# Monodisperse Cross-Linked Core−Shell Polymer Microspheres by Precipitation Polymerization

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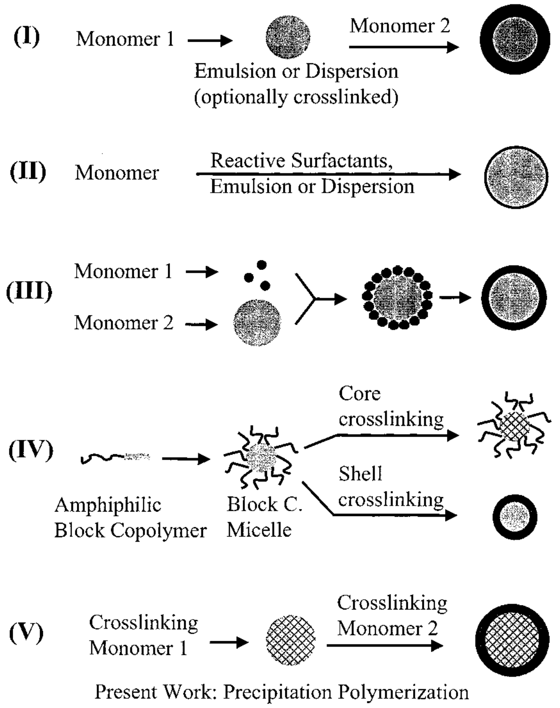
ABSTRACT: Monodisperse cross-linked core−shell polymer microspheres having diameters in the micrometer-size range were prepared by semibatch and by two-step precipitation polymerization in the absence of any stabilizer. Commercial divinylbenzenes, containing 55% or 80% divinylbenzene, were used for the core, and several functional monomers including chloromethylstyrene, monovinyl, or divinyl methacrylic monomers were incorporated into the shell. Acetonitrile and toluene/acetonitrile mixtures were used as reaction media. Depending on the type of monomer and reaction medium used, the shell could be made nonporous or porous. The particle size distribution, surface morphology, internal texture, and porosity of the resulting core−shell particles were studied. The chromatographic properties of selected particles were evaluated.

## Introduction

Core−shell heterogeneous composite polymer particles have attracted much attention since Hughes and Brown[1] first investigated their physical properties in 1961. The interesting morphology and designed surface properties of the core−shell particles have since led to numerous applications as impact modifiers, toughening agents, film aids, and as carriers and supports in the biomedical field.

Scheme 1 illustrates the common approaches to core−shell particles.

**Scheme 1**



Two-stage seeded emulsion polymerization (**I**) was the first general method developed to prepare latex particles having core−shell structure.[1−4] The first stage, or core latex preparation, was carried out either separately or in situ, and the mode of polymerization for the second stage was usually a seeded swelling batch or a semibatch process.

This process was used recently to prepare highly cross-linked latex particles.[5]

Core−shell latex particles can also be prepared by emulsion polymerization using reactive surfactants that are able to copolymerize with the monomers (**II**). The resulting copolymers typically end up as a thin shell on the surface of the particles.[6−9]

Several groups of authors reported the formation of core−shell particles by stepwise hetero-coagulation of smaller cationic polymer particles onto larger anionic polymer particles, followed by heat treatment at a temperature above the $T_g$ of the shell particles (**III**).[10−12] This method was said to give better control over certain types of composite particle morphology, as compared to the two-stage emulsion polymerizations. Core−shell particles with multilayer shells were also prepared by analogous electrostatic self-assembly strategies.[13,14]

Block copolymers can also be used to produce core−shell type polymer nanospheres (**IV**).

Ishizu's and Saito's group prepared core−shell type polymer nanospheres by cross-linking the segregated chains in the spherical microdomains of di- or triblock copolymer films[15] or micelles.[16] The core−shell type nanospheres synthesized by this method are composed of a cross-linked core, surrounded by a corona of shell chains attached with one end to the surface of the core. Core-polymerized micelles formed from diblock macromonomers carrying additional functional groups at their coronal terminus were described by Iijima et al.[17]

On the other hand, core−shell nanospheres with a cross-linked shell have been prepared by shell-cross-linking block copolymer micelles.[18,19]

The core−shell particles prepared by the methods mentioned above are all in the nanometer-size range. Similar particles in the micrometer-size range would be interesting as polymeric support materials in analytical, biomedical, and environmental applications.

Only a few reports in the literature describe polymer-based core−shell particles of micrometer-size. By use of a series of sequential seeded growth emulsion polymerizations, Rudin's group was able to prepare mono-

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disperse latex core−shell particles having diameters of 3 μm.[20] There are a few reports on core−shell particles prepared by dispersion polymerization: Laus et al.[21,22] formed monodisperse polystyrene particles of 2−10 μm in the presence of a polycarboxylic acid or polyepichlorohydrine steric stabilizer which itself then constitutes the shell. Okubo et al. conducted dispersion copolymerizations of chloromethylstyrene and styrene on polystyrene seeds which adsorbed the monomer mixture and yielded micrometer-size monodisperse polymer microspheres having chloromethyl groups in the shell.[23]

We have reported monodisperse cross-linked poly(DVB-55) microspheres having diameters of 2−8 μm prepared by precipitation polymerization in acetonitrile.[24] The use of functional comonomers including chloromethylstyrene,[25] maleic anhydride,[26] and methacrylates[27] led to the corresponding monodisperse copolymer microspheres, while the presence of a good cosolvent such as toluene led to the formation of porous microspheres.[28] In this paper, we describe the preparation of monodisperse cross-linked core−shell microspheres by precipitation polymerization, using both semibatch in situ and a two-step batch mode with core particles (**V**).

## Experimental Section

**Materials.** Divinylbenzene, 55% (DVB-55, technical grade, 55% divinylbenzene isomers), divinylbenzene, 80% (DVB-80, technical grade, 80% divinylbenzene isomers), ethylene glycol dimethacrylate (EGDMA), 3-chloromethylstyrene (CMS, 3-vinylbenzyl chloride, 70%, remainder *p*-isomer), and acetonitrile (HPLC grade) were purchased from Aldrich Chemical Co. *p*-Chloromethylstyrene (*p*-CMS, *p*-vinylbenzyl chloride) and 2,2′-azo-bis(2-methylpropionitrile) (AIBN) were obtained from Eastman Kodak Co. Toluene (Analytical Reagent grade) was received from BDH Inc. All the chemicals and solvents were used as received.

**Preparation of Monodisperse or Narrow Disperse Microspheres with Core−Shell Structure.** The apparatus used for the precipitation polymerization consists of a set of steel rollers in an insulated air chamber. The reaction vessels were placed on the rollers and rotated gently around their horizontal axes. A flexible heater pad is used along with a temperature controller to control the temperature in the air chamber during the course of polymerization. High-density polyethylene (HDPE) bottles ranging from 20 mL up to 2 L were used as reaction vessels.

Typically, the core and the shell portions of the particles were prepared in two successive reaction periods. In the first reaction period, the monomers for core (DVB-55 or DVB-80) were polymerized in neat acetonitrile to form the microspheres used as core particles. For the second reaction period, a comonomer together with AIBN, and/or a cosolvent, were introduced into the same reaction vessel, and the polymerization was allowed to resume in order to form the microsphere shells. The first reaction period could last from 4 to 24 h, depending on the size of the final particles and the core/shell ratio desired.

Alternatively, the core−shell particles were prepared by a separate precipitation polymerization using preformed, washed, and dried particles as core particles.

The typical monomer loadings, relative to the solvent, were 2−4 vol % and 1−2 vol % for the core and the shell portion preparations, respectively. Unless indicated otherwise, all experiments were carried out with an AIBN concentration of 2 wt % relative to the total monomer. The reaction medium was usually neat acetonitrile for the core preparation and either acetonitrile or toluene/acetonitrile mixtures for the shell preparation. For each reaction period, the temperature in the air chamber was ramped from room temperature to 70 °C in about 2 h and then kept at 70 °C for the desired time.

At the end of the reaction, the final particles were separated from the reaction medium, successively washed three times with tetrahydrofuran, acetone, and methanol and then dried under vacuum at 50 °C. Particle yields were determined by gravimetry.

**Characterization.** Particle size distributions were measured using a 256-channel Coulter Multisizer II with Isoton II as electrolyte. An orifice tube with an aperture of 50 μm was used for all the measurements reported here. The surface morphology of the particles was studied with an ISI DC-130 scanning electron microscope. The internal texture of the particles was studied using a JEOL 1200EX transmission electron microscope.

Pore volume, pore size distribution, and specific surface area of the particles were measured with a QUANTACHROME AUTOSORB-1 automated gas adsorption system using nitrogen at 77 K as an adsorbate.

**Column Packing and Chromatography.** Two batches of poly(DVB-55) core−shell particles with the shell prepared in a toluene/acetonitrile mixture were slurry-packed into stainless steel columns (4.6 mm i.d. and 250 mm in length) using a SHANDON HPLC Packing Pump at a constant pressure of 1600 psi. Another batch of bulk porous poly(DVB-55) particles prepared in the same toluene/acetonitrile mixture was also packed into a column in order to compare their chromatographic properties.

Column evaluations were carried out using a Waters model 590 programmable solvent delivery module with a model 441 UV/vis spectrophotometer detector operating at 214 nm. Tetrahydrofuran was used as mobile phase at a flow rate of 0.35 mL/min. Toluene, 1,2-diphenylethane, and narrow dispersed polystyrene standards with molecular weights of 580 (Polymer Laboratories) were used to test the chromatographic properties of the columns.

## Results and Discussion

A key requirement to form monodisperse microspheres by precipitation polymerization is that one of the comonomers must be a cross-linker such as divinylbenzene.[24,29] Poly(DVB-55) and poly(DVB-80) particles prepared by precipitation polymerization are highly cross-linked and, therefore, hardly swell even in good solvents. Hence, core−shell particles cannot be formed strictly by swelling these cross-linked particles with monomers and subsequently polymerizing these into a shell. On the other hand, it was confirmed by bromine addition that poly(DVB-55) particles prepared by precipitation polymerization contain more residual double bonds, as compared to the poly(DVB-55) particles prepared by conventional suspension polymerization. This is due to the poorer solvent medium and the much lower monomer concentration used in precipitation polymerizations. Those of the residual double bonds located at the surface permit the further growth of the particle by radical capture of oligomers and monomers.[29] Accordingly, addition of different comonomers during the polymerization could then lead to designed core−shell microspheres.

An important concern for such core−shell polymerizations would be to retain the particle monodispersity, and prevent secondary particle initiation. We had earlier carried out semibatch experiments to form larger poly(DVB-55) particles by precipitation polymerization with an additional supplement of DVB-55 monomer and AIBN initiator added at the end of the first period of reaction (24 h). The results showed that the particles continued to grow in the next 24 h while remaining size monodisperse.[30] We were hence interested in testing if monodisperse cross-linked core−shell particles could be prepared by precipitation polymerization, wherein ei-

**Table 1. Formation of Porous Shells on Preformed, Nonporous Core Particles**

| | core particles | | shell preparation[a] | | final particles | | porosity analysis | |
|---|---|---|---|---|---|---|---|---|
| run ID | size, $\mu$m | weight, g | core particles:monomer for shell w:w | toluene:acetonitrile v:v | size, $\mu$m | core:shell v:v | pore volume, cm$^3$/g | surface area, m$^2$/g |
| PP88−02[b] | 2.4 | 0.276 | 1:2 | 30:70 | 2.7 | 70:30 | 0.22 | 242 |
| PP88−03[b] | 2.4 | 0.272 | 1:2 | 40:60 | 2.7 | 70:30 | 0.25 | 262 |
| PP112−01[c] | 3.9 | 6.011 | 1:3 | 40:60 | 5.9 | 29:71 | 0.29 | 461 |
| PP112−02[c] | 3.9 | 4.578 | 1:4 | 40:60 | 6.2 | 25:75 | 0.32 | 508 |
| PP113[d] | | | | | 4.9 | | 0.64 | 949 |

[a] 2 vol % monomer (DVB-55) relative to the reaction medium, 2 wt % AIBN relative to the monomer. [b] 30 mL reaction vial. The reaction temperature used for the shell preparation in this series was limited to 60 °C, resulting in a low conversion during the shell-forming step. [c] 1 L reaction bottle, 24 h at 70 °C. [d] Bulk porous particles prepared in toluene/acetonitrile mixture with a toluene volume fraction of 0.4, 2 vol % monomer loading relative to the reaction medium, and 2 wt % AIBN to the monomer, in a 2 L reaction bottle, 24 h at 70 °C.

ther a second type of monomer, or else a porogen could be added during the polymerization to form a shell with properties different from those of the core. This paper describes the formation of a series of core−shell particles prepared using different monomers or polymerization conditions for the formation of core and shell portions, respectively.

**Monodisperse or Narrow Disperse Styrenic Particles with a Dense Core and a Porous Shell.** We had previously reported the preparation of nonporous poly(DVB-55) particles by precipitation polymerization in neat acetonitrile[24] and of the corresponding porous particles by precipitation polymerization in toluene/acetonitrile mixtures[28] or related solvents.[31] Mercury porosimetry[30] and nitrogen adsorption confirmed the absence of porosity in the particles prepared in neat acetonitrile. On the other hand, the particles prepared in toluene/acetonitrile mixtures were shown to have a total pore volume of up to 0.5 cm$^3$/g, depending on the amount of toluene or other porogen present. These porous particles all have a characteristic pore size distribution in the nanopore region and no macropores as indicated by nitrogen adsorption and TEM analysis and by a molecular weight cutoff, or size exclusion limit, of 500.

By combining these two polymerization conditions sequentially we should be able to prepare poly(DVB-55) particles having a dense core and a porous shell.

Our first approach involved monomer and porogen addition in situ. In a typical experiment, an acetonitrile solution containing 4 vol % monomer and 2 wt % AIBN (relative to the monomer) was polymerized at 70 °C for 6 h. At that time, an additional amount of monomer (1 vol % relative to final reaction volume), AIBN (2% relative to additional monomer), and toluene (sufficient to make the final reaction medium 40 vol % toluene) were added and the mixture polymerized for an additional 18 h at 70 °C. The particles grew from 3.48 to 4.77 $\mu$m during this second polymerization stage, and the core to shell volume ratio calculated from the diameters was 39:61.

Our second approach to building core−shell structures involved re-dispersing previously prepared, nonporous poly(DVB-55) particles in a toluene/acetonitrile mixture together with DVB-55 and AIBN, followed by a 24 h polymerization at 70 °C to form porous shells. This two-step approach gave better control over core/shell ratios, and was used unless indicated otherwise. Figure 1 compares the particle size distributions for nonporous poly(DVB-55) core particles (PP107) and the subsequent core−shell particles (PP112−01). There is no sign of secondary initiation, and the particles retained their size-monodispersity during the shell formation.

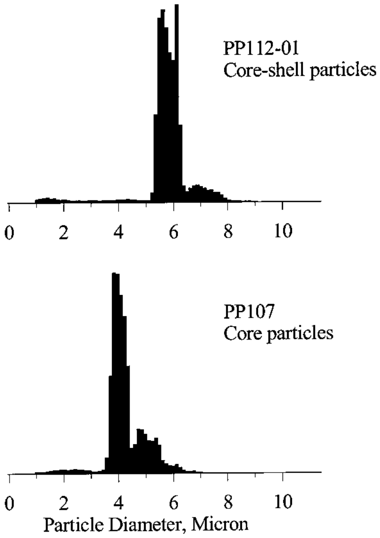

**Figure 1.** Particle size distributions for poly(DVB-55) core particles (PP107) and the subsequent core−shell particles (PP112−01) with porous poly(DVB-55) shells.

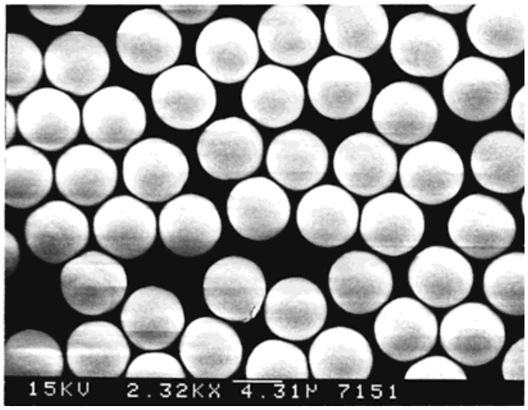

**Figure 2.** SEM image of poly(DVB-55) microspheres (PP112−02) with porous shells prepared in a toluene/acetonitrile(40/60) mixture.

The reaction conditions and porosity analyses are summarized in Table 1.

**Particle Morphology.** Scanning electron microscopy (SEM) showed both the core particles and the final core−shell particles to have spherical shapes and smooth surfaces. Figure 2 shows the SEM image of core−shell particles PP112−02 prepared using a 40/60 toluene/acetonitrile solvent mixture for the shell formation. No pores are visible in the shell surface of these particles, even in SEM images taken at higher magnification, confirming the absence of macropores.

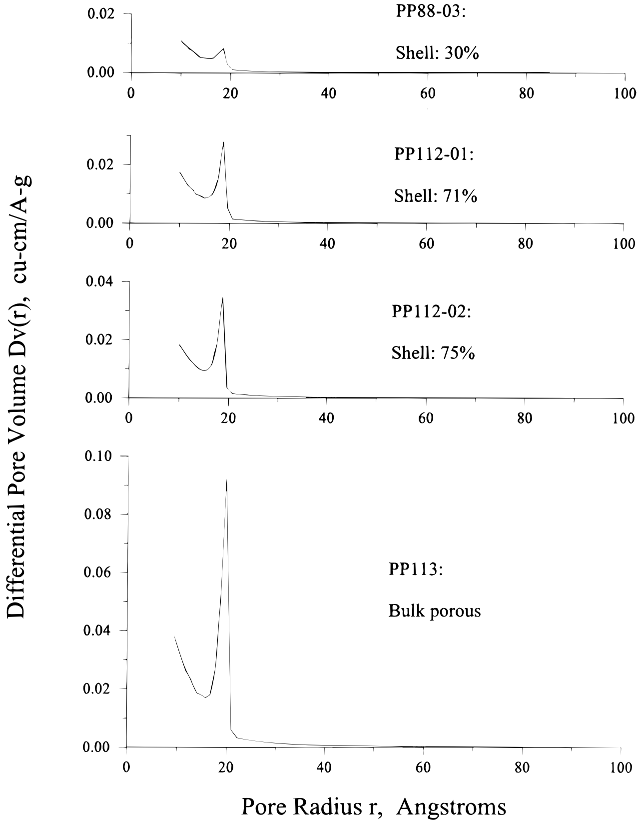

**Figure 3.** Pore size distributions for poly(DVB-55) particles with porous shells (PP88−03, PP112−01, PP112−02), and for bulk porous particles (PP113).

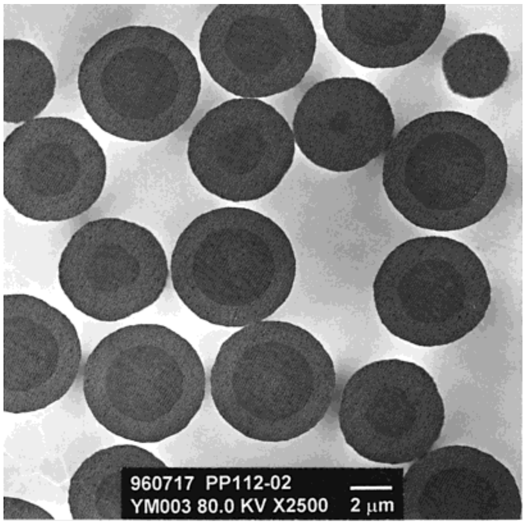

**Figure 4.** TEM micrograph of PP112-02 microspheres having dense poly(DVB-55) cores and porous poly(DVB-55) shells.

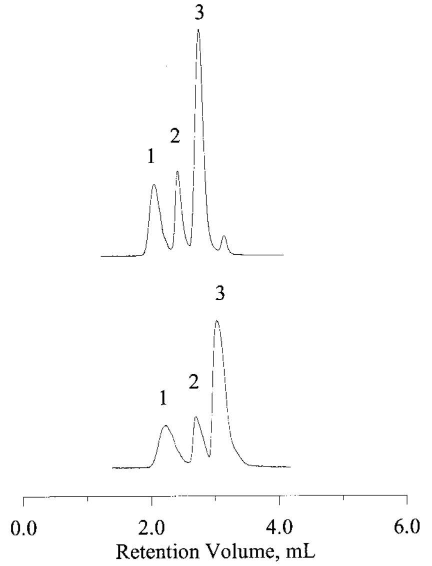

**Figure 5.** Size exclusion chromatograms from columns packed with core−shell particles PP112−02 (top) and with bulk porous particles PP113 (bottom).Solute: a mixture comprising a linear polystyrene standard (MW = 580) (1), 1,2-diphenylethane (2), and toluene (3). Column: 4.6 mm × 250 mm. Mobile phase: tetrahydrofuran. 0.5 mL/min UV detector, 214 nm.

These core−shell particles show better spherical shapes, as compared with the often oblong shapes of bulk porous particles prepared in the same toluene/acetonitrile solvent mixture. This suggests that the large surface area provided by the core particles efficiently captures the oligomers throughout the shell formation, and thus prevents homocoagulation.

**Porosity.** Poly(DVB-55) core−shell particles with their shell prepared in the presence of toluene, show porosity as indicated in Table 1. Their total pore volume and the specific surface area increase with the increasing shell percentage of the final particles. Figure 3 shows the pore size distributions for some of the core−shell particles and bulk porous particles, where all the porous portions were prepared in 40/60 v/v toluene/acetonitrile mixtures and using the same monomer loading of 2 vol %. It is notable that a narrow peak indicating a considerable amount of pores with the same size range, between 30 and 40 Å in diameter, appears for all the cases.

We used transmission electron microscopy (TEM) to study the internal, core−shell structure. The particles were embedded in an epoxy resin and microtomed to produce slices about 50 nm thick that were used directly without staining. Figure 4 shows a typical TEM image of the poly(DVB-55) core−shell particles PP112−02. The contrast between the core and the shell portions reflects the changes in density and hardness resulting from the porosity in the shells.

**Chromatographic Properties.** The core−shell particles PP112−01 and PP112−02 and the bulk porous particles PP113, with their porous portions prepared in a 40/60 v/v toluene/acetonitrile mixture, were slurry-packed into individual stainless steel columns and evaluated in terms of their chromatographic properties. A mixture of toluene, 1,2-diphenylethane, and a polystyrene standard with average molecular weight of 580 was used for this test. Figure 5 compares the size exclusion chromatograms from the column packed with porous shell particles PP112−02 and the bulk porous poly(DVB-55) particles, respectively. By comparing the ratios of the peak width at half-height to the retention volume of the toluene peak, it is apparent that the chromatographic resolution of the column packed with core−shell particles is superior to that of the column packed with bulk porous particles. The shorter diffusion paths, and the better spherical shape, of the core−shell particles compared to the bulk porous particles, likely reduce the peak broadening.

**Monodisperse or Narrow Disperse Particles with a Dense Styrenic Core and a Porous, Functional Shell.** We had previously reported the preparation of monodisperse poly(*p*-chloromethylstyrene-*co*-divinylbenzene-80) particles by direct copolymerization

**Table 2. Formation of Functional Shells on Preformed Core Particles**

| | core particles[a] | | shell preparation[b] | | final particles | | porosity analysis | |
|---|---|---|---|---|---|---|---|---|
| run ID | size, $\mu$m | weight, g | monomer composition CMS:DVB-80 | core particles:monomer for shell w:w | size, $\mu$m | core:shell v:v | pore volume, cm$^3$/g | surface area, m$^2$/g |
| PP168−01 | 3.3 | 0.050 | 10:90 | 1:5.5 | 4.7 | 35:65 | 0.22 | 240 |
| PP168−02 | 3.3 | 0.050 | 10:90 | 1:5.7 | 4.7 | 35:65 | 0.22 | 240 |
| PP168−03 | 3.3 | 0.050 | 20:80 | 1:5.8 | 4.7 | 35:65 | 0.25 | 260 |
| PP168−04 | 3.3 | 0.050 | 20:80 | 1:5.8 | 4.6 | 37:63 | 0.25 | 260 |

[a] Poly(DVB-55) core particles were prepared using 2 vol % monomer (DVB-55) relative to the reaction medium, and 2 wt % AIBN relative to the monomer. [b] Reaction medium for the shell preparation was toluene/acetonitrile (30/70 v/v).

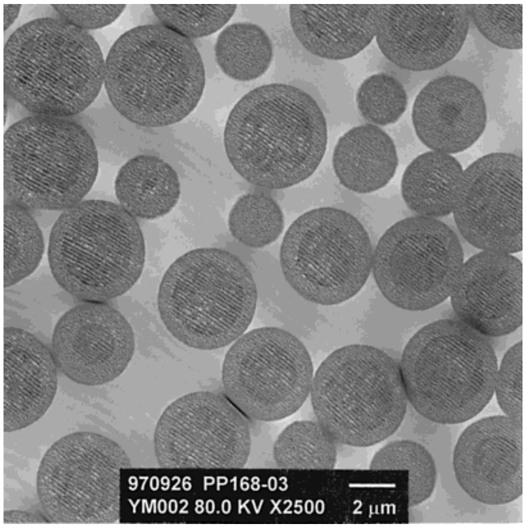

**Figure 6.** TEM micrograph of PP168−03 microspheres having poly(DVB-55) cores and porous shells with chloromethyl functional groups.

of chloromethylstyrene ($p$-CMS) with DVB-80 in neat acetonitrile. In particular, the poly($p$-CMS-*co*-DVB-80) copolymer particles prepared with $p$-CMS fractions of 0.1 and 0.2 in toluene/acetonitrile mixtures showed significant porosity. Since functional monodisperse particles are presently of substantial interest as reactive supports, we modified the above two-stage process to form core−shell particles consisting of a dense nonfunctional core and a functional and porous shell of any desired thickness.

In the first approach, a solution of 2 vol % DVB-55 and 2 wt % AIBN was allowed to polymerize in neat acetonitrile for 4 h. A sample of the narrow disperse particles taken at this time showed a diameter of 1.4 $\mu$m. After addition of 0.2 vol % $p$-CMS containing 2 wt % AIBN, and addition of 10 vol % toluene, the polymerization was continued for another 18 h. The final particles had a diameter of about 2.1 $\mu$m, indicating a 350 nm thick, porous, and functional shell.

In the second, two-step approach, nonporous poly(DVB-55) particles formed previously in a separate precipitation polymerization, were re-dispersed in an toluene/acetonitrile mixture together with CMS and DVB-55 in a volume ratio of 10/90 or 20/80, and with AIBN (2 wt % relative to monomer). Polymerization for 24 h led to the formation of monodisperse core−shell particles having defined core diameters and porous shells of desired composition (Table 2). Their pore size distributions (not shown here) are similar to those for microspheres having porous DVB-55 shells.

These functional and porous core−shell particles also have good spherical shapes and smooth surfaces (SEM images not shown). Figure 6 is a typical TEM micrograph for the core−shell particles with CMS functional groups incorporated into the porous shells. Both the effect of chlorine loading and the porosity of the shell contribute to the visual contrast between core and shell. These porous and less cross-linked shells do not exhibit the cutting artifacts visible in the cores, that are caused by the microtome knife cutting through the hard, embedded microspheres.

**Table 3. Formation of Poly(EGDMA-*co*-DVB-55) Shells on Poly(DVB-55) Core Particles**

| | core particles[a] | shell preparation[b] | final particles | |
|---|---|---|---|---|
| run ID | diameter, $\mu$m | monomer ratio EGDMA/DVB-55 | diameter, $\mu$m | core:shell, v:v |
| PP140−03 | 3.3 | 10/90 | 4.1 | 52:48 |
| PP140−02 | 3.3 | 30/70 | 4.2 | 49:51 |
| PP138−02 | 3.3 | 50/50 | 4.4 | 42:58 |
| PP140−01 | 3.3 | 70/30 | 4.5 | 39:61 |
| PP138−01 | 3.3 | 90/10 | 5.2 | 26:74 |
| PP140−04 | 3.3 | 100/0 | 5.1 | 27:73 |

[a] The poly(DVB-55) core microspheres were prepared at 2 vol % monomer loading relative to acetonitrile, with 2 wt % of AIBN relative to the monomer, and at 70 C° for 24 h. [b] 1 vol % total monomer loading, 1 wt % AIBN relative to the monomer, 24 h at 70 C° in 30 mL acetonitrile. 0.1 g of core microspheres were used in each reaction.

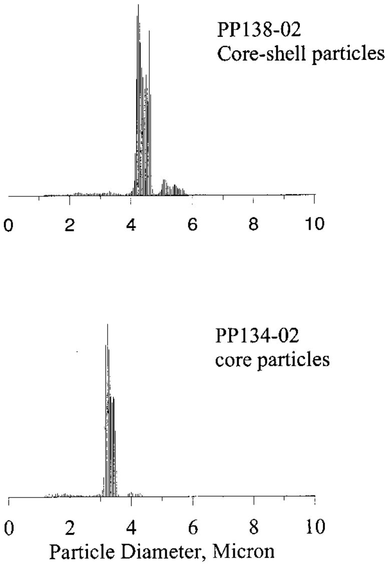

**Figure 7.** Particle size distributions for poly(DVB-55) core particles (PP134−02) and the subsequent core−shell particles (PP138−02) with poly(EGDMA-*co*-DVB-55) (1:1) shells.

Treatment of these cross-linked CMS copolymer microspheres with triethylamine in tetrahydrofuran showed that the chlorine groups on their surface could easily be replaced with nucleophiles. The resulting aminated microspheres, prepared with original CMS fractions of 0.2 and higher, easily dispersed in water, indicating the formation of quaternary ammonium salts.

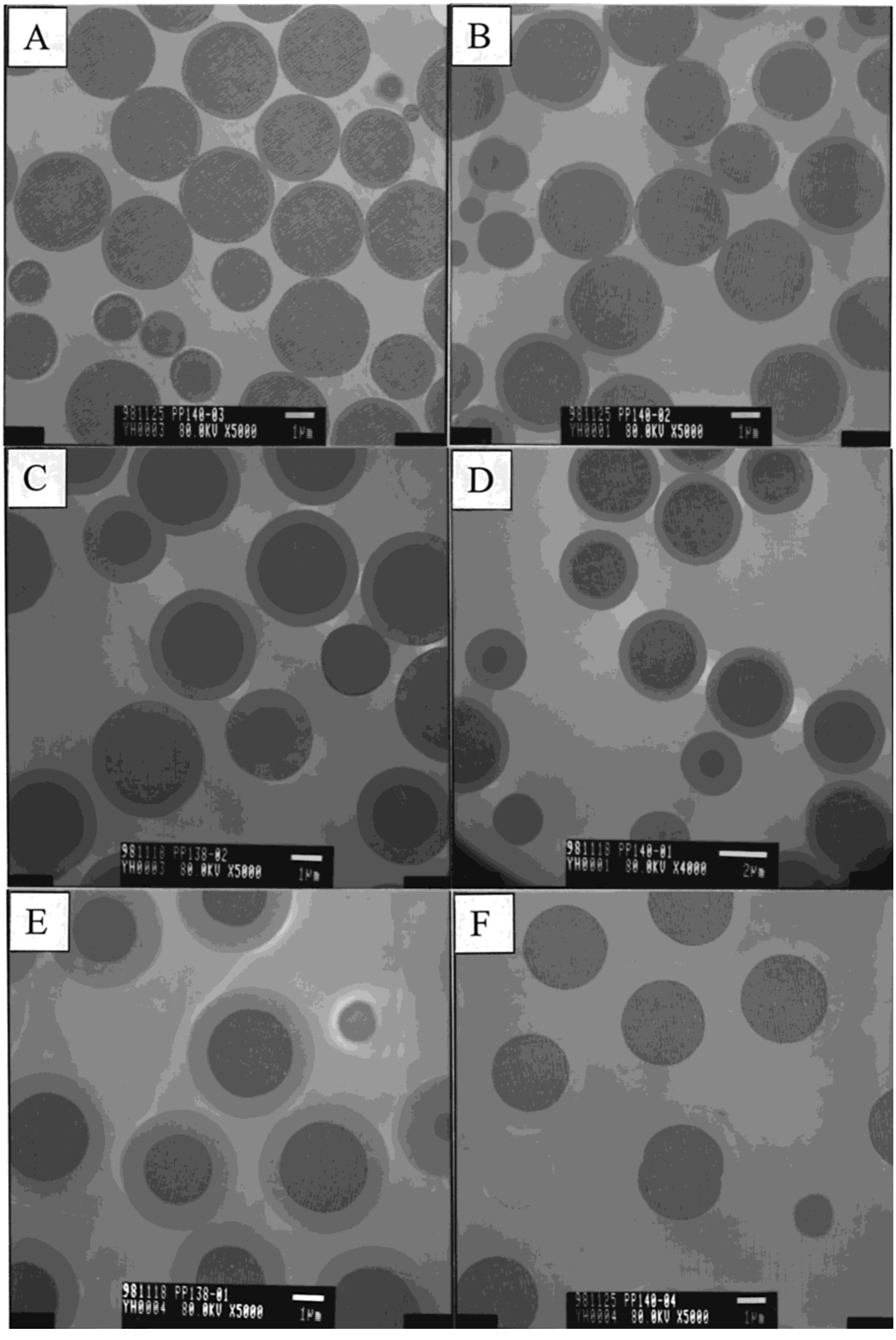

**Figure 8.** TEM micrographs of core–shell particles having poly(DVB-55) cores and poly(EGDMA-*co*-DVB-80) shells. The initial fraction of EGDMA for the shells is in ascending order: 0.1, 0.3, 0.5, 0.7, 0.9, 1.0.

**Mono- and Narrow Disperse Core–Shell Microspheres with a Methacrylate/Styrenic Shell.** Using premade monodisperse poly(DVB-55) particles as core particles, we carried out the precipitation copolymerization of ethylene glycol dimethacrylate (EGDMA) and DVB-55 to form methacrylate/styrenic shells around these styrenic core particles. The preparation conditions are summarized in Table 3.

The EGDMA volume fraction in the total monomer used for the shell formation was varied from 0.1 to 1.0. The resulting core−shell particles all have good spherical shapes and smooth surfaces, including those containing 100% EGDMA in the shell. We reported earlier that homopolymerization of EGDMA in acetonitrile did not give good spherical particles.[27] As in the case of porous poly(DVB-55) shell formation above, the large surface area of the core particles appears to prevent extended homocoagulation.

The monodispersity of the core−shell microspheres was retained during the shell formation for all these reactions. Figure 7 shows the particle size distributions for the original core particles (PP134−02) and the subsequent core−shell particles (PP138−02). Both particles have similarly narrow size distributions.

Figure 8 shows a set of TEM images of core−shell particles with a poly(DVB-55) core and poly(EGDMA-*co*-DVB-55) shells with the initial EGDMA fractions in ascending order: 0.1 (A), 0.3 (B), 0.5 (C), 0.7 (D), 0.9 (E), and 1.0 (F). It is interesting to see that while the contrast between the shell and the core portions increases as the EGDMA fraction increased in the shell, the contrast between the shells and the surrounding epoxy resin diminishes, and almost disappears for the shells consisting of 100% EGDMA (Figure 8F). This is due to the similar elemental composition and density of poly(EGDMA) and the epoxy resin.

Other monovinyl methacrylic and styrenic monomers such as glycidyl methacrylate and *tert*-butyl styrene were also successfully incorporated into microsphere shells to give monodisperse cross-linked core−shell microspheres in the micrometer-size range. These microspheres provide a range of polarities and reactivities for potential applications as supports or composite fillers.

## Conclusion

By either changing the reaction conditions in situ during the course of polymerization or by using a two-step method, we were able to form monodisperse cross-linked micrometer-size microspheres with core−shell structure by precipitation polymerization. The changes in reaction conditions include the introduction of a good cosolvent to form a porous shell on a dense core, introduction of a functional comonomer to form shells with desired functional groups, or introduction of both a good cosolvent and a functional monomer to form a porous shell with functional groups. The core size and the thickness of the shell can be easily controlled.

The porosity properties of the porous shells are similar to those of corresponding bulk porous particles. Most of the pores are in the micropore range, with the differential pore volume showing a peak at a diameter between 30 and 40 Å. Chromatographic tests of the poly(DVB) core−shell particles with a dense core and a porous shell showed chromatographic resolution superior to that of the corresponding bulk porous particles.

Particles with such unique pore size distributions may have applications as specialized separation media, or as selective sorbents. The high mechanical strength and high thermal stability of cross-linked divinylbenzene resins may also suggest applications in size or shape selective catalysis at temperatures up to 300 °C, while the clean, stabilizer-free surfaces may be important for applications in biotechnology.

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