

Narrow-Disperse or Monodisperse Crosslinked and Functional Core–Shell Polymer Particles Prepared by Two-Stage Precipitation Polymerization

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ABSTRACT: Narrow-disperse and monodisperse crosslinked core–shell polymer particles containing different functional groups, such as esters, hydroxyls, chloromethyls, carboxylic acids, amides, cyanos, and glycidyls, in the shell layers in the micrometer size range were prepared by a two-stage precipitation polymerization in the absence of any stabilizer. Commercial divinylbenzene (DVB), containing 80% DVB, was precipitation polymerized in acetonitrile without any stabilizer as the first-stage polymerization and was used as the core. Several functional monomers, including methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-hydroxyethyl methacrylate, glycidyl methacrylate,

methyl acrylate, ethyl acrylate, butyl acrylate, *t*-butyl acrylate, *i*-octyl acrylate, acrylic acid, acrylamide, acrylonitrile, styrene, and *p*-chloromethyl styrene, were incorporated into the shells during the second-stage polymerization. The resulting core–shell polymer particles were characterized with scanning electron microscopy and Fourier transform infrared spectroscopy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1776–1784, 2006

Key words: core-shell polymers; crosslinking; functional polymer; polymer microsphere; precipitation polymerization

INTRODUCTION

Spherical microparticles that consist of both organic or inorganic cores and different chemical composition shells have attracted much interest recently.¹ Usually, in the core–shell structures, the material of interest is exposed on the surfaces; that is, it forms the shell. The core has a templating function and controls the form and the size of the composite. Core–shell structures often exhibit properties that are substantially different from those of the materials building the composite, which makes them a welcome supplement to single-phase spherical particles.

The control of surface properties is central to many areas of research and in numerous commercially important technologies, ranging from biotechnology to advanced microelectronics.^{2,3} One method that has been used to control the surface properties is the use of polymeric brushes, which are prepared traditionally

from block copolymers, where one block is strongly adsorbed to the surface while the other block forms the brush layer.^{4–6} The noncovalent nature of a such grafting strategy is a weakness, however, because the desorption of the brush can subsequently occur. Additionally, the demanding block copolymer synthesis limits the choice of functional groups for the block copolymer structure. To circumvent these deficiencies, an increasing interest has been devoted to the covalent attachment of polymer chains to surfaces.⁷ This can be accomplished in a number of ways, including both a grafting-onto approach^{7,8} and a grafting-from approach.^{9,10}

Only a few reports in the literature have described polymer-based core–shell particles of a micrometer size. Through the use of a series of sequential seeded growth-emulsion polymerizations, Rundin's¹¹ group prepared monodisperse latex core–shell particles with diameters of 3 μm . There have been a few reports on core–shell particles of a micrometer size prepared by dispersion polymerization: Laus et al.^{12,13} reported the preparation of monodisperse polystyrene particles 2–10 μm in size in the presence of a poly(carboxylic acid) or a polyepichlorohydrine steric stabilizer, which itself then constituted the shell. Okubo et al.¹⁴ conducted the dispersion copolymerization of *p*-chloromethylstyrene (CMSt) and styrene (St) on polystyrene seeds, which adsorbed the monomer mixture and

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yielded micrometer-size monodisperse polymer microspheres with chloromethyl groups in the shell.

Precipitation polymerization is a unique method for affording monodisperse microspheres free of any added surfactant or stabilizer.^{15–17} Li and Stöver¹⁸ reported on monodisperse crosslinked microspheres prepared by precipitation polymerization¹⁸ and core-shell microspheres prepared by precipitation polymerization in acetonitrile with semibatch *in situ* and a two-step batch mode with core particles.¹⁹ We succeeded in obtaining monodisperse micrometer microspheres with active hydroxyl groups with a dense core and a lightly crosslinked functional shell through two-stage polymerization in the absence of any stabilizer and observed that secondary particle initiation occurred with higher loadings of 2-hydroxyethyl methacrylate (HEMA).²⁰ In this article, we report on the extension of such simple procedures for the preparation of core-shell structure polymers with different functional monomers incorporated into the shell layer without any secondary particle initiation to control the surface properties of the polymer microspheres. Such modifications should change the surface characteristics, for example, for specific binding and interactions with other materials or polymers. New application areas for such polymer particles may be visualized.

EXPERIMENTAL

Chemicals

Divinylbenzene [DVB; technical grade, 80% divinylbenzene (DVB80) isomers; Shengli Chemical Technical Factory, Shandong, China] was washed with a 5% aqueous sodium hydroxide solution and water and then dried over anhydrous magnesium sulfate before use. 2,2'-Azobis(2-methyl propionitrile) (AIBN; Chemical Factory of Nankai University) was recrystallized from 95% ethanol. The comonomers, including methyl methacrylate (MMA), methacrylate (MA), ethyl methacrylate (EMA), butyl methacrylate (BMA), butyl acrylate (BA), HEMA, ethyl acrylate (EA), and *t*-butyl acrylate (*t*-BA), were purchased from Tianjin Chemical Reagent II Co., (Tianjin, China) and were washed with a 5% aqueous sodium hydroxide solution, dried with anhydrous magnesium sulfate, and then purified by vacuum distillation. Acrylamide (AAM) was purchased from Tianjin Chemical Reagent II. and was purified by recrystallization from ethyl acetate. St and CMSt were purchased from purchased from Acros Co. and purified by vacuum-distillation before use. Glycidyl methacrylate (GMA) was purchased from Shanghai Heshibi Chemical Engineering Co., Ltd., (Shanghai, China) and was used without any further purification. Acetonitrile (Tianjin Chemical Reagent II) was dried over 4-Å molecular sieves and was distilled before use. The other reagents and solvents were used as received without any further purification.

Preparation of the monodisperse PDVB80 core by precipitation polymerization

Monodisperse crosslinked polydivinylbenzene (PDVB) was prepared as reported in our previous article.²⁰ In a typical polymerization procedure, the polymerization of DVB80 was carried out in an evaporating flask for a Büche evaporator. AIBN (0.104 g, 2 wt % compared to DVB80) was added to a solution of DVB80 (5.6 mL, 2.8 vol % relative to the total volume) in a 200 mL of acetonitrile. The flask was attached with the evaporator and evacuated and purged with nitrogen three times to remove the oxygen in the system. The flask was then immersed in a water bath 45° to a perpendicular axis and rotated around the axis at 90 rpm. The temperature of the water-bath was increased over 1.6 h from room temperature to 70°C. The initially homogeneous reaction mixture turned milky white after it reached 70°C for 1 h. The reaction was allowed to proceed for 24 h under a nitrogen atmosphere, after which 10 mL of the reaction mixture was taken out and cooled to room temperature. The resulting poly(divinylbenzene) (PDVP80) core microspheres were separated by vacuum filtration over a G5 sintered glass filter and successively washed three times with tetrahydrofuran, acetone, and ether. The particles were dried at 50°C in a vacuum oven until they reached a constant weight.

Preparation of monodisperse or narrow-disperse core-shell microspheres with different shells in the second-stage polymerization

The core particles were prepared as described in the first stage, and the conversion of DVB80 was about 60% at this stage. For the second reaction period, 0.10 g of each comonomer with different functional groups, including MMA, EMA, BMA, HEMA, GMA, MA, EA, BA, *t*-BA, *i*-octyl acrylate (*i*-OA), acrylic acid (AA), AAm, acrylonitrile (AN), St, and CMSt, together with a solution of AIBN (2 wt % relative to the comonomer), in 6 mL of acetonitrile were introduced into the previously prepared 6 mL of the core reaction mixture in a 25-mL flask. The polymerization was allowed to continue as a set of parallel syntheses to form the microsphere shell with different functional groups on the surface. The flasks were sealed and attached to a SHA-B shaker (Tianjin, China). The shaker gently agitated the samples by rolling the bottles in a horizontal position at approximate 140 rpm. The temperature used for the polymerization started with a 1-h ramp from room temperature to 70°C. The polymerization continued further for 24 h at 70°C. The core-shell particles were isolated by vacuum filtration over a G-5 sintered glass filter with three successive washings with tetrahydrofuran, acetone, and ether. The washed microspheres were dried at 50°C overnight.

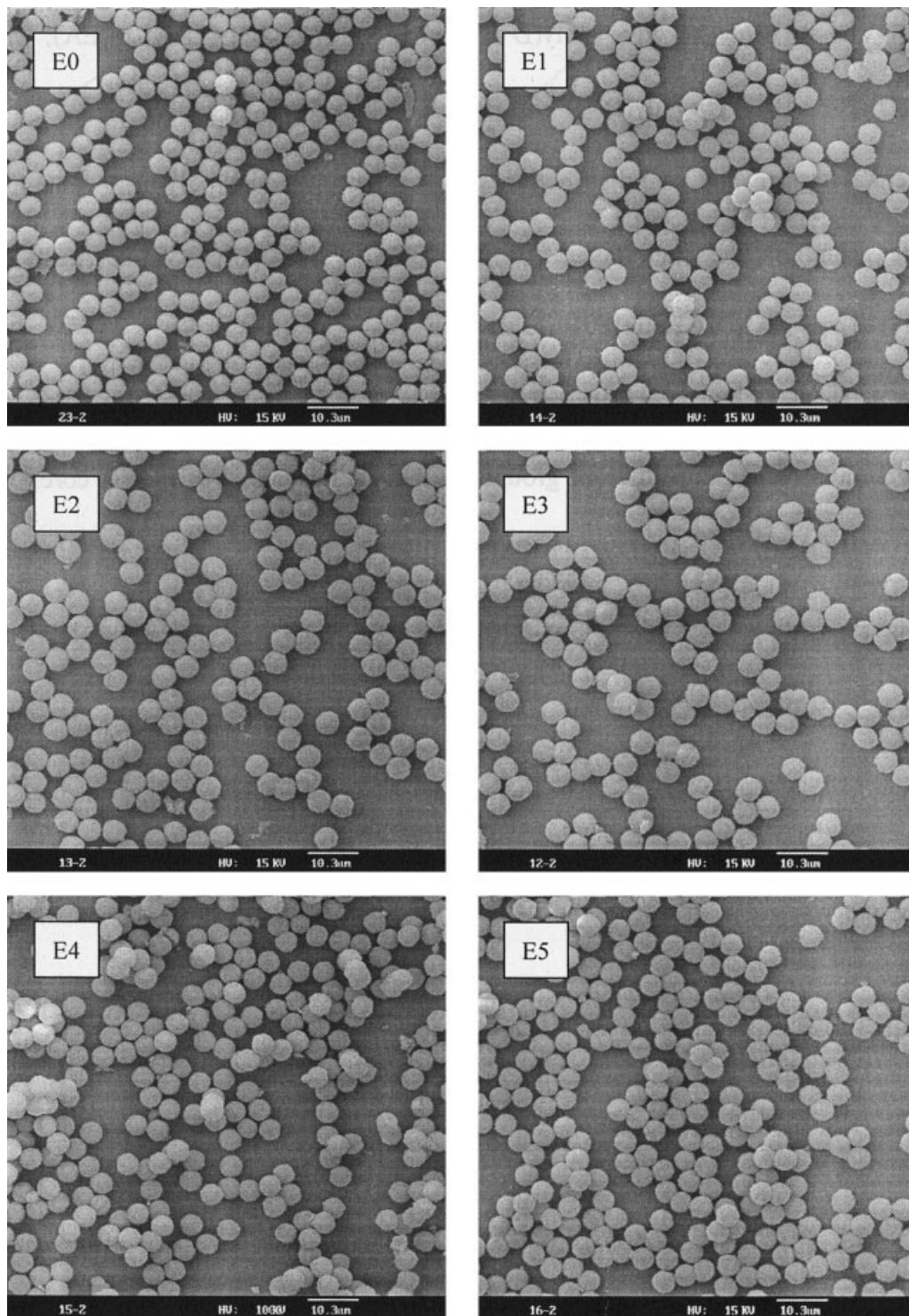


Figure 1 SEM micrographs of the poly[DVB80-co-(meth)acrylates] polymer core-shell microspheres with ester groups in the shell layer: E0 = PDVB core; E1 = poly(divinylbenzene-co-methyl methacrylate); E2 = poly(divinylbenzene-co-ethyl methacrylate); E3 = poly(divinylbenzene-co-butyl methacrylate); E4 = poly(divinylbenzene-co-glycidyl methacrylate); E5 = poly(divinylbenzene-co-2-hydroxyethyl methacrylate); E6 = poly(divinylbenzene-co-methacrylate); E7 = poly(divinylbenzene-co-ethyl acrylate); E8 = poly(divinylbenzene-co-butyl acrylate); E9 = poly(divinylbenzene-co-*t*-butyl acrylate); and E10 = poly(divinylbenzene-co-*i*-octyl acrylate).

Particle size analysis

The particle size and size distributions were determined by scanning electron microscopy (SEM) with a

scanning electron microscope (Philips-XL-30, The Netherlands). The samples were prepared by the dispersion of the particles in ethanol and the placement

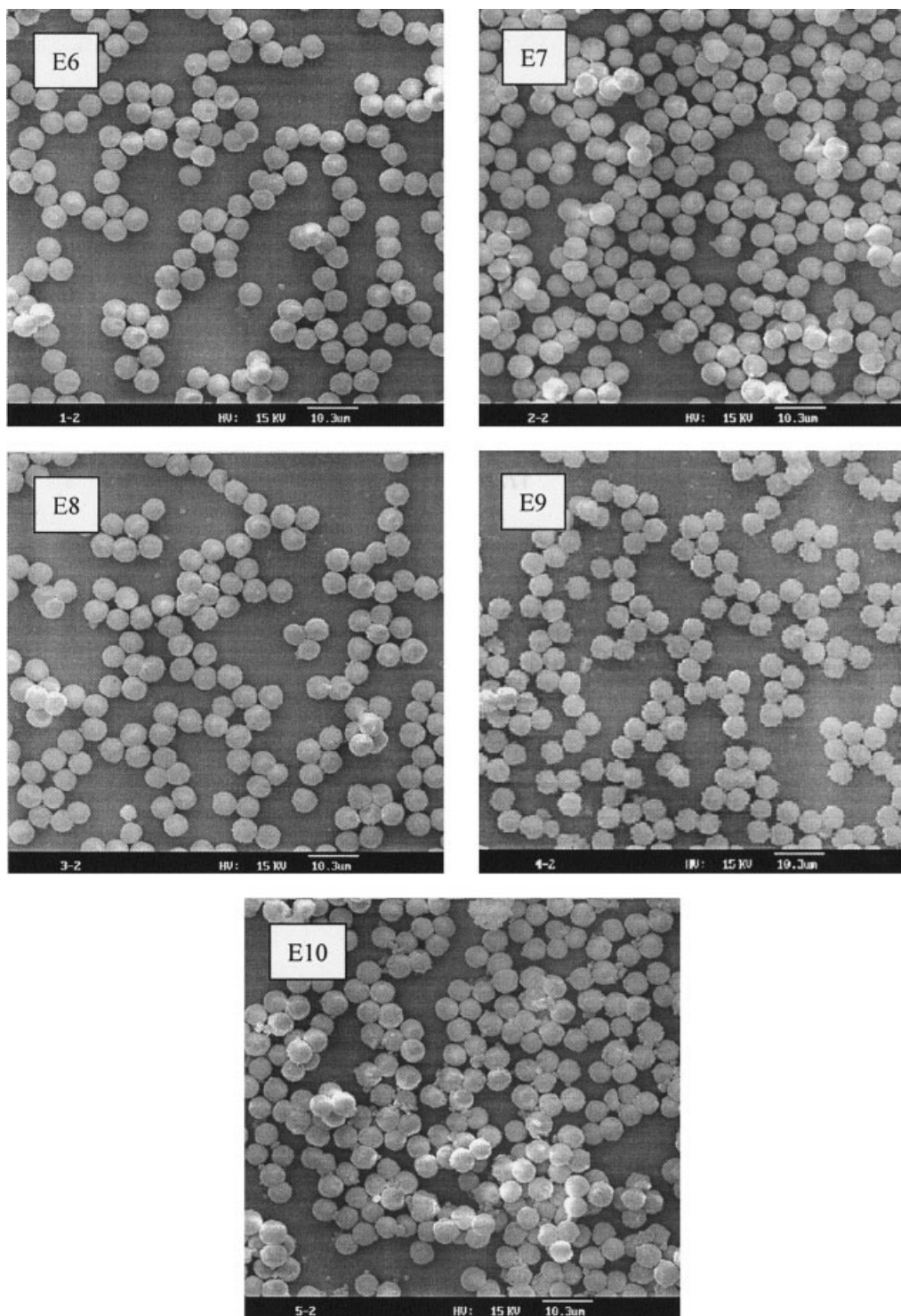


Figure 1 (Continued)

of a drop of this particle suspension on a piece of glass for an electron microscope stub with double-sided tape. The samples were dried in vacuo. All of the SEM size data reflected averages from about 100 particles each, which were calculated with the following formulas:

$$U = D_w/D_n \quad (1)$$

$$D_n = \frac{\sum_{i=1}^k n_i D_i}{\sum_{i=1}^k n_i} \quad (2)$$

$$D_w = \frac{\sum_{i=1}^k n_i D_i^4}{\sum_{i=1}^k n_i D_i^3} \quad (3)$$

TABLE I
Size and Size Distribution of the Core–Shell Structure Polymers Containing Ester Groups in the Shell Layer

Entry	Comonomer	Comonomer/DVB (v/v)	D_n (μm)	D_w (μm)	U
E0		0/0.17	4.19	4.20	1.002
E1	MMA	0.10/0.17	4.61	4.62	1.004
E2	EMA	0.10/0.17	4.95	4.97	1.004
E3	BMA	0.10/0.17	4.92	4.96	1.008
E4	GMA	0.10/0.17	4.58	4.59	1.002
E5	HEMA	0.10/0.17	4.67	4.68	1.003
E6	MA	0.10/0.17	5.04	5.07	1.006
E7	EA	0.10/0.17	4.99	5.01	1.005
E8	BA	0.10/0.17	5.01	5.05	1.008
E9	<i>t</i> -BA	0.10/0.17	5.24	5.28	1.006
E10	<i>i</i> -OA	0.10/0.17	4.93	4.99	1.012

The entries E0–E10 are defined in the caption to Figure 1.

where U is the polydispersity index, D_n is the number-average diameter, D_w is the weight-average diameter, n is the total number of the measured particles, and D_i is the particle diameter of the determined microspheres.

Fourier transform infrared (FTIR) analysis

FTIR analysis was performed on a Bio-Rad FTS 135 FTIR spectrometer. All of the samples were mixed and ground with spectroscopic-grade potassium bromide before they were placed in the sample cell, and the diffuse reflectance spectra were scanned over a range of 400–4000 cm^{-1} .

RESULTS AND DISCUSSION

Preparation of monodisperse PDVB cores

The preparation of the monodisperse PDVB cores was done as described in our previous article.²⁰ Careful optimization of the reaction conditions yield monodisperse PDVB80 cores by precipitation polymerization without any stabilizer. The SEM image of the PDVB80 core particles by precipitation polymerization in acetonitrile is shown in Figure 1, which indicated that the polymer particles had spherical shapes and smooth surfaces without any coagulation. The particle size and size distribution of the PDVB80 particles are listed in Table I, with a size of 4.19 μm and a U value of 1.002.

Preparation of narrow-disperse core–shell polymer particles with different functional comonomers

It was confirmed that polydivinylbenzene (55% DVB) particles prepared by precipitation polymerization contain more residual double bonds than that prepared by suspension polymerization due to the poor solvent medium and much lower monomer concen-

tration used in the former case.¹⁹ During the precipitation polymerization of DVB80, the conversion reached only about 60% due to the low monomer concentration and the rigid surfaces of the PDVB. The residual double bonds located at the surface permit further growth of the particle by radical capture of oligomers and monomers.²⁰ Accordingly, a series of comonomers with different functional groups was added to the second-stage polymerization, which could have then led to monodisperse core–shell polymer particles with different functional groups on the shell layer by the two-stage precipitation polymerization.

Core–shell polymer particles with ester groups on the surface

Stöver et al. reported the precipitation copolymerization of MMA and DVB to result in monodisperse microspheres.²¹ Here, we prepared monodisperse polymer particles with core–shell structures using the reactive double bonds of PDVB80 cores and comonomers containing the ester group in the shell layer by two-stage precipitation polymerization. The SEM micrographs of the prepared core–shell poly{divinylbenzene-*co*-[alkyl-(meth)acrylate]} polymer particles with ester groups in the shell layer are shown in Figure 1. The results indicate that the final core–shell microspheres had spherical shapes with smooth surfaces when MMA, GMA, EMA, HEMA, MA, and EA were used as the comonomers during the second-stage precipitation polymerization. This suggests that the large surface area of the core particles efficiently captured the oligomers throughout the shell formation to prevent homocoagulation and second-initiated particles. With the longer substituents of the pendant ester groups in the comonomers, such as BMA, BA, and *i*-OA, there were some coagula in the core–shell polymer microspheres, especially in the poly-(divinylbenzene-*co*-*i*-octyl acrylate) (with DVB80) particles.

The ratios of the comonomers to DVB80 and the size and size distribution of the core-shell microspheres with ester groups on the shell layer are summarized in Table I. All of the core-shell particle sizes increased significantly after the second-stage precipitation copolymerization. The size of the final polymer particles was determined by the conversion of the monomers and the nuclei. The particle size increased slightly from 4.19 μm for PDVB80 core to around 4.60 μm for the core-shell particles (entries E1, E4, and E5) with a monodispersity of 1.002 when MMA, GMA, and HEMA, respectively, were used as the comonomers. The size of the core-shell particles with narrow dispersity (1.004) increased to around 4.95 μm when EMA (entry E2), BMA (entry E3), MA (entry E6), EA (entry E7), BA (entry E8), and *t*-BA (entry E9) were used as the comonomers. The formation of coagula and second-initiated particles were observed with increasing size to 4.93 μm and a narrow dispersity of 1.008 when *i*-OA (Entry E10) was employed as the comonomer. The solvency of the formed polymer in the reaction system plays an essential role in the dissemination of the successful formation of a stable shape as in dispersion polymerization^{22,23} and precipitation polymerization.²⁰ With longer substituents of the pendent ester groups, the polarity of the monomer and the corresponding oligomer decrease, and the solubility of the oligomer in acetonitrile decreases, which leads to different sizes and morphologies of the core-shell polymer microspheres.

The surface modification of the ester leading to the poly[divinylbenzene-*co*-(alkyl) methacrylate] core-

shell polymers was confirmed further by FTIR spectra, as shown in Figure 2. As shown by the FTIR spectra in Figure 2 (with E0, E1, E4, and E5 shown as the samples), all of the core-shell polymer particles with ester groups on the surface had a very strong peak around 1720–1735 cm^{-1} , corresponding to the typical stretching adsorption of the carbonyl groups, and a strong peak around 1160–1260 cm^{-1} due to the asymmetrical and symmetrical stretching adsorption of C—O—C bonds in the ester groups.²⁴ For poly(divinylbenzene-*co*-2-hydroxyethyl methacrylate) particles, there was a broad strong peak at 3500 cm^{-1} , which was attributed to the vibration adsorption of hydroxyl groups.

Core-shell polymer particles with acid, amide, and cyano groups on the surface

The SEM micrographs of the prepared core-shell polymer particles containing acid, amide, and cyano group in the shell layer are shown in Figure 3.

The results indicate that the core-shell microspheres with amide groups had spherical shapes with little coagula when AAm was used as the comonomer. The size and size distribution of such particles are listed in Table II. The size of poly(divinylbenzene-*co*-acrylamide) (with DVB80) particles increased to 4.81 μm with a narrow dispersity of 1.006. The formation of the core-shell structure polymer with amide groups was confirmed further by FTIR spectra, as shown in Figure 4. The FTIR spectra had a very strong peak at 1674 cm^{-1} , corresponding to the stretching adsorption of the C=O bond of the amide group, and peaks at 3191,

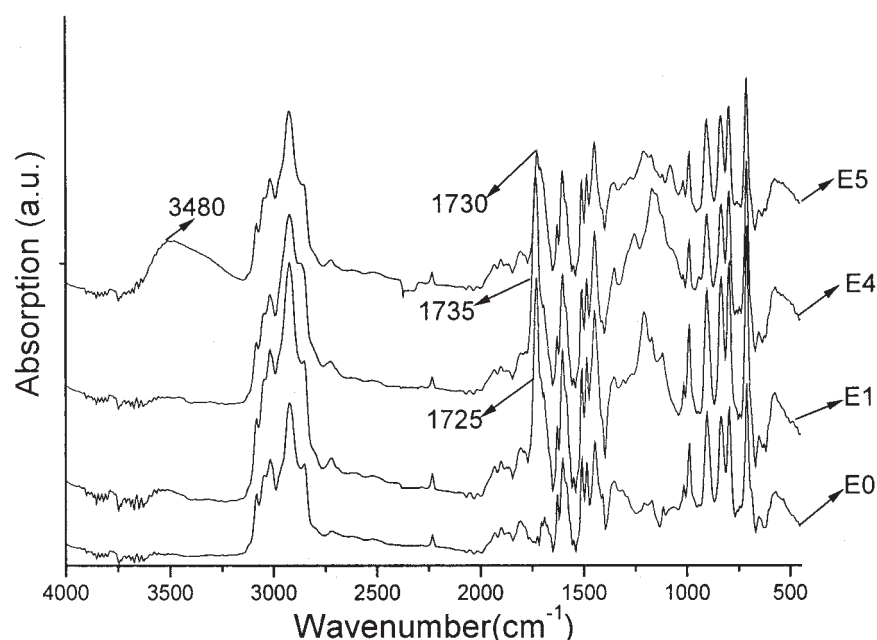


Figure 2 FTIR spectra of the poly(divinylbenzene-*co*-methacrylate) core-shell polymer microspheres with ester groups in the shell layer. See the caption of Figure 1 for the definitions of entries E0, E1, E4, and E5.

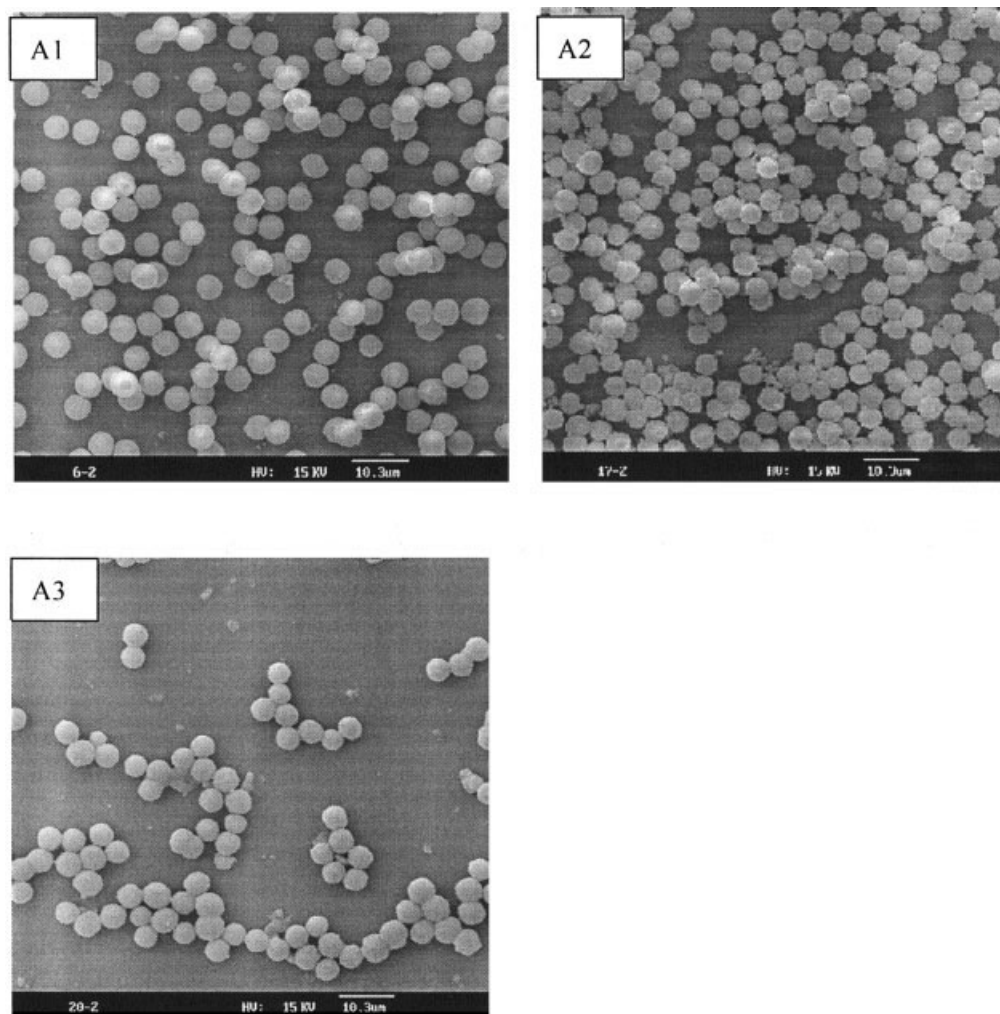


Figure 3 SEM micrographs of the core-shell polymer microspheres with different groups in the shell layer. A1 = poly(divinylbenzene-*co*-acrylamide); A2 = poly(divinylbenzene-*co*-acrylic acid); and A3 = poly(divinylbenzene-*co*-acrylonitrile).

3340, and 3475 cm^{-1} due to the adsorption of the N—H bond of the amide group.

When AN was used as the comonomer, the size of the core-shell particles increased to 4.82 μm with a narrow dispersity of 1.024 due to the higher solubility parameter of AN compared to acetonitrile. There were some coagula during the second-stage precipitation copolymerization. The FTIR spectra proved the formation of the core-shell structure with a strong peak at

2239 cm^{-1} , corresponding to the characteristic adsorption of the cyano group on the shell.

When AA was used as the comonomer, the size of the final particles increased slightly to 4.45 μm without consideration of the small second-initiated particles formed during the second-stage polymerization, as shown in Figure 3 and Table II. This was related to the strong polarity of AA and the poor solubility of the oligomers of poly(acrylic acid) (PAA) in acetonitrile

TABLE II
Size and Size Distribution of the Core-Shell Structure Polymers Containing Amide Groups in the Shell Layer

Entry	Comonomer	Comonomer/DVB (v/v)	D_n (μm)	D_w (μm)	U
A0		0/0.17	4.19	4.20	1.002
A1	AAm	0.10/0.17	4.81	4.84	1.006
A2	AA	0.10/0.17	4.45	4.50	1.011
A3	AN	0.10/0.17	4.82	4.93	1.024

A0 = PDVB core. The entries A1–A3 are defined in the caption to Figure 3.

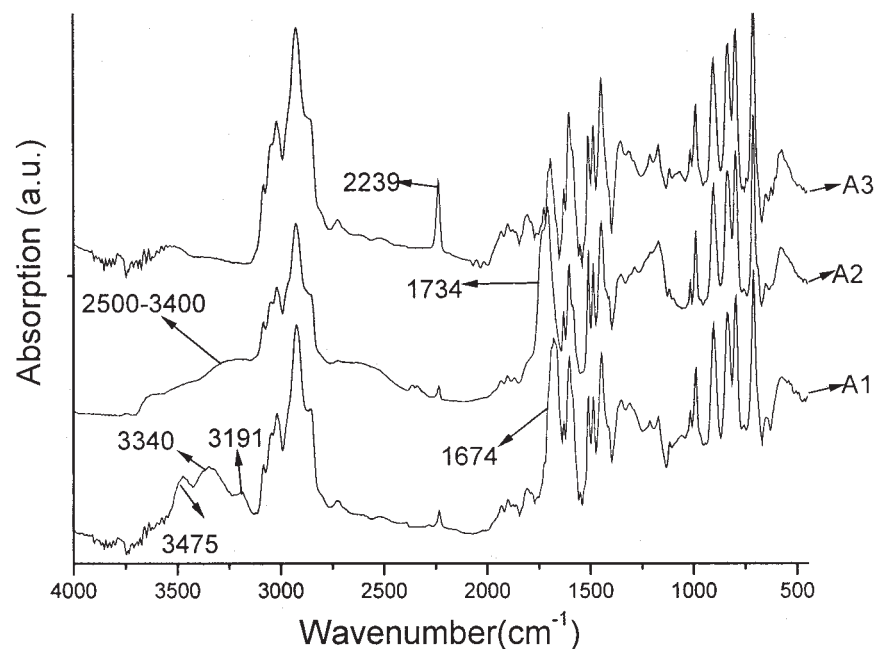


Figure 4 FTIR spectra of the core-shell polymer microspheres with different groups in the shell layer. See the caption of Figure 3 for the definitions of entries A1–A3.

that precipitated from the reaction system to form the small second-initiated particles during the second-stage precipitation polymerization.

Core-shell polymer particles with various vinyl comonomers containing different functional groups

A series of copolymerizations between the residual double bonds of the PDVB cores and vinyl comonomers containing various functional groups, such as St and CMSt, were conducted to prepare core-shell structure polymer particles. The SEM micrographs of the resulting polymer particles are shown in Figure 5.

The size and size distribution of the final particles are summarized in Table III.

When St and CMSt were used as the comonomers, the size of the obtained core-shell polymers increased to 4.91 μm for poly(divinylbenzene-*co*-styrene) (with DVB80) with a narrow dispersity of 1.009 and 4.82 μm for poly(divinylbenzene-*co*-*p*-chloromethyl styrene) (with DVB80) with a narrow dispersity of 1.006. The formation of the core-shell structure was confirmed by the presence of a peak in the FTIR spectra at 760 cm^{-1} of poly(divinylbenzene-*co*-polystyrene) (with DVB80), which was attributed to the adsorption of a

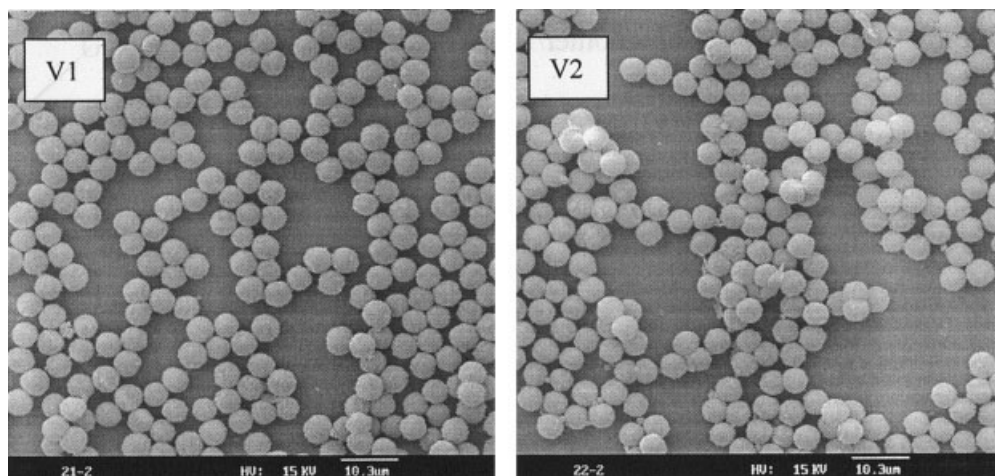


Figure 5 SEM micrographs of the core-shell polymer microspheres with vinyl comonomers containing different functional groups in the shell layer: V1 = poly(divinylbenzene-*co*-styrene); V2 = poly(divinylbenzene-*co*-*p*-chloromethyl styrene).

TABLE III
Size and Size Distribution of the Core–Shell Structure Polymers with Vinyl Comonomers Containing Different Groups in the Shell Layer

Entry	Comonomer	Comonomer/DVB (v/v)	D_n (μm)	D_w (μm)	U
V0		0/0.17	4.19	4.20	1.002
V1	St	0.10/0.17	4.91	4.95	1.009
V2	CMSt	0.10/0.17	4.82	4.85	1.006

V0 = PDVB core. The entries V1 and V2 are defined in the caption to Figure 5.

monosubstituted benzene ring.²⁴ The elemental analysis of the chloride of poly(divinylbenzene-*co-p*-chloromethyl styrene) (with DVB80) was 0.31 mmol/g, which further confirmed the success of the preparation of the core–shell polymer.

All of the previously discussed results indicate that the second comonomers with different functional groups were successfully incorporated into the shell layer. There were two kinds of competing reactions during the second-stage precipitation polymerization to form the core–shell polymer microspheres. One was the precipitation polymerization of either newly formed reacting oligomers or the comonomers on the PDVB core surface or the migration of radicals to the particle surface and their reaction with residual double bonds on the surface. The lightly crosslinked shell layers were formed in such ways to increase the particle size and incorporate the different functional groups into the shell layer. The other was a reaction between the radical themselves. In this study, the formation of narrow-disperse or monodisperse core–shell polymer particles with different functional groups in the absence of the second-initiated particles indicated that the residual double bonds on the surface of PDVB cores could efficiently capture the soluble oligomers from the solution.

CONCLUSIONS

Monodisperse or narrow-disperse crosslinked core–shell polymer microspheres with various functional groups in the shell layers were prepared by two-stage precipitation polymerization. The comonomers with different functional groups, including ester, hydroxyl, chloromethyl, carboxyl acid, amide, cyano, and glycidyl groups, were introduced into a reaction system containing a PDVB core to form the shell layers during the second-stage polymerization. The copolymerization of the functional comonomers in the second-stage precipitation polymerization could be conducted to afford monodisperse or narrow-disperse core–shell polymer microspheres without a second initiation. The residual vinyl groups on the PDVB cores efficiently captured the oligomers and monomers during

the second-stage precipitation polymerization to result in a highly crosslinked core and a lightly crosslinked shell with different functional groups in the absence of any second-initiated polymer particles.

References

- Peng, X. G.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. *J Am Chem Soc* 1997, 119, 7019.
- Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv Polym Sci* 1991, 100, 31.
- Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. *Science* 1997, 275, 1458.
- Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J Am Chem Soc* 1986, 108, 2869.
- Dan, N.; Tirrell, M. *Macromolecules* 1993, 26, 4310.
- Belder, G. F.; ten Brinke, G.; Hadziioannou, G. *Langmuir* 1997, 13, 4102.
- Jordan, R.; Graf, K.; Riege, H.; Unger, K. K. *J Chem Soc Chem Commun* 1996, 1025.
- Deutch, H. P.; Binder, J. *J Chem Phys* 1991, 94, 2294.
- Prucker, O.; Rühle, J. *Macromolecules* 1998, 31, 592.
- Wittmer, J. P.; Cates, M. E.; Johner, A.; Turner, M. S. *Europhys Lett* 1996, 33, 397.
- O'Callaghan, K. J.; Paine, A. J.; Rudin, A. *J Polym Sci Part A: Polym Chem* 1995, 33, 1849.
- Laus, M.; Lelli, M.; Casagrande, A. *Polymer* 1996, 37, 343.
- Laus, M.; Lelli, M.; Casagrande, A. *J Polym Sci Part A: Polym Chem* 1995, 33, 1849.
- Okubo, M.; Ikegami, K.; Yamamoto, Y. *Colloid Polym Sci* 1989, 267, 193.
- Romak, T. J.; Maury, E. E.; Desimone, J. M. *Macromolecules* 1995, 28, 912.
- Sosnowski, S.; Gadainowski, M.; Slomkowski, S. *Macromolecules* 1996, 29, 4556.
- Tai, E. F.; Caskey, J. A.; Allison, B. D. *J Polym Sci Part A: Polym Chem* 1986, 24, 567.
- Li, K.; Stöver, H. D. H. *J Polym Sci Part A: Polym Chem* 1993, 31, 3257.
- Li, W. H.; Stöver, H. D. H. *Macromolecules* 2000, 33, 4354.
- Bai, F.; Yang, X. L.; Zhao, Y. Z.; Huang, W. Q. *Polym Int* 2005, 54, 168.
- Li, W. H.; Stöver, H. D. H. *J Polym Sci Part A: Polym Chem* 1997, 37, 2899.
- Ober, C. K.; Hair, M. C. *J Polym Sci Part A: Polym Chem* 1987, 25, 1395.
- Horak, D.; Krustufak, M.; Spervack, J. *J Polym Sci Part A: Polym Chem* 2000, 38, 653.
- Wang, Z. H. In *Handbook for Analytical Chemistry*; Ke, Y. K.; Dong, H. R., Eds.; Chemical Industry: Beijing, 1998; Part III, p 946.