

Preparation of Monodispersed Hollow Polymer Particles by Seeded Emulsion Polymerization under Low Emulsifier Conditions

Cai-Deng Yuan,^{1,2} Ai-Hua Miao,¹ Jian-Wei Cao,¹ Yong-Shen Xu,¹ Tong-Yu Cao¹

¹Department of Polymer Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China

²School of Materials Science and Engineering, Tianjin University, Tianjin 300072, People's Republic of China

Received 30 January 2005; accepted 28 March 2005

DOI 10.1002/app.21971

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In a low emulsifier system, the MMA-BA-MAA copolymer emulsions were prepared as seed latices and the seeded emulsion polymerization of MMA-MAA-DVB was consequently carried out to prepare carboxylated core particles. The hydrophobic shell was then synthesized onto the core using styrene, acrylonitrile, and divinylbenzene as comonomers. The hollow latex particles were obtained by alkalization treatment of the core-shell latex particles. The effects of the feeding rate of monomer mixture, contents of emulsifier SDBS and crosslinking agent DVB, and ratio of the monomers during the core stage and shell stage on the morphology and volume expansion of the latex

particles were investigated. The results show that the monodispersed hollow latex particles with large size can be obtained when the feeding rate is 0.1 g/min, SDBS content is 0.15 and 0.2 wt % during the core stage and shell stage, respectively, DVB contents are 1% during the preparation of shell copolymers, and the monomer ratio of the core particle to shell layer is 1 : 8. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1505–1510, 2005

Key words: emulsion polymerization; core-shell polymers; latices; morphology; particle size distribution

INTRODUCTION

The interest in hollow polymer particles has steadily increased over the past several decades owing to their potential applications in special coatings^{1–3} or pigment,⁴ medicine control release, drug delivery or drug targeting systems,⁵ personal care formulation (such as sunscreen compositions),⁶ etc. Unlike homogeneous and solid particles, hollow polymer particles have hollows (air layers) inside the particles, and thus they have a huge interface between air and polymer particles, which have largely different refractive indexes of light. As a result, the scattering of the light occurs, and the opacity and shielding property of the coating greatly increase. Therefore, hollow polymer particles are utilized as an opacifying agent or a white pigment with excellent optical properties such as opacity and whiteness.^{7,8}

The synthetic methods leading to hollow polymer particles have been extensively investigated. One of the earliest processes for making hollow latex particles was developed in the laboratory of Rohm and Hass Co.^{9–13} Their concept involved making structured par-

ticles with core-shell morphology as precursors of end-hollow particles. Above all, the core polymer is carboxylated, and then the ionization of the carboxylated core with base under the appropriate temperature conditions expands the core by osmotic swelling to produce the hollow particles with water in their interior. A comprehensive review has been reported to summarize the preparations, properties, and applications of hollow latex particles,¹⁴ in which the osmotic swelling method and the hydrocarbon encapsulation technology have been introduced in detail. In fact, the process mentioned above is a kind of osmotic swelling method. W/O/W emulsion polymerization was also used to manufacture the hollow particles,¹⁵ in which the aqueous cores encapsulated by organic monomers were dispersed in aqueous medium and then the polymerization led to polymer particles with aqueous pores. The selection of emulsifiers is critical for the W/O/W system and it is quite difficult to prepare the monodispersed particles. The particle size and its distribution of hollow microspheres are the key parameters for applications, so control of the particle morphology has always been the focus in the field.

In the present work, the monodispersed hollow polymer latex particles with large size were prepared by multistage seeded emulsion polymerization. First, a seed emulsion with very low solid content was synthesized (called seed stage); and then the core latex

Correspondence to: C.-D. Yuan (cdyuan@tju.edu.cn).

particles were prepared by seeded emulsion polymerization on the basis of the seed (called core stage); the core-shell latex particles were obtained subsequently via seeded emulsion polymerization by using core particles as seed (called shell stage); and finally, the hollow polymer particles were produced by alkalization treatment to the above core-shell latex particles. The most important characteristic of the study is that the emulsifier dosage is much lower than its CMC, both in the seed stage and in the core stage, so the nucleation and growth of the particles are under micelle-free conditions in the whole reaction process, therefore, the homogeneous nucleation is predominant in the polymerization. The results show that micelle-free emulsion polymerization is very effective in controlling the hollow size, particle diameter, and their distributions.

EXPERIMENTAL

Materials

Styrene (St), methyl methacrylate (MMA), methacrylic acid (MAA), *n*-butyl acrylate (BA), and acrylonitrile (AN) were purified by distillation under reduced pressure in a nitrogen atmosphere and were stored in a refrigerator. Divinylbenzene (DVB) was used as crosslinking comonomer without preliminary purification. Ammonium persulfate (APS, 98.0%) and sodium dodecylbenzene sulfonate (SDBS) as initiator and surfactant, respectively, were also used without preliminary purification. NaOH was used as received. RuO₄ was used as a staining agent for the transmission electron microscope (TEM) observations. Distilled water was used.

Preparation of hollow polymer particles

Preparation of core-shell latex particles

The emulsion copolymerization was conducted in a four-neck round-bottom flask equipped with a mechanical stirrer, reflux condenser, feeding device, and nitrogen gas inlet system. The expected core-shell latex particles were prepared by seeded emulsion copolymerization according to the recipe in Table I. Seed latices were first prepared to provide control over the particle size. Core polymers were synthesized by continuous addition of the corresponding monomer mixture and aqueous solution of APS and SDBS to the seed latex in 5–6 h. Shell polymers were synthesized similarly, in which the core latex was used as seed and the feeding time was about 3–4 h.

Alkalization treatment

The latex with core-shell structure was charged into a one-neck round-bottom flask equipped with a stirrer,

TABLE I
Recipe for Seed Latex, Core Latex, and Shell Latex

Components	Seed latex (g)	Core latex (g)	Shell latex (g)
MMA	5.5	23.0	—
MAA	0.56	10.0	—
BA	6.5	—	—
St	—	—	150.0
AN	—	—	50.0
DVB	—	0.165	2.0
APS	1.0	0.281	1.6
SDBS	0.06	0.0485	0.4
Seed latex	—	50.0	—
Core latex	—	—	245.0
Distilled water	500.0	250.0	110.0
Temperature/°C	80	80	75

followed by alkalization treatment, which was carried out through the addition of a solution of sodium hydroxide to achieve pH 9. The flask was then situated into an oil bath at 100 °C, where it was stirred for 2.5 h. Finally, the flask was taken out from the oil bath and cooled to room temperature.

Latex characterization

The particle size (diameter in all cases) was obtained by nanosizer (BI-90 plus, Brookhaven) and the particle morphology was examined by TEM (H-800, Hitachi) in which RuO₄ was used as a staining agent.

RESULTS AND DISCUSSIONS

Effect of SDBS amount on morphology of hollow particles

The emulsifier SDBS plays a very important role in hollow particle preparation. In the seed stage and core stage, the dosage of SDBS should be lower than its CMC ($\sim 22.8 \times 10^{-4} \text{ mol L}^{-1}$).¹⁵ Thus, the nucleation in the seed stage was mainly through homogeneous nucleation. In other words, there were no micelles in the emulsion and the latex particles were formed and stabilized mostly by carboxylic group from unsaturated carboxylic monomer. With the growing of the latex particles, more surfactant was needed to stabilize the particles, so SDBS should be supplied gradually. In the core and shell stages, it is very important to feed more SDBS slowly and evenly. If the SDBS dosage is too high, new latex particles will be formed. As a consequence, this finally influenced both the structure and the monodispersity of the hollow particles.

As seen in Figure 1(d), the monodispersed hollow particles can be obtained when the emulsifier SDBS content is 0.15% (weight ratio to monomer, the same below) and 0.2% during the core and shell stages, respectively. When the emulsifier content becomes

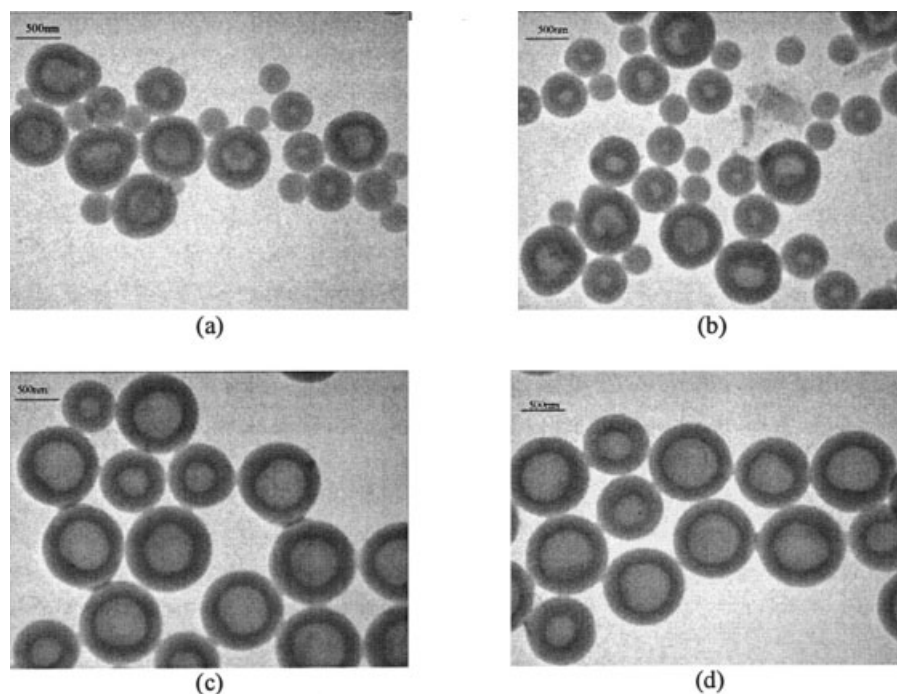


Figure 1 TEM images of hollow latex particles from different SDBS dosages during core stage and shell stage, respectively. (a) Core stage: 0.4%, shell stage: 0.4%; (b) core stage: 0.3%, shell stage: 0.3%; (c) core stage: 0.2%, shell stage: 0.2%; (d) core stage: 0.15%, shell stage: 0.2%.

higher during the core stage, new particles will be formed, finally leading to smaller hollow particles [Fig. 1(a–c)]. From the TEM images it can be concluded that in the core stage when the SDBS dosage is 0.15%, there are no micelles in the system and no new particles are formed. For the same reason, when the emulsifier dosage is higher than 0.2% in the shell stage, new particles will be formed, leading to smaller particles with no hollow structure [Fig. 1(a,b)]. Certainly, if the SDBS dosage is too low, coagulation of the particles will occur.

Effect of monomer feeding rate during carboxylated core copolymer formation

A great number of the new latex particles are produced when the feeding rate of monomer mixture is too fast during the core stage. The TEM images in Figure 2 demonstrate the characteristics of the hollow particles obtained at various feeding rate of the core monomer mixture.

As seen in Figure 2, with the decrease in monomer feeding rate, the particle size distribution of hollow polymer particles becomes narrower. As mentioned above, the emulsifier dosage in the core stage ought to be much lower than its CMC and the carboxylic monomer can play an important role in nucleation and stabilization. If the monomer feeding rate is too high in the core stage, the concentration of hydrophilic monomer with carboxylic group will be high enough

to form new particles, leading to the broader distribution of particle size. In Figure 2(a–e), we can find the bimodal or trimodal distribution for particle size, but in Figure 2(f), the particles are much larger (ca. 600 nm by TEM, ca. 900 nm of hydrodynamic diameter by nanosizer) and more monodispersed, which was synthesized under a low monomer feeding rate such as 0.1 g/min.

Effect of crosslinking agent amount on formation of hollow polymer latex particles

The addition of crosslinking agent (DVB) is necessary during the formation of shell copolymers onto the core latex particles. A proper dosage of crosslinking agent will improve the heat resistance and solvent resistance as well as the antiblocking property of the coatings. The effect of DVB content on morphology of hollow polymer particles is shown in Figure 3.

It can be concluded from Figure 3 that the particle size of the hollow latex particles and corresponding hollow percentages (volume) increase with the decrease in the content of DVB. That is to say, the enhanced swelling of the core-shell latex particle during the alkalization treatment will result in the increase in hollow percentages after water volatilization. The movement of the molecules or segments containing $-\text{COO}^-$ groups is critical to the formation of the hollow structure. The molecules or segments containing $-\text{COO}^-$ groups move toward the outside of the latex

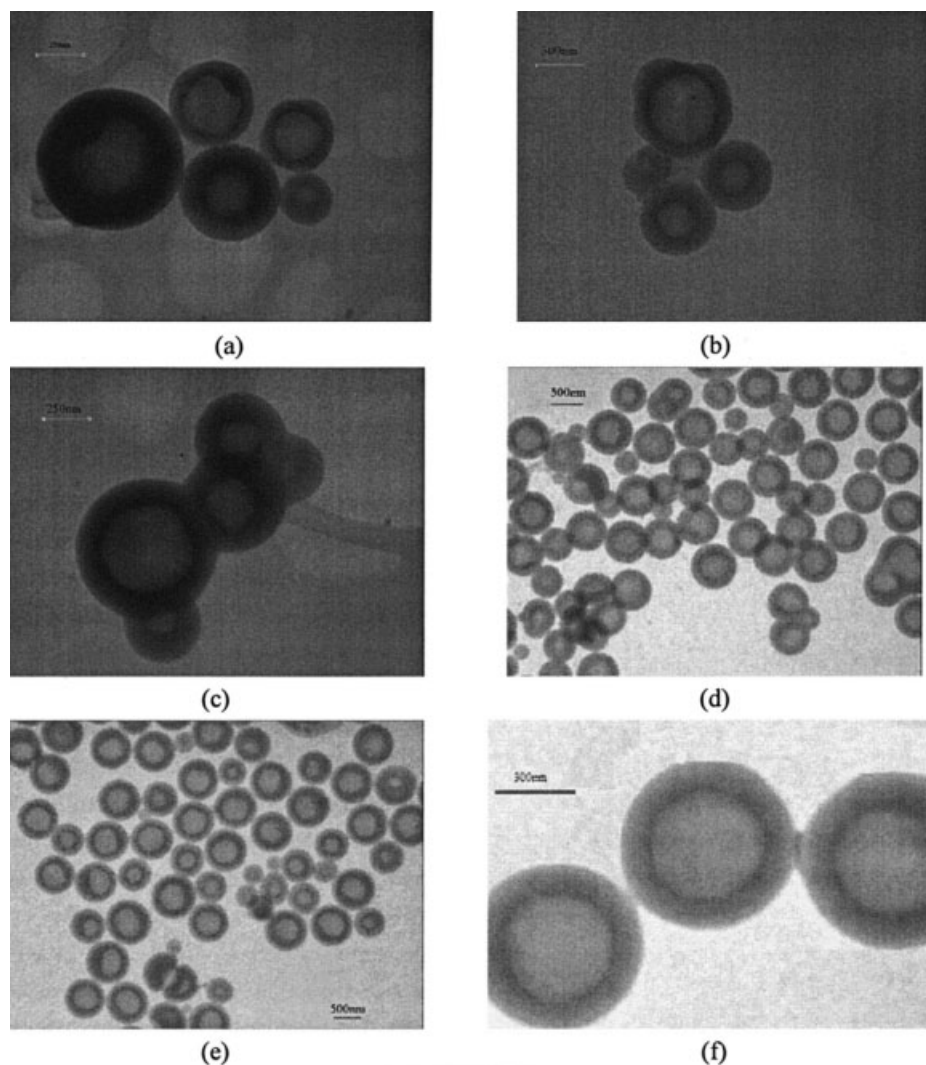


Figure 2 TEM images of hollow polymer particles under different monomer feeding rate in core stage. (a) 0.4 g/min; (b) 0.3 g/min; (c) 0.25 g/min; (d) 0.2 g/min; (e) 0.15 g/min; (f) 0.1 g/min.

particles while the alkaline solution penetrates into inside of the particles, swells, and neutralizes the core polymers when the crosslinkage of shell polymer is small. Consequently, the latex particles contain much water and electrolytes inside the particles and the volumes expand. But the increase of the crosslinkage weakens or even prevents the transfer of the molecules or segments of the polymers containing COO^- groups and finally just small pores form, or even no pores, extremely just the solid structures form inside of the particles after alkalization treatment.

The results in Figure 3 also show that the shape of the hollow particles is not regular when the contents of crosslinking agent decline to 0.8 and 0.5%, which results from the reduction of T_g of the shell polymers. Thus, it is necessary to keep the crosslinking agent at an appropriate level to assure both the regular round shape and large size of the hollows.

Effect of core-shell monomer ratio on morphology of hollow latex particles

Table II and TEM images in Figure 4 demonstrate the characteristics of the hollow particles at different shell thickness under different weight ratios of the core monomers to shell monomers.

It can be seen from Table II and Figure 4 that the volume expansion and voidage decline with the decrease in weight ratio of the core monomer to the shell monomer. This is because the shell thickness increases with the decrease in the core/shell ratio so that the alkaline solution becomes more difficult to diffuse into the interior of the core/shell particles and the segments with $-\text{COO}^-$ groups are wrapped tightly with the crosslinked shell. As a result, the movement of the molecules or segments with $-\text{COO}^-$ groups toward the outside and the swelling of the cores become more difficult as well. By contrast, when the core/shell ratio

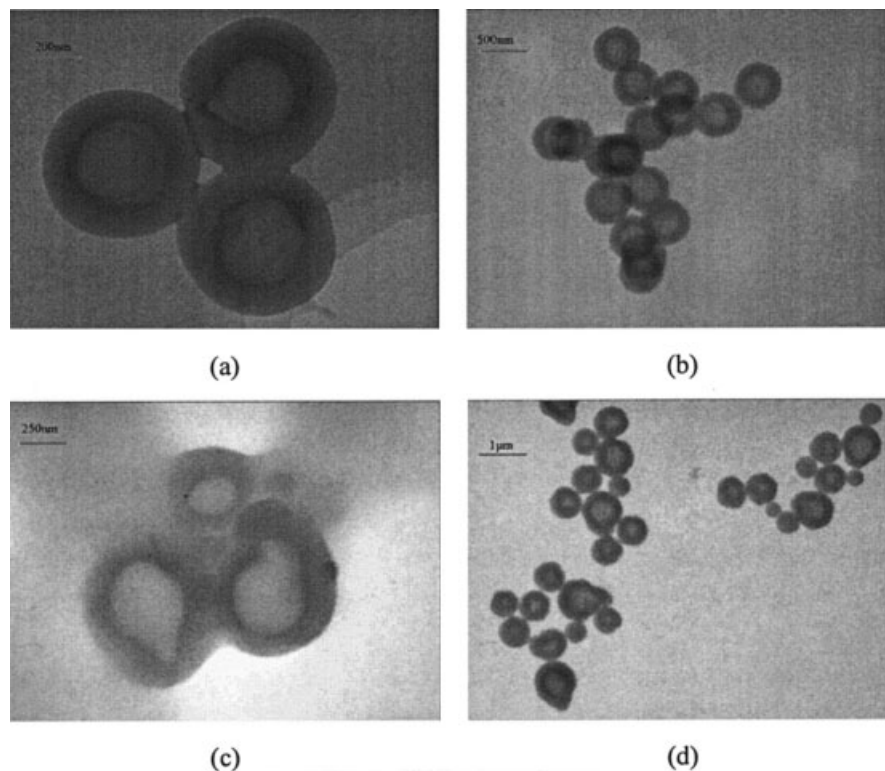


Figure 3 Influence of DVB content on morphology of hollow latex particles. DVB content (weight percentage to total shell monomer): (a) 1.5%; (b) 1.0%; (c) 0.8%; (d) 0.5%.

is 1:8 the hollow latex particles obtained keep a more preferable balance between the rigidity of the shell polymers and the hollow percentages.

CONCLUSIONS

Shell emulsion copolymerization of St, AN, and DVB onto poly (MMA-MAA-DVB) seeds was conducted, and the latex particles obtained were subjected to an alkalization treatment to form hollows. The results show that it is possible to obtain uniform hollow latex particles with large size when the MAA amount in the core copolymer achieves 30%(wt) via emulsion polymerization. During the whole polymerization process,

the feeding rate of monomer mixture, emulsifier content, crosslinking agent content, and ratio of the monomers during the core and shell polymer preparation are the main factors that affect the formation of specific morphology of the hollow particles. To obtain the uniform hollow latex particles with large size, the starve feeding technique should be adopted, the monomer feeding rate should be 0.1 g/min, and the optimum SDBS content should be 0.15 wt % and 0.2% during the preparation of the core polymer and shell polymer, respectively. The application of crosslinking agent is necessary during the formation of shell copolymers and the optimum content of DVB is 1.0%. The hollow latex particles obtained with core/shell mono-

TABLE II
Hollow Particle Characteristics under Different Core/Shell Monomer Ratios

Core/shell monomer ratio	D_p (nm)	D_{PS} (nm)	ΔV_s (%)	D_p^{TEM} (nm)	D_H (nm)	Voidage (%)
1 : 4	550.0	864.3	288.1	750.1	500	29.6
1 : 6	570.1	715.3	97.5	675.3	375	17.1
1 : 8	601.4	700.3	57.9	640	320	12.5
1 : 10	930.5	1000.1	24.2	625	250	6.4

Note. D_p , the hydrodynamic diameter of the core/shell latex particles determined by nanosizer. D_{PS} , the hydrodynamic diameter of the alkali-swollen particles determined by nanosizer. ΔV_s , the volumetric expansion of the swollen particles, defined as $(D_{PS}^3 - D_p^3)/D_p^3$. D_p^{TEM} , the diameter of the alkali-swollen particles determined by TEM. D_H , the void diameter of hollow particles determined by TEM.

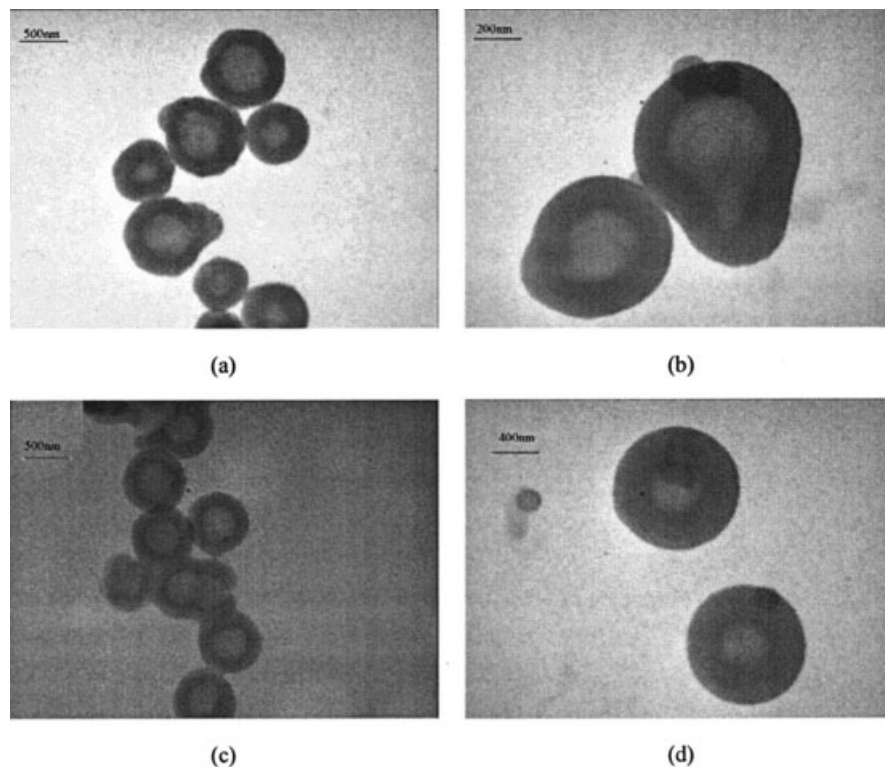


Figure 4 TEM images of the hollow particles prepared under different core/shell monomer ratios. Core/shell (weight): (a) 1 : 4; (b) 1 : 6; (c) 1 : 8; (d) 1 : 10.

mer ratio of 1 : 8 are monodispersed and keep a more preferable balance between the rigidity of the shell polymers and hollow percentages.

References

1. Fasano, D. M. Eur Pat. 0497507 (1992).
2. McDonald, C. J.; Bouck, K. J.; Chaput, A. B.; Stevens, C. J. *Macromolecules* 2000, 33, 1593.
3. Kong, X. Z.; Kan, C. Y.; Li, H. H.; Yu, D. Q.; Yuan, Q. *Polym Adv Technol* 1997, 8, 627.
4. Kawashima, N.; Sakurai, F.; Tadenuma, H. U.S. Pat. 4,972,000 (1990).
5. Pichot, C.; Delair, T.; Elaissari, A. In *Polymeric Dispersions: Principles and Applications*; Asua, J. M., Ed.; Kluwer Academic: The Netherlands, 1997; p 515.
6. Chang, C. J.; Jones, C. E.; Weinstein, B. U.S. Pat. 6,384,104 (2002).
7. Toda, H.; Takagishi, Y.; Kaino, M. U.S. Pat. 5,360,827 (1994).
8. Hoshino, F.; Nakano, M.; Someya, K.; Morita, J.; Yanagihara, T. U.S. Pat. 5,216,044 (1993).
9. Kowalski, A.; Vogel, M.; Blankenship, R. M. U.S. Pat. 4,427,836 (1984).
10. Kowalski, A.; Vogel, M.; Blankenship, R. M. U.S. Pat. 4,468,498 (1984).
11. Kowalski, A.; Vogel, M. U.S. Pat. 4,469,825 (1984).
12. Blankenship, R. M.; Kowalski, A. U.S. Pat. 4,594,363 (1986).
13. Kowalski, A.; Vogel, M. U.S. Pat. 4,880,842 (1989).
14. McDonald, C. J.; Devon, M. J. *Adv Colloid Interface Sci* 2002, 99, 181.
15. Kim, J. W.; Joe, Y. G.; Suh, K. D. *Colloid Polym Sci* 1999, 277, 252.
16. Bakshi, M. S.; Sachar, S.; Mahajan, N.; Kaur, I.; Kau, G.; Singh, N.; Sehgal, P.; Doe, H. *Colloid Polym Sci* 2002, 280, 990.