Emulsifier-Free Emulsion Polymerization of Acrylonitrile in the Presence of Poly(methyl methacrylate) Seed Particles: Influence of the Addition Mode on the Surface Morphology

Yang Guangzhi,[1,2] Liu Yang,[1,2] Jia Runping,[2] Xu Risheng,[1,2] Wang Xia,[2] Ling Licheng,[1] Yang Junhe[2]

[1]Unilab, State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China
[2]Department of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 200235, China

ABSTRACT: Acrylonitrile (AN) was polymerized in the presence of poly(methyl methacrylate) (PMMA) seed latex by both the batch and dropwise addition modes. The two addition modes both led to PMMA/polyacrylonitrile (PAN) composite particles with a core/shell structure with PMMA as the core and PAN as the shell. The shell thickness could be adjusted by a change in the amount of the second-stage AN monomer relative to the PMMA seed polymer. However, the surface morphologies of the composite polymers were quite different, which showed a rambutan-like batch mode and an urchinlike dropwise mode. The reason was considered as the different precipitation mechanisms of PAN small-particle precipitation for the batch mode and linear PAN segment growth for the dropwise mode. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 112: 410–415, 2009

Key words: composites; core-shell polymers; emulsion polymerization; morphology

INTRODUCTION

Because of their specially defined morphology, core/shell polymer particles usually have different and, in many cases, more desirable properties than composite polymers with other morphologies. Recently, some articles have reported a novel process for the fabrication of carbon nanostructured materials of carbon nanocapsules and carbon nanotubes by the treatment of core/shell polymers at high temperatures.[1–5] This method uses the different thermal properties of core and shell polymers: the core polymer is thermally decomposable, and the shell polymer is a carbon precursor. Poly(methyl methacrylate) (PMMA)/polyacrylonitrile (PAN) core/shell polymers are one of these kinds of polymers. By properly spinning PMMA/PAN core/shell polymers to fibers and then thermally processing the fibers at high temperatures, the special material of carbon nanotubes have been prepared.[4,5] This article concerns the preparation of polymer particles with a PMMA core and PAN shell by the polymerization of acrylonitrile (AN) in the presence of PMMA seed particles.

For the aforementioned method of the preparation of carbon nanostructured materials, the preparation of composite polymers with a strict core/shell morphology with a thermally decomposable polymer as the core and a carbon precursor polymer as the shell is essential. Any other possible morphologies of the composite polymers, such as hemispherical, particles with various fragmented inclusions, or inverted core–shell morphologies, are of no use to the end product. Composite polymers are usually prepared by two steps of consecutive emulsion polymerization sequences with different monomer types, where the first stage monomer (or monomers) is polymerized (copolymerized) as a seed polymer (copolymer), and then the second stage monomer (monomers) is polymerized (copolymerized) at the presence of the seed latex particles. It is well known that a wide morphology of the as-prepared composite latex can be obtained and that the particle morphology is controlled by both thermodynamic and kinetic factors.[6] The thermodynamic factors determine the

TABLE I
Recipes for the Preparation of the Latex

Symbol	Water (mL)	PMMA latex (mL)	MMA (mL)	AN (mL)	KPS (mg)	Feed rate (mL/h)
PMMA	300		10		10	Batch
PMMA/PAN-b8	100	150		8	60	Batch
PMMA/PAN-s6	100	150		6	60	3
PMMA/PAN-s8	100	150		8	60	4
PMMA/PAN-s10	100	150		10	60	5

equilibrium morphology of the final composite particle, whereas the kinetic factors determine the temporary and nonequilibrium morphology. For a definite reaction system, the equilibrium morphology is usually certain; however, the final morphology is often not the equilibrium but the nonequilibrium morphology. This situation implies that the kinetic factors are crucial for a definite system in the determination of the different final morphologies.

Among the kinetic factors, the mode of monomer addition (batch and semicontinuous) for second-stage polymerization can greatly affect the particle morphology. In the batch mode of monomer addition, all of the second-stage monomer is added to the first-stage particles at the beginning of the polymerization. In a semicontinuous (semibatch or starved dropwise) polymerization, the second-stage monomers are added continuously to the seed latex at a controlled feed rate. The critical influence of the monomer feed mode and the monomer feed rate on particle morphology has been reported in many articles.[7–11] As shown in the previous studies, a variety of morphologies may appear if only the addition method of the second-stage monomer is different.

In literature, PMMA/PAN polymers were prepared only by the batch addition mode for the second monomer.[4,12] The authors both obtained composite particles with a core/shell structure; however, the surface morphologies were different. One was smooth, and another was rambutan-like. The reason was the addition amount of AN monomer.[12] Here, we report on PMMA/PAN particles prepared by both the batch and dropwise addition mode of the AN monomer. The goal was to determine whether there was any difference in the morphologies of the obtained composite polymers. As we show, different surface morphologies were obtained with different addition modes of the AN monomer.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was provided by China National Pharmaceutical Group Corp. (Shanghai, China). The MMA was purified and neutralized with 5 wt % sodium hydroxide aqueous solution, washed with deionized water, and then passed through a column filled with active neutral aluminum oxide. AN was provided by Shanghai Guanghua Technology Corp. (Shanghai, China) and was freed of inhibitor by distillation. Potassium persulfate (KPS) as the initiator was also provided by China National Pharmaceutical Group and was used as received. All of the water used was deionized water.

Equipment

All reactions were carried out in a four-necked, round-bottom, 500-mL flask that was equipped with a stirrer, a reflux condenser, a thermometer, and a nitrogen entrance. The reflux condenser also acted as the nitrogen exit.

PMMA seed latex preparation

The PMMA seed latex was prepared by emulsifier-free emulsion polymerization by batch mode at 75°C. The reaction conditions are listed in Table I. MMA and most of the water were charged into the flask and stirred extensively. Nitrogen was introduced to remove air. When the temperature was reached, KPS dissolved in the rest of the water was injected. The reaction was continued for 4 h and then finished.

Polymerization of the PMMA/PAN latex

The PMMA/PAN composite latex was prepared by the methods of both batch and dropwise emulsifier-free seeded emulsion polymerizations at 70°C under the conditions listed in Table I. For batch mode, PMMA latex was first mixed with AN monomer and most of the water. Nitrogen was introduced to remove air. When the temperature reached a determined point, KPS dissolved in the rest of the water was injected. The reaction was continued for 4 h and then finished. For dropwise mode, AN was dropped into the solution at a constant rate. After AN was dropped over, the reaction was continued for 2 h and then finished.

Characterization

The PMMA latex and PMMA/PAN latex were diluted to appropriate concentrations, dropped and

dried on carbon-coated copper grids, and then directly observed by scanning electron microscopy (SEM; Quanta, 200F, 20 kV, Holland) and transmission electron microscopy (TEM; JEM, 2100, 200 kV, Japan). After freeze drying, the resulting PMMA and PMMA/PAN powders were characterized by X-ray photoelectron spectroscopy (XPS; PerkinElmer PHI 5000C, USA).

RESULTS AND DISCUSSION

Surface morphology

The morphologies of the PMMA and PMMA/PAN prepared by the batch mode and dropwise mode are illustrated by SEM in Figure 1. Figure 1(a) shows that the PMMA microspheres used as the seed particles were uniform, round, and surface-smooth, with diameters varying between 200 and 210 nm. For the preparation of PMMA in water initiated by KPS, MMA was, to some extent, water-soluble; the monomers polymerized in the aqueous phase to oligomeric radicals with sulfate end groups. When the oligomeric chains grew to a critical length, they precipitated from aqueous solution and formed polymer particles. The sulfate groups of KPS were surface-active and could form micelles in the polymerization, so KPS served as not only as an initiator but also as a stabilizer.[13] This enabled PMMA to form monodisperse, stable polymer particles with a smooth surface. Figure 1(b,c) shows the PMMA/PAN composite polymers prepared by the second monomer batch and dropwise addition modes, respectively. The two kinds of polymers both had an increased particle diameter of about 250 nm and an unsmooth, anomalous surface morphology. The surface of PMMA/PAN-b8 particles prepared by the batch monomer addition mode here looked like many small precipitated PAN particles adhered and coated on the outer surface of the core polymer, which was similar to that reported by Shi et al.,[12] who did a series of experiments and nominated the morphology as anomalous of rambutan-like. The edges of the PAN particles here were not as distinct as that of the reference; the reason may be the direct examination by SEM without any sputter coating of gold. However, this does not damage our conviction of their consistency. According to Figure 1(c), on the surface of the PMMA/PAN-s8 particles prepared by the dropwise monomer addition mode, no small PAN particles were found; the surface of PMMA/PAN-s8 was more flocky than that of PMMA/PAN-b8 and looked like many linear PAN fragments grown and coated on the outer surface of the PMMA.

Figure 2 shows the TEM photographs of the PMMA and the PMMA/PAN prepared with the
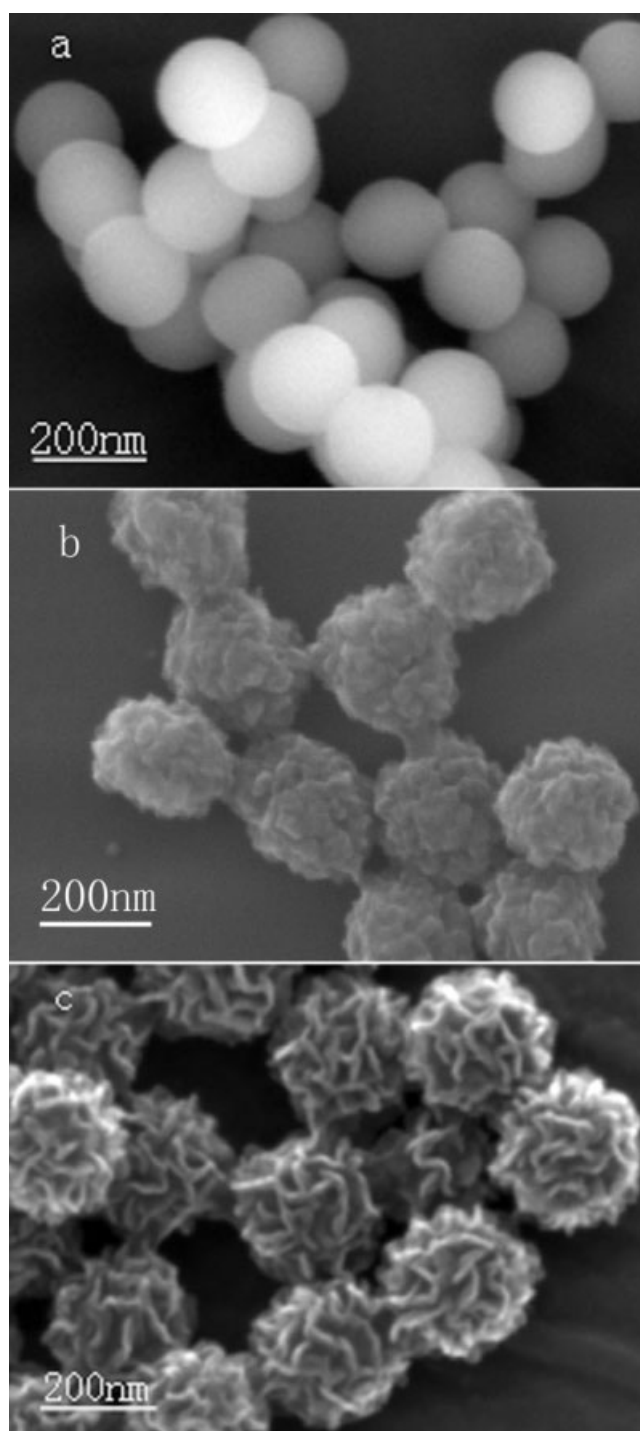
Figure 1 SEM images of polymerized microspheres: (a) PMMA, (b) PMMA/PAN-b8, and (c) PMMA/PAN-s8.

batch mode and dropwise mode. The images further identified the diameter increase of the PMMA/PAN from PMMA and the different morphologies between PMMA/PAN-b8 and PMMA/PAN-s8. Under TEM observation, the PMMA/PAN-s8 particles had many thorns extending out and had a morphology like an urchin. However, for the
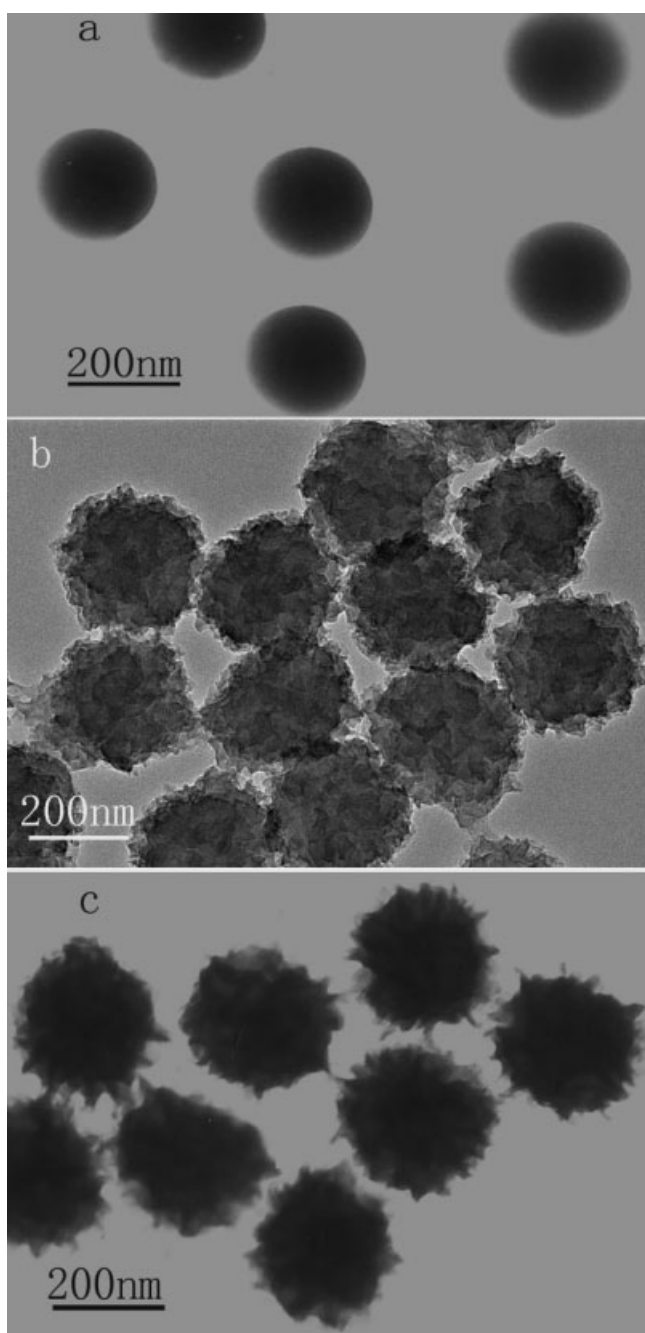
Figure 2 TEM micrographs of polymer latex: (a) PMMA, (b) PMMA/PAN-b8, and (c) PMMA/PAN-s8.

PMMA/PAN-b8 particles, the extensions were only small particles, and no linear thorns were found.

Because of these observations, for the emulsifier-free emulsion polymerization of AN in the presence of PMMA seed particles, the addition mode of AN had a great influence on surface morphology. The batch mode led to small PAN particles adhering to PMMA particles, whereas the dropwise mode led to PAN growing as linear segments on the surface of the seed particles. This may be explained by the for-

mation mechanism. For the batch mode, when AN monomers were charged into the reaction flask and mixed with seed latex, as highly water-soluble monomers, all of the monomers were present in the aqueous phase. Because the polymerization rate of AN was fast and PAN had zero cosolubility with both the AN monomer and water, PAN created many oligomers, which grew to a critical chain length, collided with each other, collapsed to globular structures, and then precipitated to the surfaces of the seed particles. For the dropwise mode, AN monomers were dropped to the reaction flask, the amount of AN monomers in the reaction solution was very small, and so the amount of polymerized PAN oligomers. The growing oligomers of PAN had little chance to collide with each other to form small PAN particles but had more chances to collide with seed particles and precipitated on their surfaces when they obtained a critical chain length. So it was possible that PAN first precipitated as a chain and then continued to grow. For the emulsifier-free seeded polymerization of AN, the crystalline nature of PAN led to a highly unsmooth surface morphology, and the zero cosolubility of PAN with water and AN led to a great influence of the addition mode on the PAN growing mechanism on the seed polymer surface.
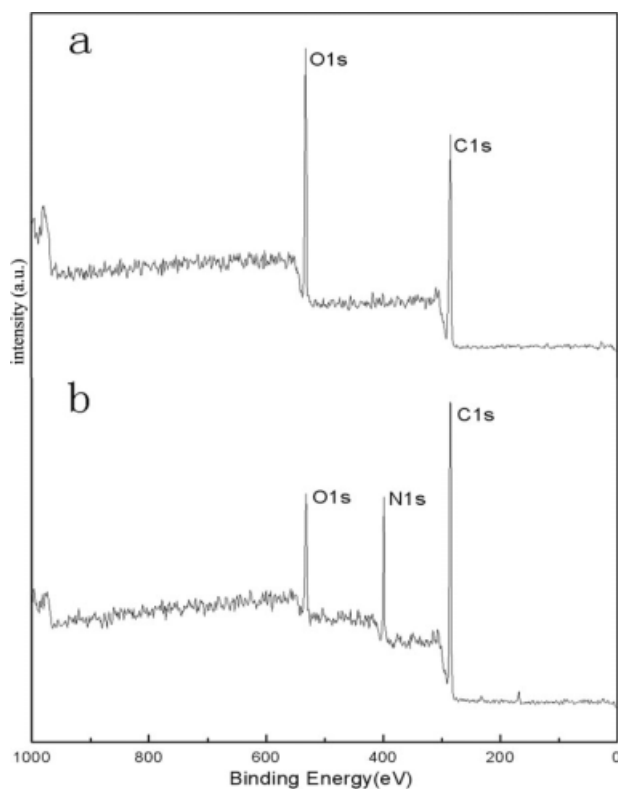
Identifying the core–shell structure

As previously said, the main aim of the preparation of the PMMA/PAN composite particles was to fabricate carbon nanostructured materials with a strict core/shell structure, with PMMA as the core and PAN as the shell being essential. Further characterizations were made to justify whether PAN was on the surface of the PMMA particles. Shi et al.[12] used TEM of ultrathin cross section and XPS to identify the core/shell structure of a series of PMMA/PAN particles prepared by batch mode. Here, we just provide the experiments of identifying the core/shell morphology of the PMMA/PAN particles prepared by the dropwise mode. Because PMMA and PAN did not have light contrast with each other under TEM observation, direct observation could not show the difference between PMMA and PAN. The solvent extraction method was used to remove the core polymers from the core/shell composite materials.[14] Here, excess tetrahydrofuran was charged into PMMA/PAN-s8 latex as an extraction solvent to remove PMMA. After a long period of extensive stirring, the solution was dropped and dried on carbon-coated copper grids for TEM observation. As shown in Figure 3, after the removal of PMMA, hollow PAN particles remained, which illustrated that PMMA was really the core and PAN was coated on the outer surface of the PMMA particles. The hollow
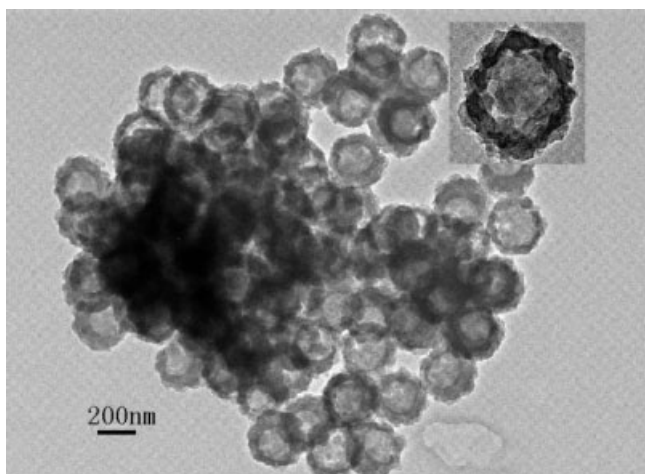
Figure 3 TEM micrograph of PMMA/PAN-s8 latex after extraction.

PAN did not show an urchinlike morphology; the reason may have been that the PMMA dissolved in the solution precipitated on the surface of the PAN after the drying of the latex on the copper grids.

XPS characterization was also done for PMMA and PMMA/PAN-s8 particles after freeze drying. As shown in Figure 4, N atoms originating from the PAN molecules appeared for the outermost layer of the PMMA/PAN-s8 particles. The intense increase

in N atoms and decrease in O atoms for the PMMA/PAN-s8 particles compared to that of the PMMA particles illustrated that PAN was located at the outer particle surface. The weight content of PMMA was calculated to be about 80% by the assumption that the C, N, and O atoms only originated from the PAN and PMMA molecules.

Influence of the amount of AN

Shi et al.[12] reported that their prepared composite particle size increased with increasing AN amount for the batch mode polymerization during the second stage. The same phenomenon was found for the dropwise mode polymerization. According to Figures 1(c) and 5(a,b), the particle size of the resulting polymers increased from 220 to 280 nm with increasing amount of AN monomers. For PMMA/PAN-s6, with a low AN amount relative to the PMMA polymer, the size of the linear PAN fragments was small, whereas for PMMA/PAN-s10, with a high amount of AN monomers, the size of the linear PAN fragments was large, and the anomalous morphology was further developed.

Figure 4 XPS spectra of (a) PMMA and (b) PMMA/PAN-s8 powders.
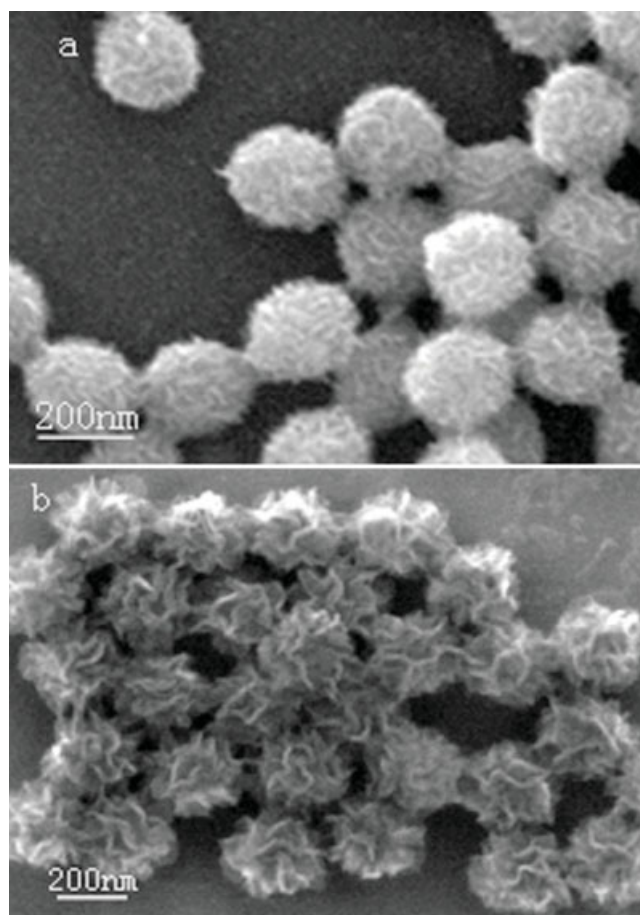
Figure 5 Micrographs of (a) PMMA/PAN-s6 and (b) PMMA/PAN-s10 latex particles.

CONCLUSIONS

For the emulsifier-free polymerization of AN in the presence of PMMA seed particles, the batch and dropwise addition modes had no visible effect on the core/shell structure of the resulted composite particles with PMMA as the core and PAN as the shell. By changing the AN monomer amount, we could adjust the shell thickness of PAN to a different size. However, different addition modes of the AN monomers had a great influence on the surface morphology of the resulting particles. Batch mode led to a rambutan-like morphology and the dropwise mode led to an urchinlike surface morphology of the PMMA/PAN polymers. The reason was considered to be the different polymerization mechanisms of the PAN small-particle precipitation for the batch mode and the linear PAN segment growth for the dropwise mode. When they are used to fabricate carbon nanostructured materials, the different surface morphologies may affect the interconnections of the resulting products, which will be discussed elsewhere.

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