

Initiation of Surface Graft Polymerization by Ceric Ions on Polymer Microspheres

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ABSTRACT: The surface graft polymerization of acrylamide on poly(styrene-*co*-acrylonitrile) copolymer microspheres by the initiation of ceric ions was studied. The grafting was verified by IR spectra and X-ray photoelectron spectroscopy measurements. The resultant microspheres with surface-grafted polymer chains were employed in the preparation of polymer-microsphere-supported palladium

composite particles. The composite particles were then studied by transmission electron microscopy and X-ray diffraction. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 936–940, 2003

Key words: graft polymers; composites

INTRODUCTION

Polymer microspheres with surface functionality (surface functional groups or surface chains) have found extensive applications in biology, medical analysis, coatings, catalysts, and so on.^{1–5}

Emulsion copolymerization with functional monomers such as acrylic acid and acrylonitrile (AN) and dispersion copolymerization with suitable macromonomers have been the main methods of preparing polymer microspheres with surface functional groups and surface chains, respectively. The former, however, has limitations and difficulty in controlling the quantity and distribution of functional groups,^{6,7} whereas the latter has limitations in preparing suitable macromonomers.⁸ In view of surface modifications on fibers or membranes, surface grafting has been one of the most useful and effective methods of rendering surface functionality and, therefore, has been applied widely.^{9–11} Works on the surface modification of cellulose membranes via graft polymerization by the initiation of ceric ions have been reported extensively. Graft polymerization is generally presumed to result from radical sites generated on the backbones of polymer chains. Therefore, the initiation of graft polymerization is thought to result from radicals formed on the cellulose molecular backbone because of the oxidation of ceric ions with functional groups in cellulose macromolecules such as —OH. However, works on

surface graft polymerization on polymer microspheres by the initiation of ceric ions are rarely reported.

In this work, the surface graft polymerization of acrylamide (AAM) on poly(styrene-*co*-acrylonitrile) [P(St-*co*-AN)] copolymer microspheres by the initiation of ceric ions was attempted for the preparation of functional polymer microspheres with surface polymer chains. These surface chains might then be employed as stabilizers for surface-deposited metal particles. The prerequisite for surface grafting is the presence of surface functional groups such as hydroxyl or cyano groups.¹² For this end, the emulsifier-free emulsion copolymerization of styrene (St) with AN was employed for the preparation of polymer microspheres with some surface cyano groups. Afterward, the surface graft polymerization of AAM was carried and found to be feasible. This method provides a versatile approach for preparing functional polymeric microspheres with various surface-grafted chains. The resultant polymer microspheres were used to prepare polymer-microsphere-supported palladium composite particles, which may have potential applications in the area of catalysis.^{13,14}

EXPERIMENTAL

Materials

St and AN were purified by distillation under reduced pressure. Ammonium persulfate (APS) was analytical-grade and was used as supplied. AAM (≥98.5%), ceric ammonium nitrate (CAN), and nitric acid were used without further purification.

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TABLE I
Conditions for the Preparation of St-AN Copolymer Microspheres

Sample	St (g)	AN (g)	APS (g)	H ₂ O (mL)	Temperature (°C)	Time (h)	Diameter (nm)
St-AN	12	12	0.084	200	70	7	446

Preparation of P(St-co-AN) copolymer microspheres

P(St-co-AN) copolymer microspheres (abbreviated St-AN) were prepared by the emulsifier-free emulsion copolymerization of St with AN with APS as an initiator. The recipe of the copolymerization is given in Table I. The preparation procedure was reported earlier.¹⁵ The polymerization was carried out at 70°C for 7 h under a nitrogen atmosphere. The microspheres obtained were first purified by dialysis for 1 week and then collected by centrifugation.

Graft polymerization of AAM on St-AN microspheres

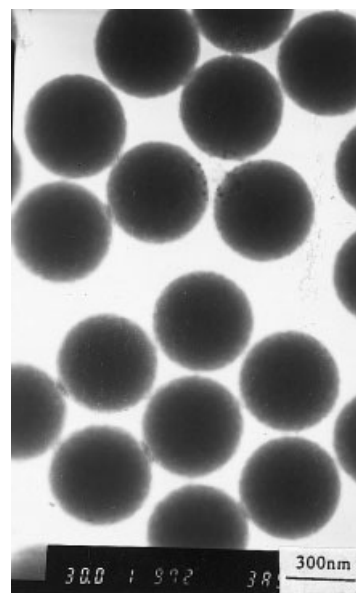
In a typical experiment, a solution of CAN in 1M nitric acid (0.1M, 3 mL) was added to a dispersion solution of AAM (3 g) and St-AN microspheres (0.5 g) in 47 mL of H₂O. The reaction was carried out at 50°C for 4 h under a nitrogen atmosphere. The product designated (St-AN)AAM was purified by the centrifugation being repeated.

Polymer-microsphere-supported palladium composite particles

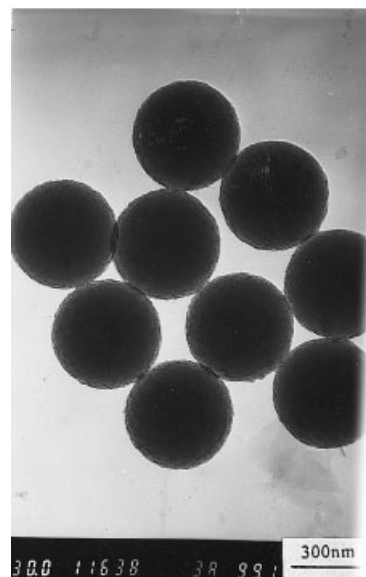
The composite particles were prepared by the refluxing of an ethanol/H₂O solution of Pd₂Cl in the presence of (St-AN)AAM microspheres. The detailed procedure was similar to that reported earlier.¹⁶ The weights of the (St-AN)AAM microspheres and Pd₂Cl were about 0.4 g and 15 mg, respectively. The resultant composite particles were filtered and then dried below 40°C.

Characterization

The morphology of the microspheres was observed by transmission electron microscopy (TEM) with a Hitachi 800 microscope. IR spectra were recorded on a Vector 22 IR spectrometer with KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an Escalab Mark II system with a residual pressure of 3×10^{-9} mbar. A Mg K α radiation source ($h\nu = 1253.6$ eV) was used with an overall energy resolution of 1.0 eV. The microspheres were in powder form for the XPS measurements. X-ray diffraction (XRD) was carried out on a X-ray diffractometer (Y-4Q, China).



(a)



(b)

Figure 1 TEM photographs of (a) St-AN copolymer microspheres and (b) (St-AN)AAM microspheres.

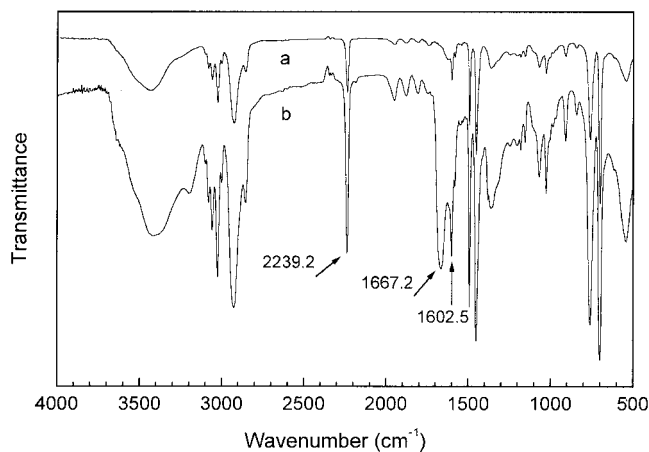


Figure 2 IR spectra of (a) St-AN microspheres and (b) (St-AN)AAM microspheres.

RESULTS AND DISCUSSION

Surface graft polymerization of AAM by the initiation of ceric ions

TEM observations

Figure 1 shows typical TEM micrographs of St-AN microspheres before and after grafting. In Figure 1(a), the St-AN microspheres are spherical in shape and monodisperse in size. After grafting, the diameter of the microspheres increases [from 446 to 470 nm; see Fig. 1(b)], and the surface becomes rougher. These observations suggest the formation of a new phase on the surface of St-AN microspheres after the grafting reaction.

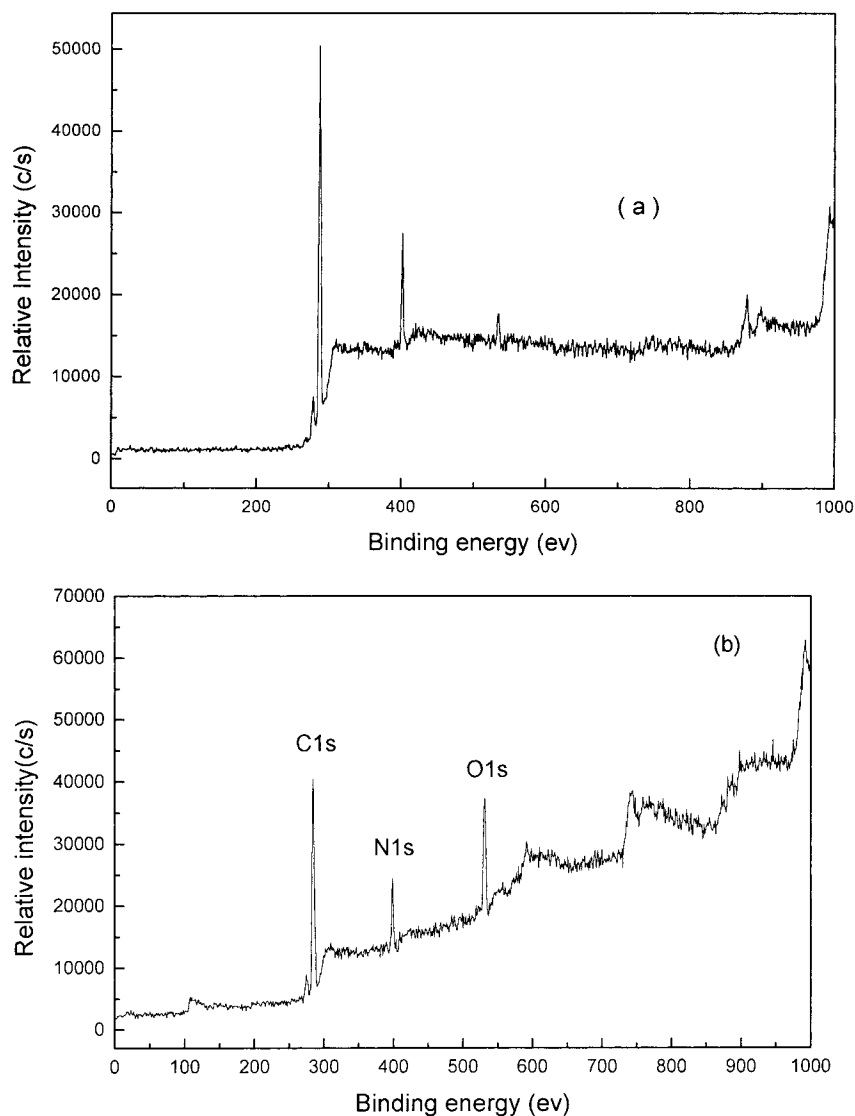


Figure 3 Full-scan spectra of (a) St-AN microspheres and (b) (St-AN)AAM microspheres.

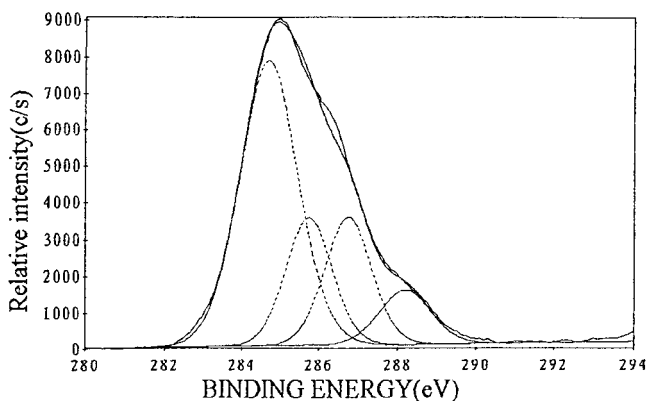


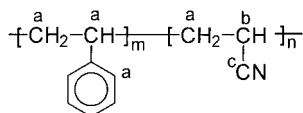
Figure 4 Curve-fitted C1s spectrum of (St-AN)AAM microspheres.

IR spectra

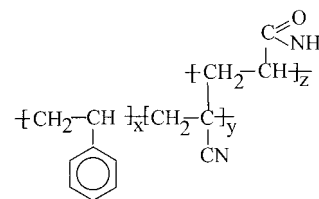
The IR spectra of St-AN microspheres before and after grafting are shown in Figure 2. In Figure 2(a), except for the typical bands of polystyrene, a characteristic peak at 2237 cm^{-1} is due to the presence of CN groups. This confirms the copolymerization of St with AN in St-AN copolymer microspheres. After grafting [Fig. 2(b)], a strong adsorption at 1667 cm^{-1} , assigned to the carbonyl bond in CONH₂ groups,¹⁷ appears, indicating the grafting of AAM on the surface of St-AN microspheres.

XPS analysis

XPS was employed to study the surface composition variations of St-AN microspheres after the grafting reaction. The full-scan spectra of St-AN and (St-AN)-AAM microspheres are shown in Figure 3. The C1s spectrum of (St-AN)AAM is shown in Figure 4. In Figure 3, the O1s signal is much stronger in intensity in the (St-AN)AAM microspheres than in the St-AN microspheres. This observation indicates the formation of an oxygen-containing phase on the surface of the St-AN microspheres after the grafting of AAM. As seen in Figure 4, the curve-fitted C1s spectrum of the (St-AN)AAM microspheres shows four peaks. The first three peaks at binding energies (BEs) of 284.7, 285.8, and 286.8 eV are attributed to three different carbons (a, b, and c, respectively) in the backbone structure of the St-AN copolymer microspheres, as shown in Scheme 1.¹⁵ However, a new and quite strong peak at BE = 288.2 eV can be observed in



Scheme 1



Scheme 2

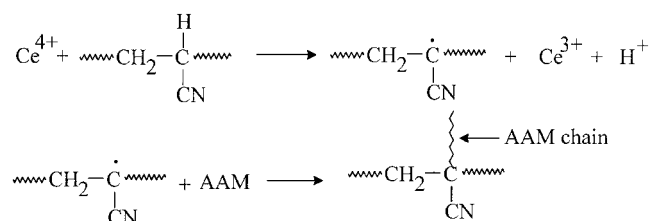
Figure 4 for the (St-AN)AAM microspheres. This peak can be attributed to carbon in CONH₂ groups.¹⁶

The combination of all of these results confirms the occurrence of the ceric-ion-initiated graft polymerization of AAM on the surface of St-AN microspheres, which results in the formation of surface-grafted polyacrylamide chains.

Under the assumption of the surface molecule backbone structure indicated in Scheme 2 for the (St-AN)-AAM microspheres, the grafting extent was then calculated from the curve-fitted results of the C1s spectrum of (St-AN)AAM in Figure 4. The X:Y:Z ratio of 1:4.3:5.1 suggested a graft of about one AAM on one AN unit. The grafting mechanism was tentatively assumed to proceed as shown in Scheme 3, similar to that for hydroxyl groups.¹⁸ That is, the hydrogen at the position of the tertiary carbon was abstracted by ceric ions, and a radical was yielded on the copolymer backbone, which then initiated the polymerization of AAM therein.

Polymer-microsphere-supported palladium composite particles

The surface-grafted polymer chains on the microspheres may be employed to protect and stabilize ultrafine metal particles such as nanometer particles and, therefore, prevent their mutual agglomeration and air oxidation. Consequently, the (St-AN)AAM microspheres were used to prepare microsphere-supported palladium composite particles. A typical TEM micrograph of such composite particles is shown in Figure 5. Nanometer palladium particles (5–20 nm) are clearly attached to the surfaces of the microspheres. Some of them are buried in the surface layer structure, and these are most likely attributable to surface-grafted polymer chains. These observations



Scheme 3

imply that the surface-grafted polymer chains are applicable for stabilizing metal particles on the surfaces of microspheres.

The XRD pattern of the composite particles is shown in Figure 6. Except for the scattering of polymer microspheres around $2\theta = 22^\circ$, three additional peaks appear at $2\theta = 40.0$, 46.4 , and 67.8° , which are attributed to (111), (200), and (220) planes of palladium, respectively. The results confirm the formation and deposition of zero-valent palladium particles on the surfaces of (St-AN)AAM microspheres.^{19,20}

CONCLUSIONS

The surface graft polymerization of AAM by the initiation of ceric ions on St-AN copolymer microspheres was studied and found to be feasible. Both IR spectra and XPS results confirmed the occurrence of surface graft polymerization. These polymer microspheres with surface-grafted polymer chains were then used to prepare microsphere-supported palladium composite particles. TEM observations indicated the distribution of nanometer palladium particles buried in the surface layer structure, implying the stabilization of metal particles by grafted polymer chains.

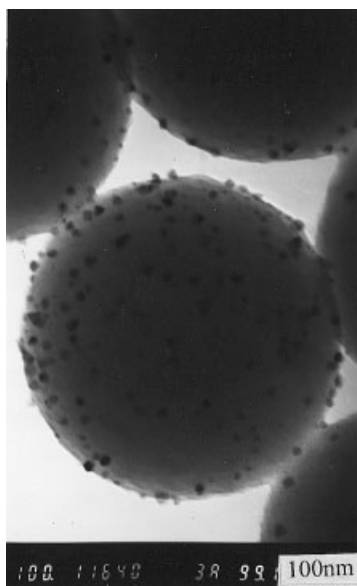


Figure 5 TEM photograph of (St-AN)AAM/Pd composite particles.

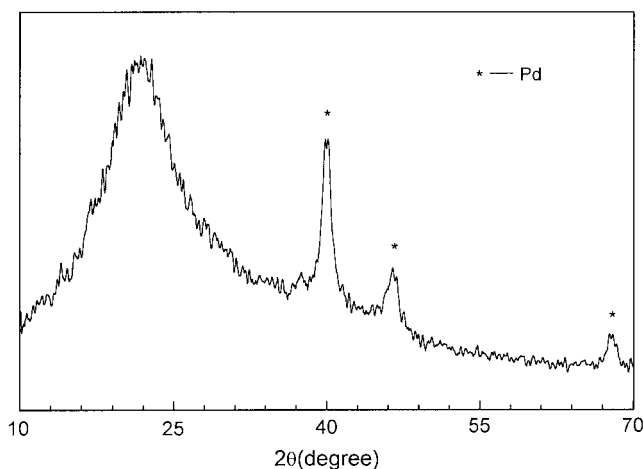


Figure 6 XRD profile of (St-AN)AAM/Pd composite particles.

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