Amphiphilic Particles with Hydrophilic Core/Hydrophobic Shell Prepared via Inverted Emulsions

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SYNOPSIS

An aqueous solution of acrylamide, its crosslinker (N,N'-methylenebisacrylamide), and an oxidant (ammonium persulfate) was first used to prepare an inverted concentrated emulsion in hexane. Span 80, which is soluble in hexane, was employed as a dispersant. The polymerization of acrylamide in the concentrated emulsion was greatly accelerated by introducing an aqueous solution of a reductant (sodium metabisulfite); it started at room temperature and was completed in a few seconds, resulting in a pastelike product. The system thus obtained was subsequently diluted with hexane containing a hydrophobic monomer. When styrene was used as the hydrophobic monomer, cumene hydroperoxide (which, together with sodium metabisulfite present in the dispersed phase, constitutes the initiator for the polymerization of styrene) was dissolved in the continuous phase. When vinylidene chloride was employed as the hydrophobic monomer, no additional initiator besides sodium metabisulfite and ammonium persulfate already present in the hydrophilic phase had to be employed. The use of initiators which are present only in the hydrophilic phase, and hence also at the interface between this phase and hexane, ensured the polymerization of the hydrophobic monomer as shells that encapsulate the polyacrylamide latexes. Under the proper conditions, a porous outer shell can be generated, which makes the hydrophilic chains present inside accessible. Such hydrophilic core/hydrophobic porous shell particles can be dispersed in water, where they remain stable for a long time, and in hydrophobic liquids, where they remain stable for at least 24 h. For this reason, we call these kinds of particles amphiphilic particles. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

New materials can be produced by combining two different polymers. The greater the difference between the two polymers, the more likely synergistic properties will result from the combination. For this reason, the combination of a hydrophilic and a hydrophobic polymer has received attention in recent years. The combination of hydrophilic and hydrophobic polymers can be achieved via block, graft, or random copolymerization[1-3]; interpenetrating or semi-interpenetrating networks[4,5]; and hydrophilic–hydrophobic composites based on concentrated emulsions[6] or colloidal pathways.[7] Since both hy-

drophilic and hydrophobic chains or domains are associated in such materials, amphiphilicity can be achieved, which can find wide applications in membrane separation,[8] controlled release,[9] drug delivery,[10,11] etc. It was reported[12] that a remarkable amphiphilicity can be achieved by preparing hydrophilic core/hydrophobic shell particles. A hydrophilic core of poly(triethylvinyl benzylammonium chloride) (PEVAC) was encapsulated with a porous hydrophobic shell of polydivinyl benzene. The particles thus prepared have been used for the immobilization of catalysts and employed in some catalytic processes.[13] Hydrophilic core/hydrophobic shell particles have also been prepared by seeded emulsion polymerization in water, in which copolymers of methyl methacrylate and methacrylic acid were used as the hydrophilic core and polystyrene as the hydrophobic shell.[14,15] The goal was to achieve a complete and uniform encapsulation with a hy-

Table I   Preparation Conditions of the Samples

| Figure Number | Hydrophilic Phase[a] | | Coating Monomer | | | | |
	AAM (g)	MBA (g)	Hexane (g)	Styrene (g)	DVB (g)	VDC (g)	Coating Time (h)
1	2	0	3	0.5	0.5	—	8
2 (a)	2	0.1	No subsequent coating applied				
2 (b)	2	0.2	No subsequent coating applied				
3	2	0.1	3	—	—	3	8
4	2	0.1	0	1.0	1.0	—	8
5	2	0.1	3	1.0	1.0	—	8
6	2	0.1	6	1.0	1.0	—	8
7 (a)	2	0.1	3	1.5	1.5	—	8
7 (b)	2	0.1	3	0.5	0.5	—	8
8	2	0.1	3	1.0	1.0	—	4
9	2	0.1	3	—	—	1	8

[a] The hydrophilic phase contains also 2 g water and 0.06 g ammonium persulfate. After the concentrated emulsion was prepared, and aqueous solution of 0.06 g sodium metabisulfite in 0.5 g water was introduced.

drophobic shell of a hydrophilic core. As a result, the hydrophilic core was unaccessible.

In the present article, a novel, simple procedure to prepare hydrophilic core/hydrophobic shell particles via inverted emulsions is proposed. An aqueous solution of a hydrophilic monomer (acrylamide) and its crosslinker (N,N'-methylenebisacrylamide) con-

Figure 1   Particle morphology of a sample based on uncrosslinked polyacrylamide (see Table I).

taining ammonium persulfate as initiator was first used to prepare a concentrated emulsion in hexane. The polymerization of acrylamide in the concentrated emulsion generated a pastelike product. After it was diluted with hexane containing a hydrophobic monomer, the system became a suspension of water-swollen polymeric particles. Depending on the nature of the hydrophobic monomer, either only the initiators used for the polymerization of acrylamide and present in the system could be employed, or another one had to be introduced in the hydrophobic phase. Since either all the initiators or some of them were present in the swollen particles (and hence also at the interface between the two phases), the polymerization of the hydrophobic monomer occurred on the surface of the polyacrylamide (PAAM) latexes. By selecting proper coating conditions, a porous shell structure could be achieved, which made the hydrophilic chains present inside accessible and thus ensured the amphiphilicity of the particles.

EXPERIMENTAL

Materials

Styrene (St, 99%), vinylidene chloride (VDC, 99%) and divinyl benzene (DVB, tech, 80%) were filtered through an inhibitor removal column before use. Acrylamide (AAM, 99%), N,N'-methylenebisacrylamide (MBA, 99%), hexane (95%), ammonium persulfate (APS, >98%), sodium metabisulfite (SMBS, >97%), cumene hydroperoxide (CHPO, tech, 80%),
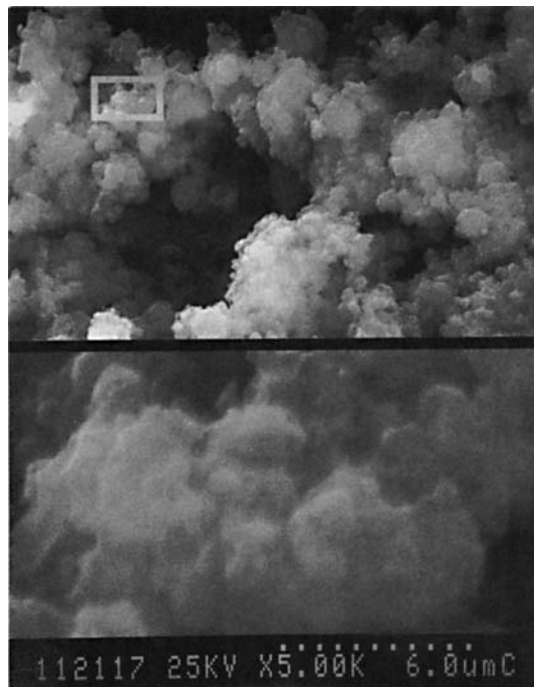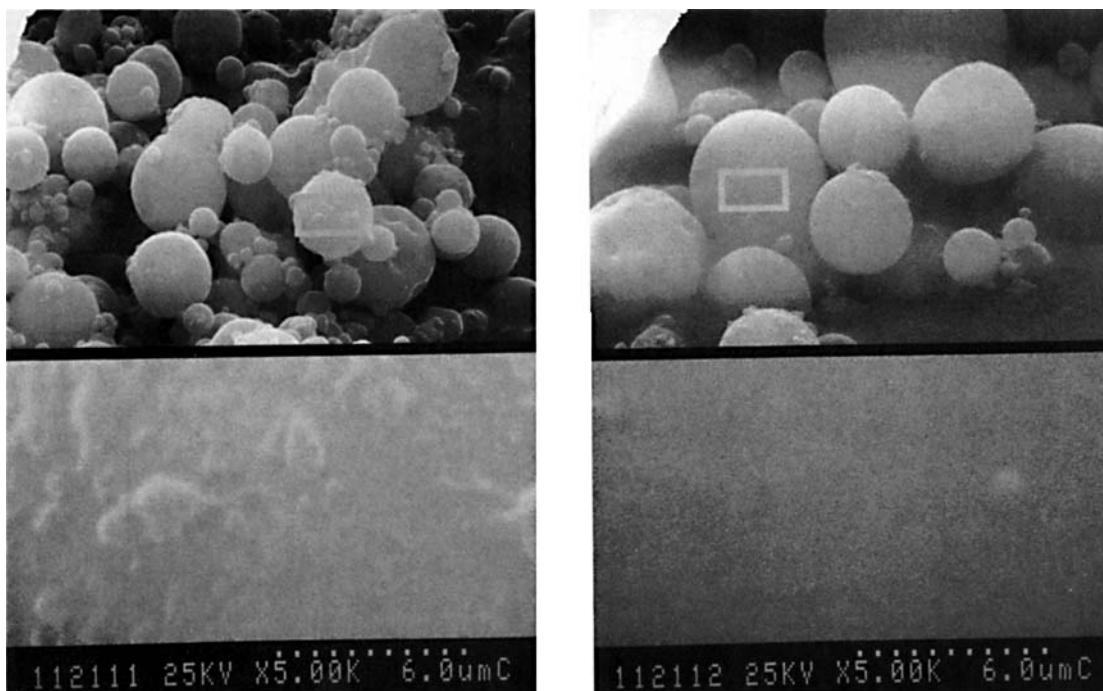
Figure 2 Particle morphologies of polyacrylamide latexes. AAM/MBS weight ratio: (a) 100/5; (b) 100/10 (see Table I).

and sorbitan monooleate (Span 80) were used as received. All chemicals were purchased from Aldrich, except Span 80, which was purchased from Fisher. Water was distilled and deionized.

Preparation Procedure

A flask containing a magnetic stirring bar was sealed with a rubber septum and kept in an ice bath below 5°C. The air inside was replaced with nitrogen. Hexane (containing 0.1 g/g Span 80), which constitutes the continuous phase of a concentrated emulsion, was introduced into the flask through the rubber with a syringe (when amounts smaller than 0.1 g/g of Span 80 were used, the emulsion became unstable). The dispersed phase, an aqueous solution of AAM, MBA, and an oxidant (APS), was subsequently introduced dropwise with stirring, until its volume fraction became 0.8. After the concentrated emulsion was formed, an aqueous solution of a reductant (SMBS) was injected into the flask. After the reductant solution was uniformly dispersed, the flask was removed from the ice bath. The polymerization of AAM started at room temperature and was completed in a few seconds. The pastelike product obtained was washed with methanol and dried in a vacuum oven until constant weight. We found that the weight ratio of the polyacrylamide thus

obtained to the acrylamide monomer was always higher than 0.95; hence the polymerization of acrylamide in the concentrated emulsion was almost complete. After the paste was diluted with hexane, either VDC or a mixture of St, its crosslinker DVB, and another oxidant (CHPO) was added. The flask was then introduced into a thermostated water bath at 30°C for VDC or 60°C for St, for various lengths of time (4, 6, and 8 h), to allow the polymerization of the hydrophobic monomer to occur on the surface of the PAAM latexes. The product thus obtained was washed with methanol and dried in a vacuum oven.

Scanning Electron Microscopy (SEM)

A small amount of the powder sample was glued on a SEM holder and then coated with a thin film of gold. The surface morphology was examined by SEM (Hitachi S-800).

Elemental Analysis

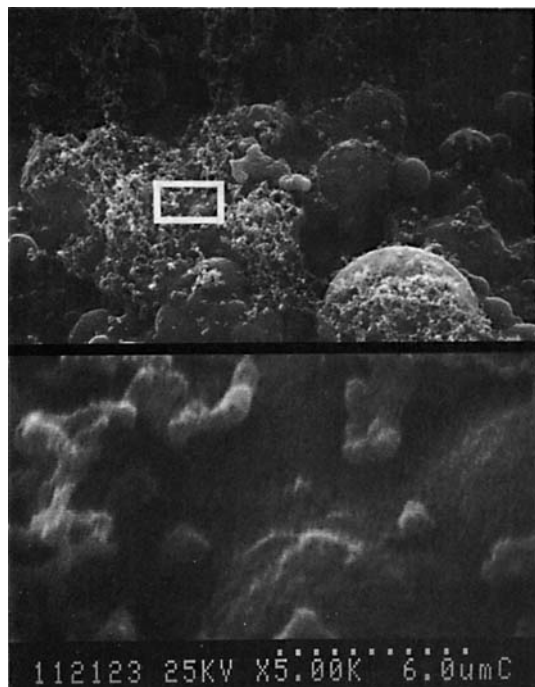Elemental analysis was performed by Quantitative Technologies Inc., Whitehouse, NJ.

Figure 3 Particle morphology of a sample possessing a netlike PVDC coating (see Table I).

RESULTS AND DISCUSSION

Various preparation conditions were employed; they are listed in Table I. In the present article, PAAM latexes were prepared mainly via the concentrated emulsion method.[6,16] A concentrated emulsion differs from the conventional emulsion in that the volume fraction ϕ of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangements of monosize spheres). The volume fraction ϕ = 0.8 was employed. Inverted emulsions with a lower ϕ were also tried. We found that the greater the volume fraction of the continuous phase (hexane), the slower the polymerization rate. When ϕ was between 0.5 and 0.7, more than 1 h was necessary to complete the polymerization of AAM. When ϕ was lower than 0.4, the polymerization lasted as long as 48 h. When the volume fraction of the dispersed phase was in the concentrated emulsion range, the polymerization took place almost instantaneously.

In the range of concentrations employed, the monomer concentration in the dispersed phase (aqueous solution of AAM, MBA, and oxidant) had no detectable effect on the polymerization rate. Different monomer/water weight ratios—1/1, 1/1.5, 1/2, and 1/4—were employed, and almost the same polymerization rate was observed. To remove the

water easily after the reaction was completed, a ratio of 1/1 was selected. When the monomer/water weight ratio was greater than 1/1, the subsequent dilution of the polymerized concentrated emulsion with hexane and hydrophobic monomer became difficult because of its high viscosity.

The initiator had an important effect on the polymerization rate. AAM could be polymerized using only APS as an initiator. However, the addition of a reductant (SMBS) greatly accelerated the polymerization. In our experiments, a concentrated emulsion based on APS alone completed the polymerization of AAM in 8 h at room temperature. If an aqueous solution of SMBS was added to the concentrated emulsion, the polymerization was finished almost instantaneously. However, the reductant could not be introduced together with the oxidant before the concentrated emulsion was prepared, because the monomer would have polymerized immediately.

To obtain individual latexes, a suitable crosslinking of the PAAM was necessary. Indeed, if not properly crosslinked, the latexes formed lumps, and, as shown in Figure 1, the hydrophobic polymer could coat in the subsequent stage only the surface of the lumps and not those of the latexes. The particle morphologies of Figure 2 are based on AAM/MBA weight ratios of 100/5 and 100/10, respectively (see
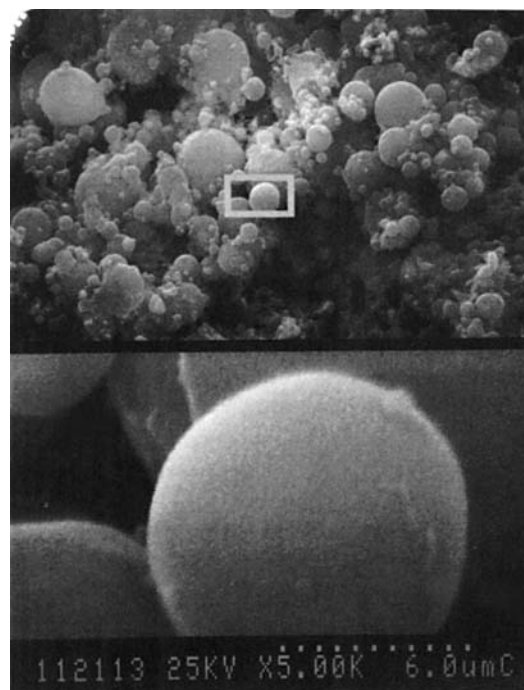

Figure 4 Particle morphology of polyacrylamide/polystyrene in the absence of hexane (see Table I).
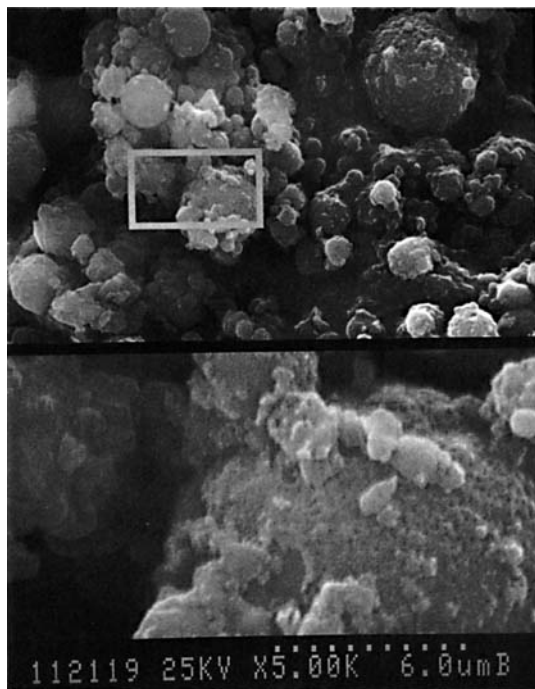
Figure 5 Particle morphology of a sample possessing a netlike PS coating (see Table I).

Table I for other details) and show that individual particles were obtained in both cases. The particles based on an AAM/MBA weight ratio of 100/10 are larger and possess a smoother surface than those based on 100/5. Most of the samples in the present study were prepared with an AAM/MBA weight ratio of 100/5.

With a 100/5 AAM/MBA weight ratio, individual particles were obtained only via the concentrated emulsion pathway. In diluted emulsions, the particles would still stick to one another to some extent. This occurs because in a dilute emulsion, the stirring stimulates the collisions among the polymerizing particles. However, in the case of a concentrated emulsion, the thin films between the particles are not strongly affected by the stirring and the particles maintain their individuality.

After the prepared PAAM latexes were diluted with hexane, a hydrophobic monomer was added to the system. Two monomers were employed—namely, VDC or St (the latter containing a cross-linker, DVB). For the systems based on VDC, no additional initiator besides those soluble only in water and used for the polymerization of AAM (APS and SMBS) were needed. The VDC polymerization is initiated on the surface of the PAAM particles because the initiator is present in the hydrophilic phase. For the systems involving St, the aforemen-

tioned redox pair had to be strengthened with an additional oxidant, CHPO, which (being hydrophobic) was dissolved in the oil phase. Since the polymerization of styrene is initiated by CHPO and SMBS together, but by neither of them individually, the polymerization is initiated on the latex surface.

After the polymerization of the monomer was initiated on the surface of the PAAM particles, the polymer molecules could either grow there *in situ* or in the oil phase, near the place where they were initiated. Since both the monomer and the continuous medium are hydrophobic, the latter is more likely to occur. The growing polymer molecules will remain in the oil phase until the latter can no longer dissolve or swell them because of their increasing molecular weight, degree of crosslinking, or crystallinity. Then the hydrophobic polymer will precipitate on the surface of the PAAM latexes as tiny particles, and thus shells with holes will be generated. A poly(vinylidene chloride) (PVDC) coated sample is presented in Figure 3. One can see that the sample is coated with a clear, netlike PVDC structure. Because the VDC homopolymer is crystalline and insoluble in both its monomer and in hexane, the PVDC chains are readily precipitated as small crystallites.

For the samples based on styrene, the solubility of polystyrene (PS) in the oil phase plays an even
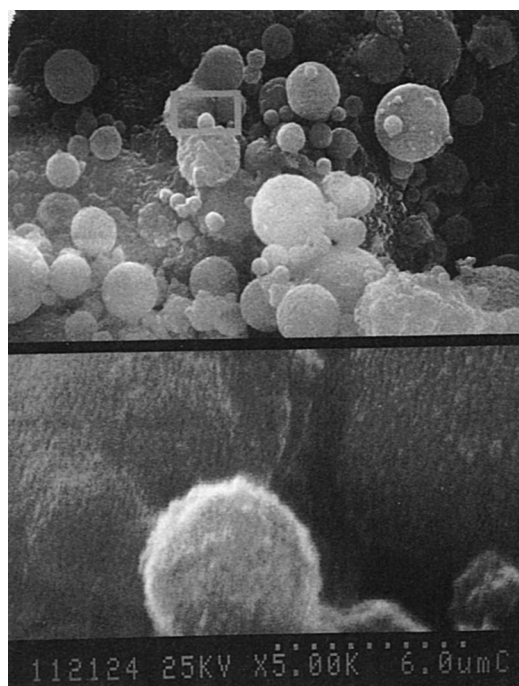

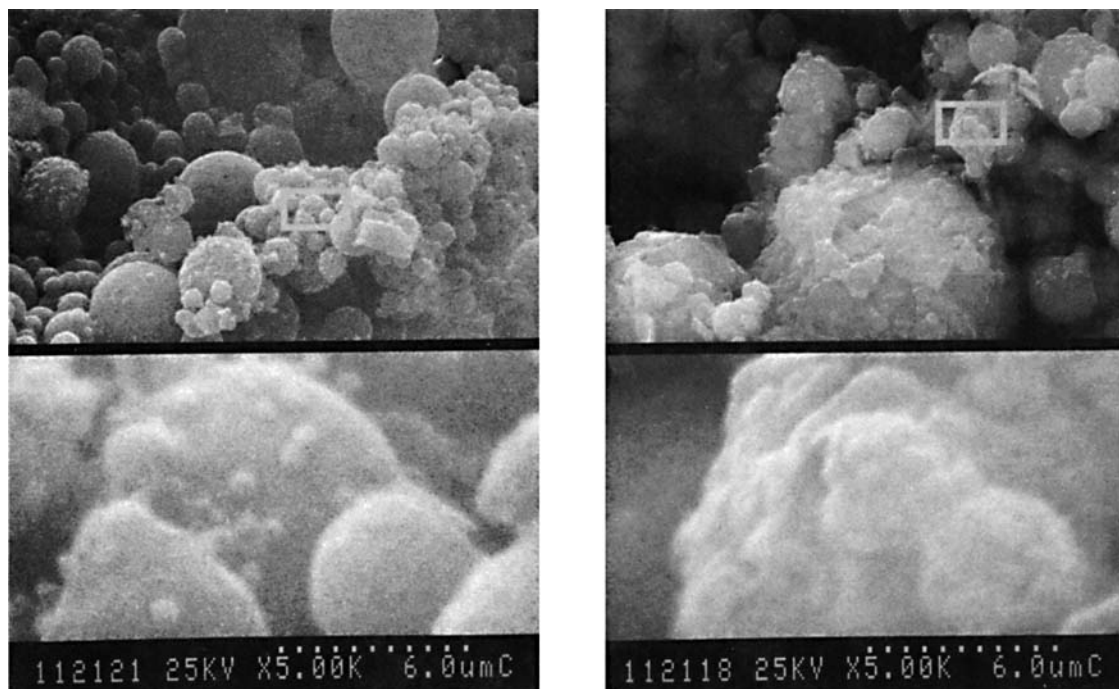**Figure 6** Particle morphology of a sample obtained with a large amount of hexane (see Table I).

Figure 7 Particle morphologies of samples with different monomer concentrations. PAAM/hexane/St/DVB weight ratio: (a) 2/3/1.5/1.5; (b) 2/3/0.5/0.5 (see Table I).

more important role than for PVDC, because both styrene and DVB dissolve or swell the polymer. In a system diluted only with styrene and DVB, the crosslinked PS, dispersed in the hydrophobic phase, aggregated to form individual particles which did not deposit on the surface of the PAAM latexes (Fig. 4). The addition of a large proportion of hexane (which is a solvent for styrene and DVB monomers, but a nonsolvent for PS) in the oil phase reduces the solubility of PS in the latter, and for this reason tiny PS particles are deposited on the surface of PAAM latexes. In a system in which the PAAM/hexane/St/DVB weight ratios were 2/3/1/1, the coating was composed of a large number of tiny particles loosely packed and having holes, as shown in Figure 5. When an even larger amount of hexane was employed (i.e., for PAAM/hexane/St/DVB weight ratios of 2/6/1/1; Fig. 6), the coating consisted of even smaller particles, more uniformly distributed.

Consequently, there are conditions under which a netlike coating can be achieved, which allows the hydrophilic core to be accessible to a hydrophilic medium. The particles of Figure 5 could be dispersed easily both in water, where they remained stable for a long time, and in hydrophobic media, where they remained stable for at least 24 h; for this reason they can be called amphiphilic particles.

When the amphiphilic particles with PAAM core/PS shell were dispersed in water, the PAAM cores had swollen and became semitransparent. The unswollen hydrophobic shells had the appearance of a large number of white spots scattered in the suspension. When the particles were dispersed in toluene, the thin, swollen PS shell could not ensure a stability as high as that in water. However, when the outer shell completely encapsulated the core, as in Figure 6, the particles could be dispersed in toluene but not in water.

Figure 7 shows that the thickness of the coating layer varies dramatically with the monomer concentration. The samples in Figure 7(a,b) were prepared with PAAM/hexane/St/DVB weight ratios of 2/3/0.5/0.5 and 2/3/1.5/1.5, respectively. The latexes in Figure 7(a) are only partially covered with a thin PS layer, and those in Figure 7(b) are completely covered with a thick layer. Although the same amount of monomer was used for the samples of Figures 5 and 6, the coating is thinner in Figure 6, because the monomer in the continuous phase was diluted with a double amount of hexane.

The coating time (the time used for the polymerization of the hydrophobic monomer) is also important. The sample in Figure 8 was coated under the same conditions as that in Figure 5, but
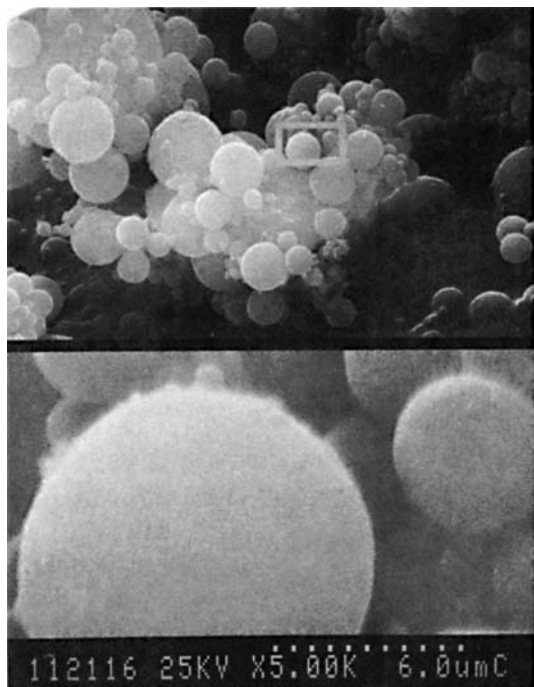
Figure 8 Particle morphology of a sample obtained after a short coating time (see Table I).
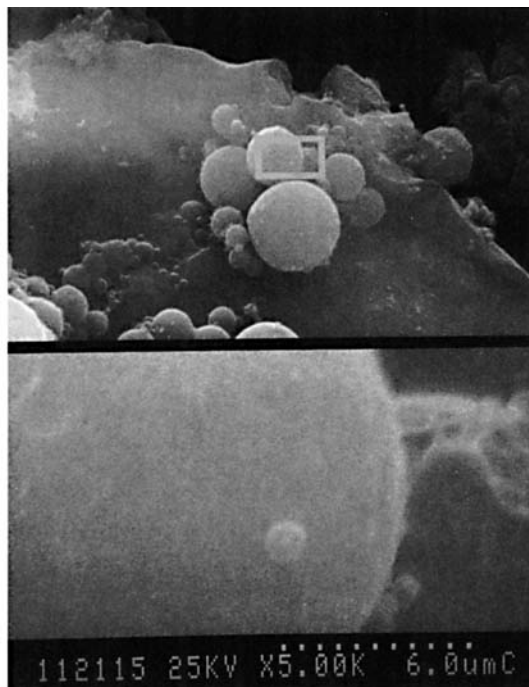

Figure 9 Particle morphology of a sample obtained with a low concentration of VDC (see Table I).

for a shorter polymerization time (4 vs. 8 h); therefore, the coating layer has only a moderate thickness.

In the case of VDC, the effects of monomer concentration and coating time were as in the previous case. The samples in Figures 3 and 9 were prepared with PAAM/hexane/VDC weight ratios of 2/3/3 and 2/3/1, respectively. In Figure 3, the PVDC shell has a netlike structure; in contrast, in Figure 9, only a few netlike domains can be identified. The effect of the coating time on the PVDC coating is reflected in the results of the elemental analysis, which are presented in Table II (which shows that the longer the coating time, the higher the Cl wt % in the samples).

CONCLUSION

Hydrophilic core/hydrophobic shell particles were prepared via an inverted emulsion method. Polyacrylamide latexes were first obtained, using a concentrated emulsion of acrylamide in hexane as precursor. Subsequently, hexane and a hydrophobic monomer were introduced into the polymerized concentrated emulsion, and the polyacrylamide latexes were coated, through surface-initiated polymerization, with a hydrophobic polymer. In proper conditions, tiny particles of hydrophobic polymer are present on the surface of polyacrylamide latexes as a netlike shell. The netlike structure of the outer shell makes the hydrophilic chains present inside accessible to the outside me-

Table II Elemental Analysis of Some Samples

Samples	AAM (g)	MBA (g)	Hexane (g)	VDC (g)	Coating Time (h)	N (Wt %)	Cl (Wt %)
a	2	0.1	3	1	8	15.73	1.92
b	2	0.1	3	1	6	15.71	1.33
c	2	0.1	3	1	4	15.90	1.12

dium. Because such particles can be compatible with both water and oil phases, we call them amphiphilic particles.

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