]= 2.0Wt%, [PEO-VB]= 1.6Wt%, [SDS]= 0.6Wt%, [AIBN]= 0.2Wt%, V_{EtOH}: V_{H_2O}= 90: 10)

The structure of amphiphilic microsphres was characterized by IR spectroscopy and the result was shown in Fig. 4, which included the IR spectra of Polystyrene (PSt), PEG and amphiphilic microspheres. The result indicated PEG had a strong peak near 1100cm^{-1} which is a characteristic peak of ether bond; the amphiphilic microspheres also had a peak in middle strength near 1100cm^{-1}, which proved the amphiphilic microspheres were the copolymer of styrene and PEO-VB.

The experimental results showed that average size of amphiphilic microspheres ranging from 0.5μm~ 1.5μm could be prepared under different polymerization condition. The effect of concentration of PEO-VB on the diameter of amphiphilic microspheres was shown in Fig. 5. The result showed that the diameter of amphiphilic microspheres decreased with the increase of PEO-VB concentration for PEO-VB acted as a dispersant in polymerization.

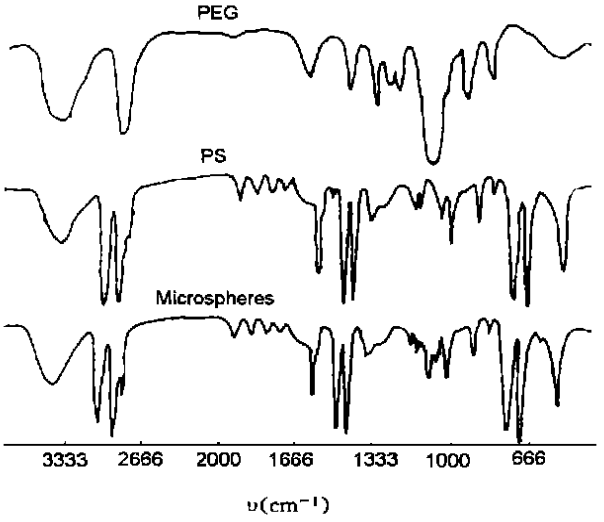
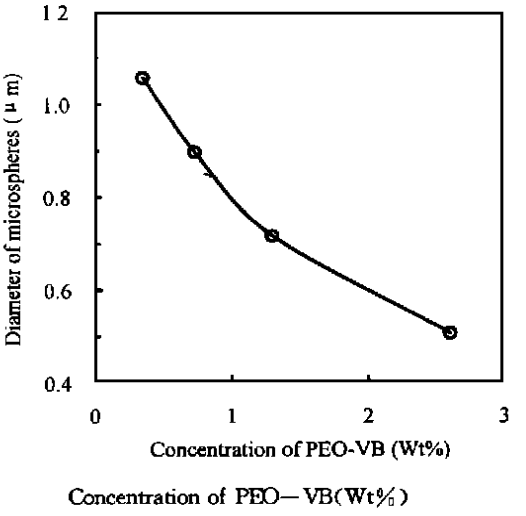


Fig. 4　IR Spectra of PEG, PS, Amphiphilic Microspheres.



Concentration of PEO—VB(Wt%)

Fig. 5　Effect of PEO- VB Concentration on the Diameter of Microspheres

[styrene]= 15.8%; [PVP]= 2.0Wt%; [SDS]= 0.6Wt%; V_{EtOH}: V_{water}= 90: 10; [AIBN]= 0.2Wt%

Acknowledgement: The project was supported by the Hongkong Polytechnic University, the Youth Researcher Foundation of Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences and The Youth Researcher Foundation of Di? Ao Group, Chinese Academy of Sciences

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两亲高分子微球的合成与表征

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摘要　通过苯乙烯和聚氧乙烯大分子单体的共聚,合成了粒径在 0.5μm~ 1.5μm的两亲高分子微球。随着聚氧乙烯大分子单体浓度的增加,微球粒径减小。通过扫描电镜, IR等分析手段对微球进行了表征。

关键词　苯乙烯　聚氧乙烯　共聚　分散聚合　大分子单体