

Polymer Microspheres with Surface Chains Prepared by Dispersion Copolymerization Using Poly(oxyethylene) Macromonomer

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ABSTRACT: Polymer microspheres were prepared by dispersion copolymerization of styrene with poly(oxyethylene) (peo) macromonomer. A dispersion terpolymerization of styrene, PEO macromonomer and acrylic acid was also conducted to prepare polymer microspheres with both surface carboxyl groups and PEO polymer chains. The microspheres thus obtained were characterized with TEM, IR, and X-ray photoelectron spectroscopy analyses. Palladium nanopar-

ticles were then formed on the surface of these copolymer microspheres forming polymer/metal nanocomposites which were then studied by TEM and X-ray diffraction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2732–2736, 2002

Key words: dispersion copolymerization; PEO macromonomer; nanocomposites

INTRODUCTION

Recently, considerable interest has been concentrated on the development of polymer particles by dispersion polymerization.^{1–7} These particles have extensive applications in the fields of medical diagnostics, liquid chromatography, enzyme immobilization, and drug delivery.^{8–10}

Stabilizers are essential to the dispersion polymerizations which provide stability for the particles. Apart from the classical stabilizers, macromonomers are found to be effective stabilizers and therefore receive much attention in the literature.^{11–13} Of various macromonomers, poly(oxyethylene) macromonomer (PEO) belongs to a very important class of macromonomers.

The dispersion polymerization of PEO macromonomer with oil-soluble monomers such as styrene was found to be a useful method for preparation of stable polymer microspheres.^{14–16} Different from the conventional dispersion polymerization or copolymerization, the amphiphilic macromonomer PEO acts not only as comonomer, but also as stabilizer.

Generally, dispersion polymerization is a heterogeneous process, by which polymer particles are formed from the initially homogeneous reaction medium in the presence of a suitable steric stabilizer. The reaction medium is therefore selected to act as precipitant for

the copolymer formed (or hydrophobic segments of the graft copolymer) and as a good solvent for the low molecular weight comonomer, macromonomer, and the hydrophilic branches of the graft copolymer¹⁷. The initiation of dispersion polymerization is a two-step process. It starts in the continuous phase by the primary radicals derived from an initiator. The second step begins in the polymer particles by entering oligomer radicals.

According to the homogeneous nucleation theory,¹⁸ the polymerization or copolymerization starts in the homogeneous reaction medium and forms oligomer radicals. The solubility of these oligomer radicals is a function of the monomer type, the molecular weight, and the copolymer composition. Oligomers with molecular weight higher than the critical value precipitate and form primary particles. These primary particles agglomerate until stable particles are formed. This point is referred to as the critical point (or the critical conversion) and it appears when all polymer particles contain a sufficient amount of surface-active groups or amphiphilic (e.g., PEO) chains at the surface to provide colloidal stability.

The microspheres produced by dispersion copolymerization with macromonomers contain surface graft macromonomer chains. These graft chains might be employed to stabilize metal nanoparticles on the surface of polymer microspheres and to prevent their mutual agglomeration.

In this work, polystyrene-based microspheres with macromonomer surface-graft polymer chains were prepared by dispersion copolymerization by using

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TABLE I
Conditions for Dispersion Copolymerization of St with MAPEO Macromonomer^a

Sample No.	St (g)	MAPEO (g)	AA (g)	AIBN (g)	Et/H ₂ O (ml, v/v ⁹ : 1)	Diameter ^b (nm)
PEO1	10	1.0		0.2	100	350–550
PEO2	10	1.5		0.2	100	250–400
PEO3	10	3.0		0.2	100	120–270
PEO4	10	1.5	0.5	0.2	100	100–300

^a Polym. Temp., 65°C; polym. time, 24 h.

^b Because of polydispersity in particle size, the value here is only an indication of range of particle diameter.

PEO macromonomer. Then, the polymer microsphere-supported metal nanocomposites were formed by reducing palladium ions in the presence of polymer microspheres.^{19,20} Initial work regarding the preparation and characterization of the microspheres and nanocomposites is reported here.

EXPERIMENTAL

Materials

Commercially available styrene (St) and acrylic acid (AA) were purified by distillation under reduced pressure. Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Palladium chloride (PdCl₂) was of analytical grade and used as supplied. Poly(oxyethylene) capped with methyl group at one end (designated as MePEO, commercial sample from Fluka, 5000 g/mol) was used to prepare PEO macromonomer. All other chemicals were purchased from the Shanghai Chemical Reagent Plant in Shanghai, China.

PEO macromonomer synthesis

Methacryloyl chloride was prepared by reaction of methacrylic acid (MAA) with thionyl chloride. MePEO was dried under vacuum at melting state before use. The methacryloyl-terminated PEO macromonomer was prepared according to the following procedure: to a well-stirred solution of MePEO and Et₃N in dichloromethane (DCM) at ice-water bath, the methacryloyl chloride in DCM was dropped very slowly for 1.5 h. After all of the methacryloyl chloride was added (1.5 h later), the reaction proceeded for 1 h at 0°C, and then for 24 h at room temperature. The precipitates formed were filtered off. The macromonomer was obtained by precipitation of the filtrate into excess of diethyl ether, filtered off, and then dried at room temperature under vacuum. The PEO macromonomer (designated as MAPEO) thus obtained was characterized by ¹H-NMR spectrum.

¹H-NMR (CDCl₃), δ (TMS, ppm): 3.38 (3H, OCH₃); 1.95 (3H, CH₃); 3.61 (4nH, OCH₂CH₂O); 4.3 (2H, COOCH₂); 5.58 and 6.13 (2H, CH₂=C).

Dispersion polymerization

Two batch polymerizations (St-MAPEO, St-MAPEO-AA) were carried out in ethanol/water mixture (v/v 9 : 1) at 65°C for 24 h under nitrogen atmosphere. The recipes for the polymerizations are listed in Table I. Polymer microspheres were collected by centrifugation.

Polymer microspheres supported palladium nanocomposites

About 0.5 g of copolymer particles was dispersed in 25 mL ethanol by sonification. Into this solution, an acid solution of 25 mg PdCl₂ in 25 mL water was added. The mixture was stirred for 1 h at room temperature and then refluxed for 2 h. The dispersion was dialyzed against water for 24 h and then dried below 40°C.

Characterization

The morphologies of both the copolymer microspheres and the composite particles were observed on a Hitachi-800 microscope. IR spectra were recorded on a VECTOR-22 IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB MARK system with the overall energy resolution of 1.0 eV. X-ray diffraction (XRD) analysis was carried out on a X-ray diffractometer (Y-4Q, China).

RESULTS AND DISCUSSION

Dispersion polymerization

Effect of PEO macromonomer concentration

The morphologies of the polymer microspheres were observed by TEM. The typical micrographs of these microspheres are shown in Figure 1. Unexpectedly, the microspheres, though spherical in shape, are quite polydisperse in size. The ranges of the particle diameters for the microspheres are listed in Table I. Examination of Figure 1 and Table I provides the following results: (1) With increase in the amount of PEO mac-

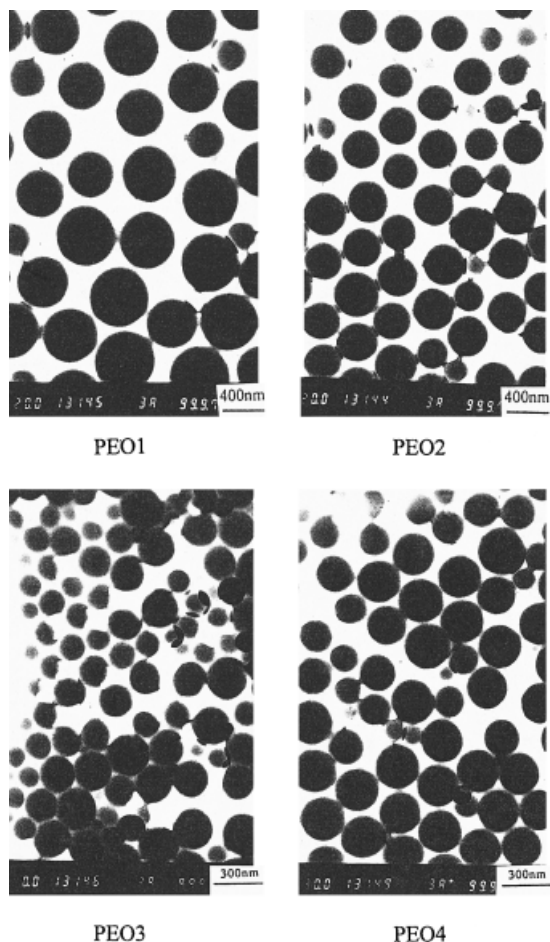


Figure 1 TEM micrographs of the copolymer microspheres.

romonomer in the polymerization feed, the particle diameter, though polydisperse, shows a clear trend of significant decrease; (2) In the dispersions of lower amounts of PEO macromonomer as in PEO1 and PEO2, the polydispersity of the particle size is decreased (e.g., the particles are more homogeneous in size); (3) The fraction of microspheres with small size is quite low in each dispersion. In addition, comparison of PEO2 and PEO4 clearly indicates that addition of AA into the initial polymerization feed significantly decreases the particle size, suggesting that hydrophilic carboxylic acid monomer contributes to the stabilization of polymer microspheres in the present dispersion polymerization. The decrease in particle size with an increase in the amount of PEO macromonomer in the polymerization feed as observed in Figure 1 and Table I is obviously due to the finding that more macromonomer can stabilize more particles. The polydispersity in particle size observed in the present dispersions might be owing to subsequent nucleation,²¹ which undoubtedly needs further investigation.

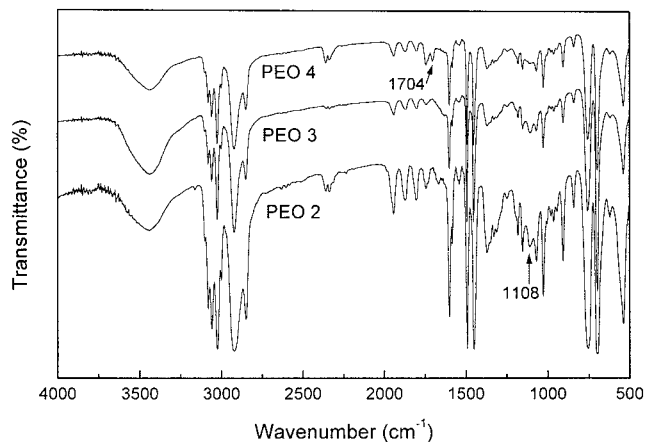


Figure 2 IR spectra of the copolymer microspheres.

Composition analyses of the polymer microspheres

The IR spectra of the PEO2 to PEO4 microspheres are shown in Figure 2. The peak at 1108 cm^{-1} is attributed to the C—O—C linkage of PEO macromonomer. Further evidence for this linkage was obtained from $^1\text{H-NMR}$ spectra. The signal at 3.6 ppm was observed for the microspheres.²² These results proved the copolymerization of St with MAPEO macromonomer. For PEO4, a peak at 1704 cm^{-1} appears in the IR spectrum (see Fig. 2). This peak is attributed to carboxyl group in AA unit, indicating copolymerization of AA with St and MAPEO in the PEO4 microspheres.^{23,24}

As is accepted, the macromonomer functions not only as a comonomer, but more importantly, as a stabilizer in the dispersion copolymerization. Thereafter, the macromonomer tends to stay on the surface of the microspheres. XPS was therefore employed to study the surface structure of the PEO3 and PEO4 copolymer microspheres. Full-scan spectra of both microspheres are shown in Figure 3. The main elements, as detected by XPS on the surface of the microspheres, are carbon and oxygen (hydrogen cannot be detected by XPS). Evidently, in PEO3 the oxygen comes from

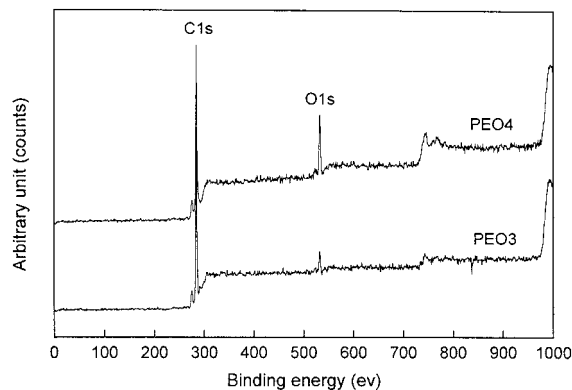


Figure 3 XPS full-scan spectra of the copolymer microspheres.

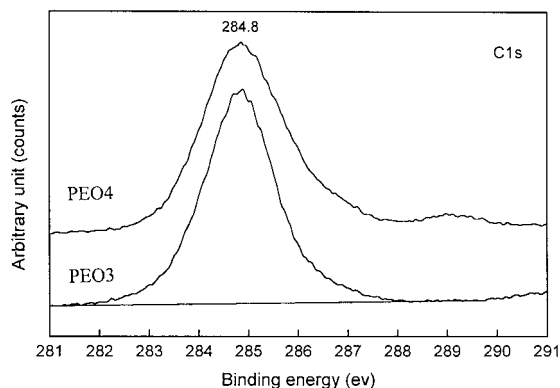


Figure 4 XPS C1s spectra of the copolymer microspheres.

PEO macromonomer. Comparison of PEO3 and PEO4 in Figure 3 shows a much stronger O1s signal in PEO4. This result indicates more oxygen content on the surface of PEO4 microspheres, which is most probably due to the presence of AA units on the microsphere surface. The C1s spectra of both the microspheres are shown in Figure 4. The C1s peak shifts toward the side of higher binding energy (BE). The curve-fitted C1s spectra are shown in Figures 5 and 6. In Figure 5, the presence of two types of carbons can be seen at binding energies of 284.8 and 286.1 eV, respectively. The former is attributable to the carbons in C—C and C—H linkage; whereas the latter is attributable to carbons in C—O—C linkage that derive from the PEO macromonomer. These results confirm the grafting of PEO macromonomer on the surface of PEO3 copolymer microspheres. In Figure 6, three peaks are obtained at binding energies of 284.8, 286.1, and 289.2 eV. The first two peaks are the same as in Figure 5. The third peak undoubtedly comes from carbons in carboxyl groups, which proves the presence of the AA unit on the microsphere surface. The XPS results here convincingly confirm the presence of both the carboxylic groups and the PEO macromonomers on the surface of PEO4 microspheres. The microspheres belong to an interesting kind of surface-functionalized poly-

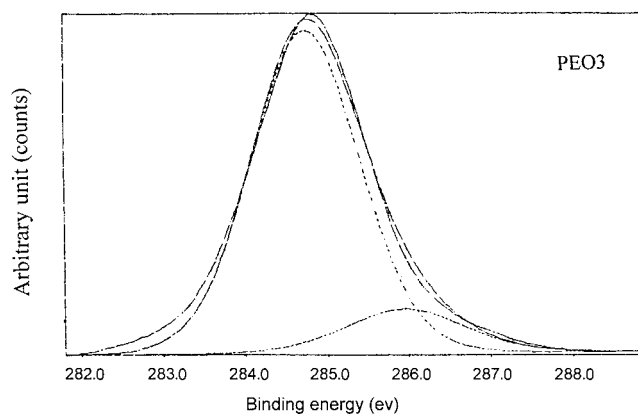


Figure 5 Curve-fitted C1s spectrum of PEO3.

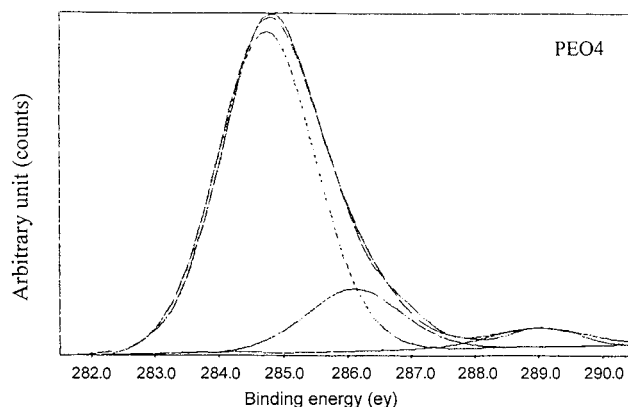
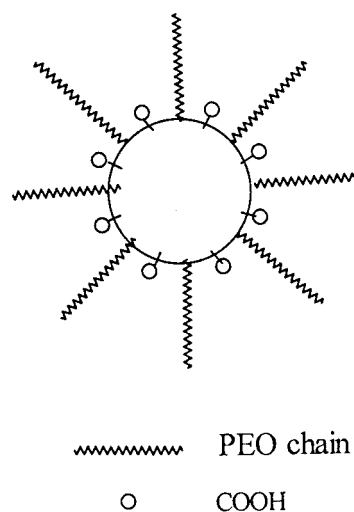


Figure 6 Curve-fitted C1s spectrum of PEO4.

mer microspheres. That is, the microsphere surface is not only covered with functional groups but also with macromonomer polymer chains, as depicted in Scheme 1.

Microsphere supported palladium nanocomposites

As discussed above, both the PEO3 and the PEO4 microspheres have macromonomer chains grafted on the surface. One function of the polymer chains, together with surface functional groups as in PEO4 microspheres, lies in protecting and stabilizing metal nanoparticles, therefore, preventing them from mutual agglomeration and air oxidation. For this end, both the PEO3 and the PEO4 microspheres were then used to prepare microsphere-supported palladium nanocomposites. Typical TEM micrographs of such nanocomposites are shown in Figure 7. It is interesting to see that nanometer palladium particles (5–20 nm) closely attached to the surface of the microspheres. Large fractions of them are buried into the surface layer which are most probably attributed to mac-



Scheme 1

romonomer chains grafted on the surface. The observations here imply that the surface polymer chains are stabilizing nanoparticles.

An XRD pattern of the nanocomposites based on PEO3 microspheres is shown in Figure 8. As well as the scattering of polymer microspheres around $2\theta = 21^\circ$, three additional peaks appear at $2\theta = 40^\circ$, 46.4° , and 67.3° , which are attributed to (111), (200), and (220) planes of palladium, respectively. The result confirms formation of zerovalent palladium particles on the surface of the microspheres.

Stabilization of other inorganic nanoparticles on the surface of such copolymer microspheres, and the interaction between surface structure and nanoparticles, are under investigation together with the catalytic activity of the nanocomposites.

CONCLUSION

Polymer microspheres with surface-grafted polymer chains were prepared by dispersion copolymerization using PEO macromonomer. By dispersion terpolymerization of St, PEO macromonomer, and AA, a type of surface-functionalized copolymer microspheres with both surface carboxyl groups and PEO chains were obtained. Such polymer microspheres with surface-grafted polymer chains were then used to prepare microsphere-supported palladium nanocomposites. TEM observation indicated that nanometer palladium

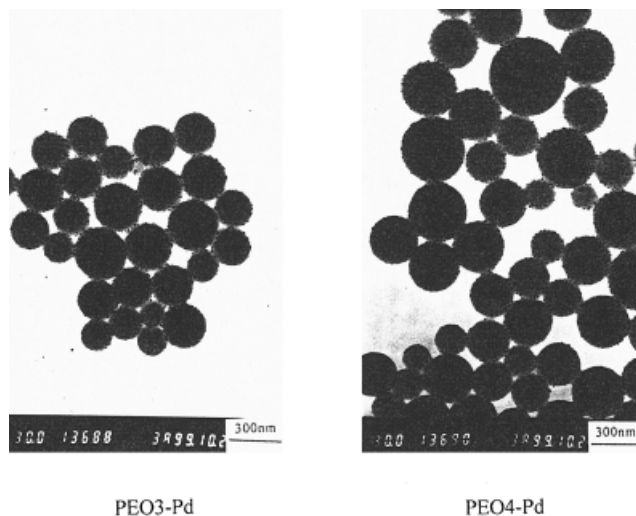


Figure 7 TEM micrographs of microsphere supported palladium nanocomposites.

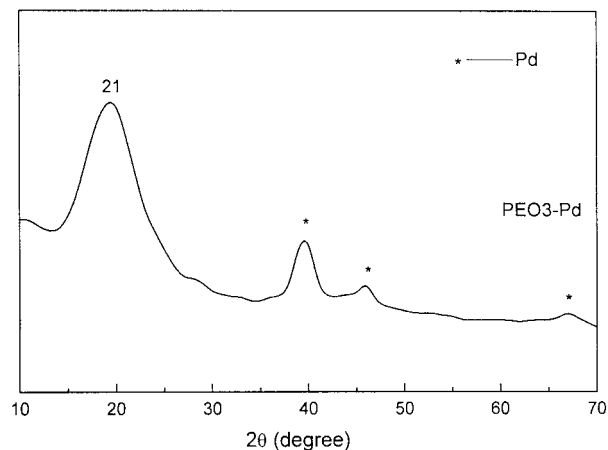


Figure 8 XRD profile of PEO3-Pd nanocomposites.

particles were buried into the surface layer, implying stabilization of nanoparticles by grafted polymer chains.

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