Macromolecular Research, Vol. 16, No. 4, pp 329-336 (2008)

In-Situ Synthesis of PS/(-)Silica Composite Particles in Dispersion Polymerization Using An (±) Amphoteric Initiator

Deok Ryul Hwang, Jinho Hong, Jeongwoo Lee, and Sang Eun Shim*

Department of Chemical Engineering, Inha University, 253 Yonghyundong, Namgu, Incheon 402-751, Korea

Received October 29, 2007; Revised February 5, 2008; Accepted February 11, 2008

Abstract: Core/shell (±)PS/(-)silica nanocomposite particles were synthesized by dispersion polymerization using an amphoteric initiator, 2,2′-azobis [*N*-(2-carboxyethyl)-2,2-methylpropionamidine] ($HOOC(CH_2)_2HN(HN=)C(CH_3)_2CN=NC(CH_3)_2C(=NH)NH(CH_2)_2COOH$), VA-057. Negatively charged (-6.9 mV) silica was used as the stabilizer. The effects of silica addition time and silica and initiator concentrations were investigated in terms of polymerization kinetics, ultimate particle morphology, and size/size distribution. Uniform hybrid microspheres with a well-defined, core-shell structure were obtained at the following conditions: silica content = 10-15 wt% to styrene, VA-057 content=above 2 wt% to styrene and silica addition time=0 min after initiation. The delay in silica addition time retarded the polymerization kinetics and broadened the particle size distribution. The rate of polymerization was strongly affected by the silica content: it increased up to 15 wt% silica but then decreased with further increase in silica content. However, the particle size was only marginally influenced by the silica content. The zeta potential of the composite particles slightly decreased with increasing silica content. With increasing VA-057 concentration, the PS microspheres were entirely coated with silica sol above 1.0 wt% initiator.

Keywords: polystyrene, silica, colloids, dispersion polymerization, core-shell.

Introduction

Recently, the synthesis of polymer/inorganic composite particles has received much attention because such hybrid particles can possess combined properties of both incorporated inorganic materials and base polymers. Furthermore, the combined materials exert much enhanced mechanical, chemical, thermal, electrical, and optical properties due to their unique 3-dimentional structure.[1-3] Accordingly, many results have been presented about the synthesis and properties of colloidal organic/inorganic composite materials. Various inorganic materials have been employed, including titanium dioxide,[4] copper oxide,[5] magnetic oxide,[6] aluminum hydroxide,[7] alumina,[8] clay,[9] carbon black[10] and so on. Among them, silica is the most studied model system since it has a long-standing history as the reinforcing filler in classical plastic or rubber materials. Currently, silica/polymer hybrid particles find diverse applications in bio-materials and structural materials in aerospace, electronics, and sensors.

These polymer/silica composite particles are generally produced by the incorporation of colloidal silica at the beginning of various heterogeneous polymerizations such as conventional emulsion, miniemulsion, soap-free emulsion, and dispersion polymerization.[11-16]

In such processes, silica is chemically or physically manipulated to form a shell or core layer for a desired purpose. In synthesizing well-defined controllable core/shell structure of silica composite particles, chemistry between silica surface and host polymer is important.

In order to improve the encapsulation efficiency, *i.e.*, compatibility, the surface of silica particles is often modified by using hydrophobic silane coupling agents[17,18] since hydrophobic vinyl monomers are generally used in heterogeneous polymerizations in an aqueous phase. In such cases, surface-modified colloidal silica is embedded in the composite particles, resulting in silica as the core. By utilizing the negative surface charge of silica particles, a positive surface charge is endowed to the polymer particles to maximize an electrostatic attraction between silica sol and polymer colloids. For this method, a cationic initiator, azobisisobutyramidine dihydrochloride, has been successfully used for the capsulation of silica particles by dispersion[13,19] or emulsion polymerization.[20] The use of cationic initiator drastically increases the silica adsorption efficiency up to 40 wt% based on polymer. If there is no electrostatic attraction by using a neutral initiator, a negligible amount of silica, *ca* 1 wt%, is adsorbed. Furthermore, severely coagulated particles in a resin form is obtained when a negative initiator is

---

*Corresponding Author. E-mail: seshim@inha.ac.kr

used due to electrostatic repulsion between silica and polymer particles.[13] Additionally, the use of basic comonomers such as 4-vinylpyridine[12,21] and 1-vinylimidazole[22,23] has been known to form a strong acid-base interaction with acidic (due to hydroxyl groups) silica particles, which substantially increases silica adsoprtion efficiency on the surface of ultimate polymer particles.

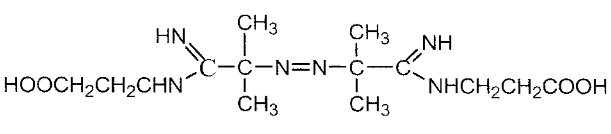
Recently, amphoteric initiators have been employed in emulsion polymerization to produce monodisperse polystyrene (PS) and poly(methyl methacrylate) microspheres in aqueous media.[24-29] In these articles, the amphoteric initiators bearing both positively and negatively ionizable groups have been effectively used for stabilizing polymer colloids.

We have found that an amphoteric initiator, 2,2′-azobis [*N*-(2-carboxyethyl)-2,2-methylpropionamidine] ($HOOC(CH_2)_2HN(HN{=})C(CH_3)_2CN{=}NC(CH_3)_2C({=}NH)NH(CH_2)_2COOH$), VA-057, is completely soluble in methanol and used this type of initiator in dispersion polymerization of styrene.[30] In this study, we extended the utilization of the amphoteric initiator to synthesize silica/PS hybrid microspheres in dispersion polymerization which is a now widely used method to produce micron-sized polymer micropheres.[31,32] The effects of addition time of silica and the concentrations of silica and initiator are investigated in terms of polymerization kinetics, ultimate particle morphology, and size/size distribution.

Experimental

Materials. Styrene (99%, Kanto Chemical, Japan) was purified using a basic inhibitor removal column (Aldrich, USA) and stored at -5 °C prior to use. 2,2′-Azobis [*N*-(2-carboxyethyl)-2,2-methylpropionamidine] (VA-057, Wako Chemicals, Japan) were used as initiator without further purification. The chemical structure of VA-057 is shown in Scheme I. Reagent grade methanol (Samchun, Korea) was used as the polymerization medium. Negatively charged colloidal silica (NANOS-AM20) having a zeta potential of -6.9 mV at pH 7.0 (diluted in distilled and deionized water), an average diameter of 25 ± 5 nm, and a specific surface area of 150 m^2/g was kindly donated from ABCNanoTech Co., Korea and used without any surface modification. The as-received silica sol dispersed in water (20 wt%) had pH of 10.0.

Polymerization. The dispersion polymerization of styrene with silica sol was conducted in methanol with VA-057 as an initiator. 20 g methanol was poured into the reaction vessel and 2 g styrene, 10 wt% relative to the medium, was charged. The various amounts of silica sol were added to the vial. The net amount of silica was varied from 5 (0.1 g) - 20 (0.4 g) wt% relative to styrene. In some cases, the preweighed silica was added after the initiation of polymerization in order to find optimum time for silica addition. When the temperature of reactants in the reactor reached 60 °C, the VA-057 dissolved in aliquot of methanol was added to the reaction system. The amount of VA-057 was varied from 0.5 to 3.0 wt% relative to styrene. The polymerization was carried out in 50 mL scintillation vial with the stirring at 300 rpm under nitrogen atmosphere at 60 °C. The recipe and the parameters are given in Table I. After completion of the polymerization, the colloidal solution was washed with methanol in order to remove unreacted species.



Scheme I. Chemical structure of VA-057.

Characterization. A Hitachi SEM (Scanning Electron Microscopy) S-4300 was used to observe the morphology of PS/silica composite particles. The number-average particle diameter (D_n) and the coefficient of variation (C_v) of particle diameter were measured by a particle size analyzer (LS230®, Beckman Coulter, USA). To measure the zeta-potential, the rinsed composite particles were redispersed in water (pH of nearly 7.0) and measurement was performed on a zeta-potential analyzer (Zetasizer4 1308, Malvern). The rinsed composite particles were dried in a vacuum oven and thermogravimetric analysis was performed on TGA Q50 (TA Instrument, USA). Conversion was measured gravimetrically and the rate of polymerization was achieved by taking the first-order derivative from the conversion vs time curve.

Results and Discussion

Addition Time of Silica. Basically, the adsorption phenomenon in this dispersion polymerization is ascribed to the electrostatic attraction between negative charges (-) on the surface of silica sol and both negative and positive charges (±) of the polymer microspheres. The surface charge of polymer particles originates from the reaction between the amphoteric initiator and propagating polymer chains, which further grow to stable polymer colloids. In series of experimental setup, key parameters which would affect the degree of silica adsorption on polymer particles were chosen, including the addition time of silica, concentration of silica sol, and the amount of the amphoteric initiator. The formulation with summarized results is listed in Table I.

First, the addition time of silica sol was varied from 0 to 60 min after dispersion polymerization was initiated. Zero means that silica was added to the polymerization system prior to initiation. In this investigation, the amount of silica was fixed at 12.5 wt% to styrene. When the silica sol is present before the polymerization starts, the conversion curve follows a typical dispersion polymerization kinetics. However, as the silica addition time is delayed after initiation, the polymerization rate becomes sluggish and the final conversion also decreases as seen in Figure 1. This can be understood in terms of the role of silica sol as a stabilizer in

Table I. Polymerization Parameters for the Synthesis of (-)Silica/(±)PS Composite Microspheres and Summarized Results

Run	Conc. of Silica (wt%)	Conc. of Initiator (wt%)	Addition Time of Silica (min)	D_n^a (μm)	C_v^b (%)
1	12.5	2	0	1.04	12.1
2	12.5	2	5	1.09	14.4
3	12.5	2	10	1.13	28.7
4	12.5	2	30	1.15	41.7
5	12.5	2	60	1.17	42.1
6	5	2	0	1.04	15.7
7	7.5	2	0	1.02	15.1
8	10	2	0	1.22	16.8
9(1)	12.5	2	0	1.04	12.1
10	15	2	0	0.91	17.0
11	20	2	0	0.91	18.2
12	12.5	0.5	0	0.99	22.4
13	12.5	1	0	1.09	15.1
12(1)	12.5	2	0	1.04	12.1
15	12.5	3	0	1.17	16.8

[a]Number-average diameter. [b]The coefficient of variation.

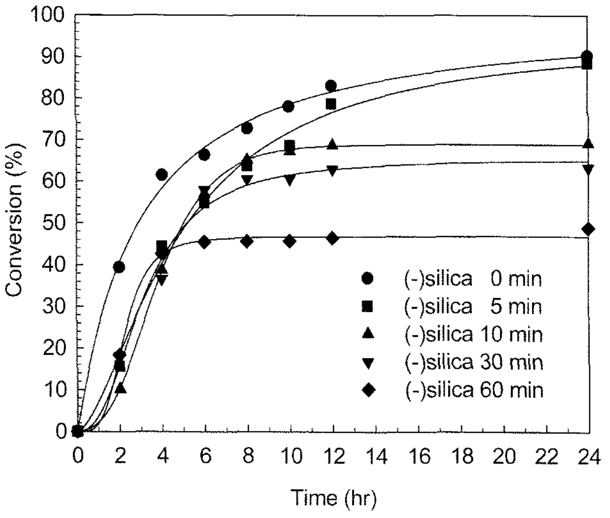


Figure 1. Effect of different addition times of (-)silica 12.5 wt% relative to styrene on the conversion of dispersion polymerization.

dispersion polymerization. When charged silica sol particles are present in the dispersion polymerization system, they adsorb on the forming polymer microspheres due to the columbic interaction, thereby the polymer particles are stabilized and further individually grow to discrete particles. If the external stabilizer is absent at the moment when growing oligomeric chains precipitate to form polymer particles, the stabilization is limited with the only aid of amphoteric initiator. In the lack of stabilization, primary polymer nuclei are destabilized and polymerization rate is retarded. If serious destabilization occurs, the particles undergo coagulation, finally leading to gelation. Dispersion polymerization is relatively more sensitive than other heterogeneous polymerizations to the reaction conditions such as the existence of oxygen in the reactor and the formulation of the ingredients. Especially, a slight change in the concentration of a single polymerization ingredient in the formulation turns out a dramatic variation in the uniformity of ultimate particles. Moreover, the retardation of polymerization rate especially in a nucleation stage causes the broadening of final particle size distribution.

In Figure 2, the SEM micrographs of the ultimate silica/PS hybrid microspheres are displayed in which the composite particles are prepared with different addition times of silica sol. When silica sol is present before nucleation, 0 and 5 min, fairly monodisperse composite particles are resulted. As the addition time of silica is delayed, small secondary particles are generated (10 min) and eventually the particle size becomes quite broad (30 and 60 min). The D_n/C_v of the particles are 1.04/12.1, 1.09/14.4, 1.13/28.7, 1.15/41.7, and 1.17 μm/42.1% for the addition time of silica, 0, 5, 10, 20, and 60 min, respectively. It is noted that the turbidity occurs at approximately 10–20 min after injection of the initiator. Therefore, it is evident that the particle size distribution becomes greatly broad when the silica sol is injected after initiation of the dispersion polymerization. In the cases of 30 and 60 min, the C_v's are 41.7 and 42.7%. In our previous study on the synthesis of positively charged silica/negatively charged PS hybrid particles by conventional emulsion polymerization initiated by potassium persulfate in water,

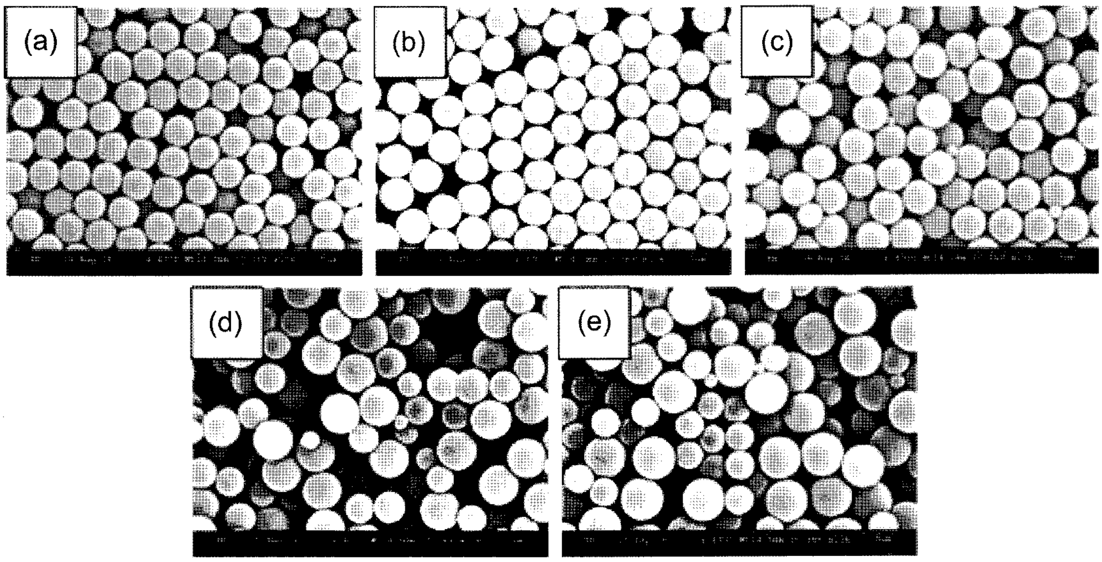


Figure 2. SEM micrographs of (-)silica coated PS microspheres prepared with different addition times of silica 12.5 wt% relative to styrene. (a) 0, (b) 5, (c) 10, (d) 30, and (e) 60 min.

the particle formation was significantly suppressed when silica sol was present in the beginning of polymerization, 0 min. In that case, collapsed particle morphology due to the lack of colloidal stability was obtained.[33]

The addition time of silica greatly affects conversion and particle size distribution, however it does not influence the adsorption efficiency as determined from TGA analysis (Figure 3). Based on the above results, the addition time of silica was determined to 0 min.

Varying Concentration of Silica. Polymerization was conducted in the presence of an increasing amount of silica from 5 to 20 wt% relative to styrene. Figure 4 represents the effect of the concentration of silica on the polymerization kinetics. With 5 wt% silica, the conversion is very low so that the final conversion reaches only 38.9% at 24 h. Since silica acts as a stabilizer in this system, ordinary polymerization is not achieved at low concentration of silica due to the lack of colloidal stability in dispersion polymerization. Above 7.5 wt% silica, the final conversions exceed 90% at 24 h and the conversion tends to become greater with the amount of silica as shown in Figure 4(a). Figure 4(b) shows the rate of dispersion polymerization with respect to the amount of silica. The lines in Figure 4(a) were achieved by fitting the experimental conversion data using the Marquardt–Levenberg algorithm in SimgaPlot®. Then, the rate of polymerization was calculated by taking the first-derivative of each curve from Mathematica®. At 5 wt% silica, the rate of polymerization is quite slow and it substantially increases with the amount of silica above 7.5 wt%. However, the rate of polymerization is reduced at 20 wt% silica since the nucleation is hindered by the possible aggregation of silica at a high concentration. Truly, the maximum rates of polymerization are 1.24×10^{-3}, 3.98×10^{-3}, 3.99×10^{-3}, 4.09×10^{-3}, 4.69×10^{-3}, and 3.52×10^{-3} mol/L·s for 5, 7.5, 10, 12.5, 15, and 20 wt% silica, respectively. In order to obtain the fastest polymerization, the optimal quantity of silica can be chosen from 12.5 to 15 wt% to styrene.

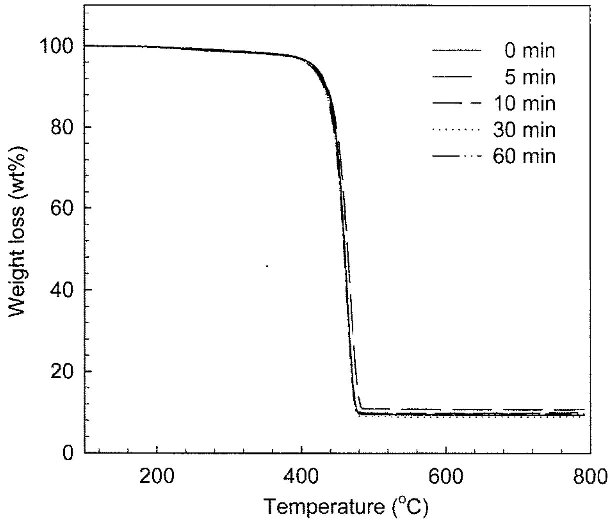


Figure 3. TGA thermograms of (-)silica/PS composite microspheres prepared with different addition times of silica 12.5 wt% relative to styrene.

The particle size distribution of the PS/silica composite particles prepared with an increasing amount of silica is shown in Figure 5. The distribution of the particles is unimodal and narrow for all concentrations of silica from 5 to 20 wt%, which suggests that (-) silica effectively serves as the stabilizer in dispersion polymerization initiated with the amphoteric initiator. The D_n/C_v of the particles are 1.04/15.7, 1.02/15.1, 1.22/16.8, 1.04/12.1, 0.91/17.0, and 0.91

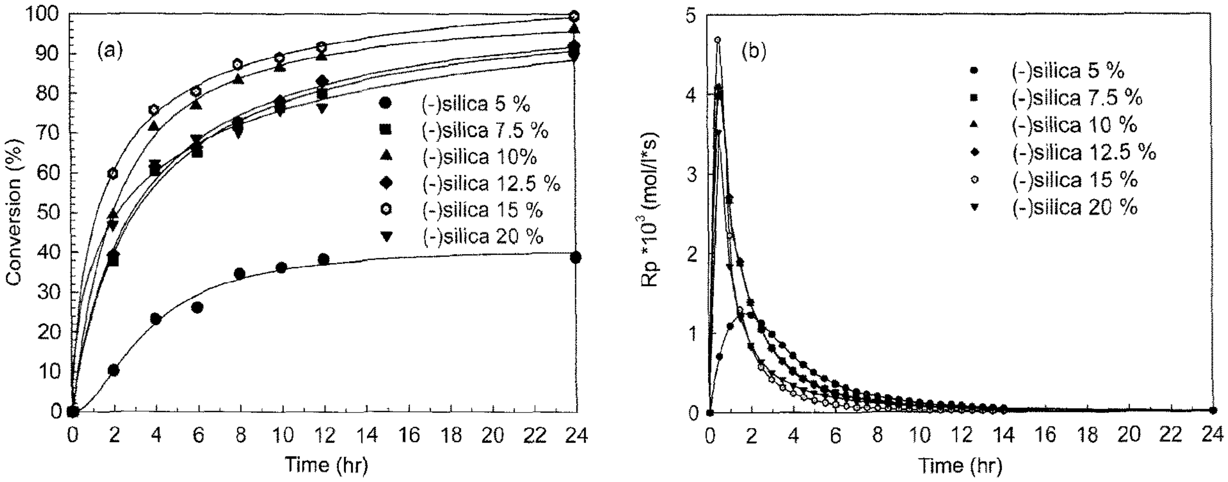


Figure 4. Effect of different concentrations of (-) silica relative to styrene on the (a) conversion and (b) rate of dispersion polymerization.

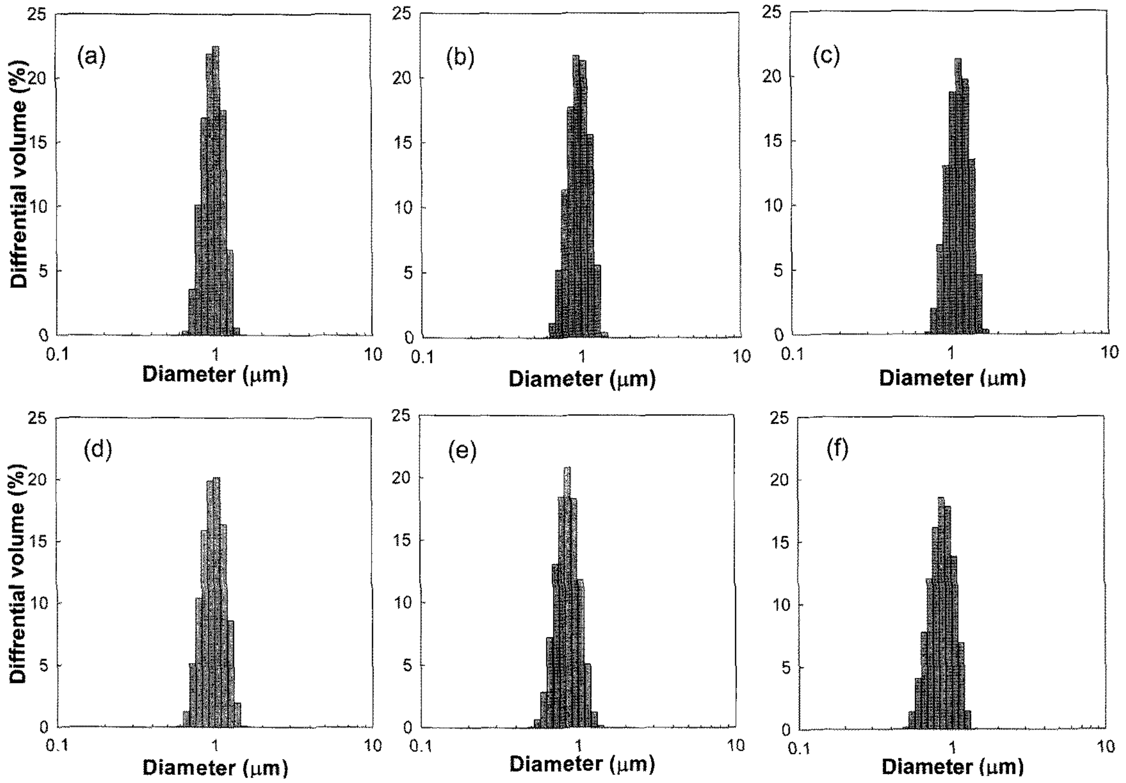


Figure 5. Particle size distribution of PS/(-)silica composite particles with different concentrations of silica injected after 0 min from the initiation; (a) 5, (b) 7.5, (c) 10, (d) 12.5, (e) 15, and (f) 20 wt% relative to styrene.

μm/18.2% for the concentration of silica, 5, 7.5, 10, 12.5, 15, and 20 wt%, respectively. The result indicates that the average size and uniformity of the composite particles are marginally influenced by the amount of silica as the stabilizer. The most common stabilizer used in dispersion polymerization is poly(vinylpyrrolidone; PVP) without doubt.[34] Paine *et al.*[35] have reported the size of PS decreases with an increasing amount of PVP to the power of -0.33, -0.36, and -0.27 for PVP with molecular weight of 10,000, 40,000, and 360,000 g/mol, respectively. Unlike PVP, the influence of the concentration of silica as the stabilizer on the variation of the size of particles is negligible in this system. In the case of PVP, PVP molecules serve as initiation sites enabling grafting reaction so that chemical grafting of PVP with polymer chains abruptly increases the molecular weight of growing oligomers which further results in the small particle size. On the other hand, the effect of the silica concentration on the size variation of the ultimate particles is marginal

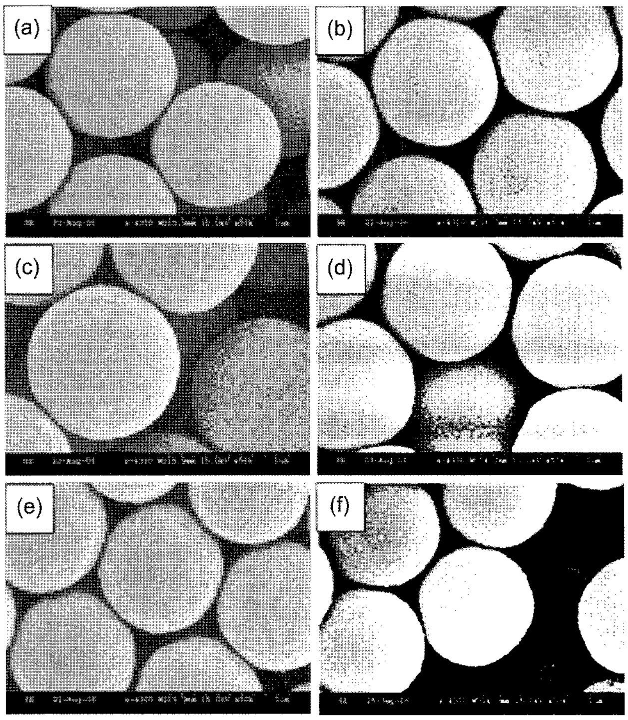


Figure 6. SEM micrographs of (-)silica coated PS microspheres prepared with different concentrations of silica injected after 0 min from the initiation; (a) 5, (b) 7.5, (c) 10, (d) 12.5, (e) 15, and (f) 20 wt% relative to styrene.

since silica particles exert only physical absorption.

Figure 6 depicts the morphology of the PS/silica composite particles prepared with an increasing amount of silica (refer to Supporting Information for a low magnification). The existence of colloidal silica particles adsorbed on the PS microspheres is evident for all hybrid microspheres. At 5 and 7.5 wt% silica contents, the surface coverage by silica is not complete so that some bare PS surfaces are observed. At 20 wt% silica, it is seen that the surface of PS microspheres is adsorbed by excess amount of silica. Therefore, the optimum range of silica content can be judged from 10 to 15 wt%, and preferably 10-12.5 wt% in order to achieve complete coverage of PS microspheres by silica particles. It is noted that the thickness of the silica shell is the same as the pristine silica particles, i.e., 25 nm.

Adsorption of (-)silica on (±)PS microspheres changes the surface nature of composite particles. The state of surface charge with the incorporated silica content is investigated by measuring the zeta potential of PS/silica hybrid particles suspended in water (Figure 7). The zeta potentials of bare silica sol and bare PS particles prepared by VA-057 in the absence of silica are -6.9 and +10.2 mV at pH 7.0, respectively. For measuring zeta potential of PS microspheres without silica, neat PS particles were prepared by conventional dispersion polymerization using 1 wt% VA-057 (0.1 g) and 10 wt% PVP (1 g) to styrene (10 g) in methanol (100 mL) at 60 °C for 24 h. With increasing silica amount from 5 to 20 wt%, the zeta potential steadily decreases from -2.0 to -4.7 mV. Since the zeta potential of silica sol is only -6.9 mV, that of composite particles changes within that limit.

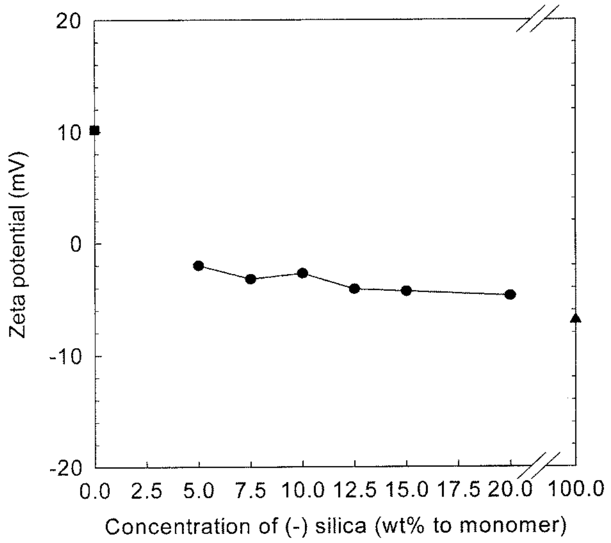


Figure 7. Zeta potential of PS/(-)silica composite particles with different concentrations of silica in methanol; (■) only PS particles, (●) PS/(-)silica composite particles, and (▲) only silica particles.

Varying Concentration of Initiator. Determined from the previous sections, the optimum condition for the synthesis of evenly (-)silica adsorbed uniform (±)PS microspheres is 12 wt% silica present at the beginning of polymerization. Here, the concentration of VA-057 initiator was changed from 0.5 to 3.0 wt% with respect to styrene. In Figure 8, polymerization kinetics in terms of the amount of initiator is demonstrated. As expected, the conversion with time increases with the amount of VA-057. At 0.5 and 1.0 wt% VA-057,

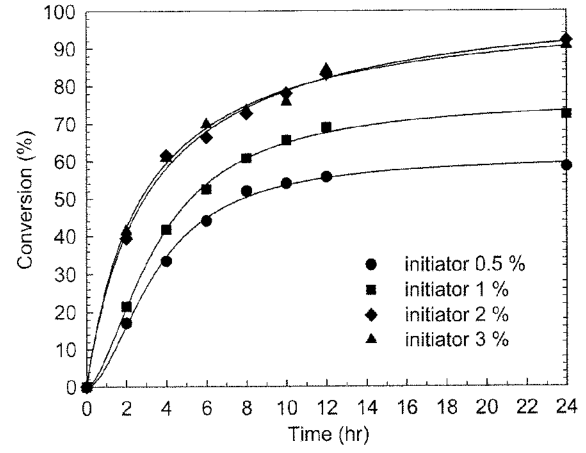


Figure 8. Effect of different concentrations of initiator on the conversion of dispersion polymerization of styrene/(-)silica. 12 wt% silica to styrene was added before the initiation of polymerization.

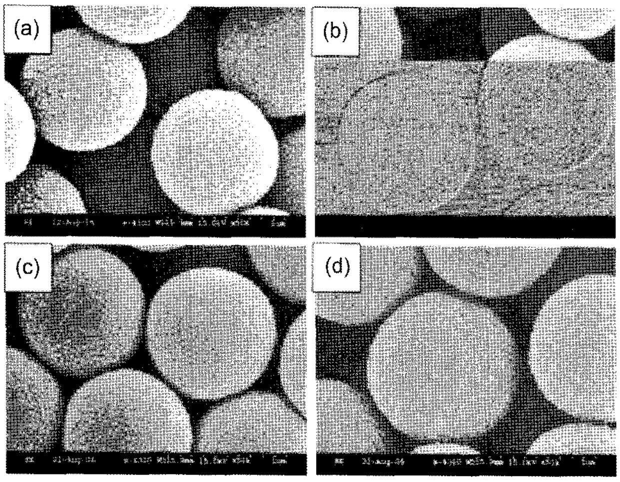


Figure 9. SEM micrographs of (-)silica coated PS microspheres prepared with different amounts of initiator; (a) 0.5, (b) 1.0, (c) 2.0, and (d) 3.0 wt% VA057. 12 wt% silica to styrene was added before the initiation of polymerization.

final conversions are quite low, 58.5 and 72.4% at 24 h, respectively. High conversions above 90% are obtained above 2 wt% VA-057. Above 2 wt% initiator, the polymerization kinetics shows a similar behavior. Therefore, 2 wt% VA-057 seems to be sufficient to achieve satisfactory conversion. Figure 9 presents the effect of VA-057 on morphology of silica (12.5%) adsorbed PS microspheres. At 0.5 wt%, the discrete silica sol particles on the surface of PS microspheres are clearly observed due to the incomplete coverage by silica due to insufficient surface charges on PS microspheres to attract silica particles. From 1.0 wt% VA-057, the PS microspheres are entirely adsorbed by silica sol particles leaving no bare PS surface. The D_n/C_v of the particles are 0.99/22.4, 1.09/15.1, 1.04/12.1, and 1.17 μm/16.8% for the concentration of VA-057, 0.5, 1.0, 2.0 and 3.0 wt% to styrene, respectively. The average diameter of the composite particles slightly increases with the initiator concentration, which is typical in dispersion polymerization. In case of high concentration of initiator, the molecular weight of oligomers in a nucleation stage becomes low, which reduces the number of primary particles. The small number of nuclei in turn grows to larger particles with the help of copious supply of monomer. Considering the conversion and morphology together, 2 wt% VA-057 is adequate to prepare well-defined (-)silica/(±)PS shell/core hybrid microparticles.

Conclusions

The core/shell (±)PS/(-)silica nanocomposite particles are synthesized by dispersion polymerization using an amphoteric initiator, 2,2′-azobis[*N*-(2-carboxyethyl)-2,2-methylpropionamidine] ($HOOC(CH_2)_2HN(HN{=})C(CH_3)_2CN{=}NC(CH_3)_2C({=}NH)NH(CH_2)_2COOH$), VA-057. It has been found that this water-soluble initiator completely dissolves in methanol. The PS microspheres having the amphoteric nature by means of VA-057 are synthesized and silica sol with negative surface charge (-6.9 mV) adsorbs on the growing PS microspheres for imparting colloidal stability. When the silica sol is present before the polymerization starts, the conversion curve follows a typical dispersion polymerization kinetics. However, as the silica addition time is delayed after initiation, the polymerization rate becomes sluggish and the final conversion also decreases since silica serves as the stabilizer in this system. Moreover, the retardation of polymerization rate especially in a nucleation stage causes broadening of final particle size distribution. When the concentration of silica is varied from 5 to 20 wt% to styrene, it is seen that the polymerization rate strongly depends on the amount of silica. At 5 wt% silica, the rate of polymerization is quite slow and it substantially increases with the amount of silica above 7.5 wt%. However, the rate of polymerization is reduced at 20 wt% silica due to the possible aggregation of silica at a high concentration. Since silica acts as a stabilizer, ordinary polymerization with high conversion over 90% is achieved above 7.5 wt% silica. The number-average diameter of the composite particles is 1.02±0.20 μm and the size and uniformity of the ultimate particles are marginally influenced by the amount of silica. Between 10 and 15 wt% silica, the complete coverage of PS microspheres by silica particles as a shell layer is attained. The zeta potential of the composite slightly decreases with the amount of silica. When the initiator concentration is increased from 0.5 to 3.0 wt% at a fixed amount of silica, 12.5 wt%, it has been found that the conversion with time increases with the amount of VA-057. High conversions above 90% are obtained above 2 wt% VA-057. Above 2 wt% initiator, the polymerization kinetics shows a similar behavior. From 1.0 wt% VA-057, the PS microspheres are entirely adsorbed by silica sol particles and the average diameter of the composite particles slightly increases with the initiator concentration, which is typical in dispersion polymerization.

Acknowledgement. This work was supported by Inha University Research Grant 2006.

References

(1) S. Yin, T. Sato, and A. M. El-Toni, *J. Colloid Interf. Sci.*, **300**, 123 (2006).
(2) Z. Zhong, Y. Yin, B. Gates, and Y. Xia, *Adv. Mater.*, **12**, 206 (2000).
(3) Y. Meng, D. Chen, and X. Jiao, *J. Am. Chem. Soc.*, **7**, 18 (2006).
(4) C. H. M. Caris, L. P. M. van Elven, A. M. van Herk, and A. L. German, *Br. Polym. J.*, **21**, 133 (1989).
(5) C. Huang, *J. Colloid Interf. Sci.*, **170**, 275 (1995).
(6) X. Li and Z. Sun, *J. Appl. Polym. Sci.*, **58**, 1991 (1995).
(7) H. T. Oyama, R. Sprycha, Y. Xie, R. E. Partch, and E. Matijevic, *J. Colloid Interf. Sci.*, **160**, 298 (1993).
(8) S. J. Park and E. Ruckenstein, *Polymer*, **31**, 175 (1990).

(9) X. Huang and W. J. Brittain, *Macromolecules*, **34**, 3255 (2001).

(10) M. Bakhshaee, R. A. Pethrick, H. Rashid, and D. C. Sherrington, *Polym. Commun.*, **26**, 185 (1985).

(11) E. Bourgeat-Lami and J. Lang, *J. Colloid Interf. Sci.*, **210**, 281 (1999).

(12) C. Barthet, A. J. Hickey, D. B. Cairns, and S. P. Armes, *Adv. Mater.*, **11**, 408 (1999).

(13) A. Schmid, S. Fujii, and S. P. Armes, *Langmuir*, **22**, 4923 (2006).

(14) I. Sondi, T. H. Fedynshyn, R. Sinta, and E. Matijevic, *Langmuir*, **16**, 9031 (2000).

(15) M. J. Percy, J. I. Amalvy, D. P. Randall, and S. P. Armes, *Langmuir*, **20**, 2184 (2004).

(16) F. Tiarks, K. Landfester, and M. Antonietti, *Langmuir*, **17**, 5775 (2001).

(17) E. Bourgeat-Lami and J. Lang, *J. Colloid Interf. Sci.*, **197**, 293 (1998).

(18) F. Corcos, E. Bourgeat-Lami, C. Novat, and J. Lang, *Colloid Polym. Sci.,* **277**, 1142 (1999).

(19) K. Yoshinaga, T. Yokoyama, Y. Sugawa, H. Karakawa, N. Enomoto, H. Nishida, and M. Komatsu, *Polym. Bull.*, **28**, 663 (1992).

(20) M. Chen, S. Zhou, L. Wu, S. Xie, and Y. Chen, *Macromol. Chem. Phys.*, **206**, 1896 (2005).

(21) M. J. Percy, C. Barthet, J. C. Lobb, M. A. Khan, S. F. Lascelles, M. Vamvakaki, and S. P. Armes, *Langmuir*, **16**, 6913 (2000).

(22) M. Chen, L. Wu, S. Zhou, and B. You, *Macromolecules*, **37**, 9613 (2004).

(23) M. Chen, S. Zhou, B. You, and L. Wu, *Macromolecules*, **38**, 6411 (2005).

(24) S.-J. Fang, K. Fujimoto, S. Kondo, K. Shiraki, and H. Kawaguchi, *Colloid Polym. Sci.*, **278**, 864 (2000).

(25) S.-J. Fang and H. Kawaguchi, *Colloid Polym. Sci.*, **280**, 984 (2002).

(26) S. Gu, H. Akama, D. Nagao, Y. Kobayashi, and M. Konno, *Langmuir*, **20**, 7948 (2004).

(27) S. Gu, S. Inukai, and M. Konno, *J. Chem. Eng. Jpn.*, **35**, 977 (2002).

(28) S. Gu, S. Inukai, and M. Konno, *J. Chem. Eng. Jpn.*, **36**, 1231 (2003).

(29) Y. Yamada, T. Sakamoto, S. Gu, and M. Konno, *J. Colloid Interf. Sci.*, **281**, 249 (2005).

(30) J. Lee, J. U. Ha, S. Choe, and S. E. Shim, *J. Colloid Interf. Sci.*, **298**, 663 (2006).

(31) H. Namgoong, D. J. Woo, and S. H. Lee, *Macromol. Res.*, **15**, 633 (2007).

(32) K. C. Lee and S. Y. Lee, *Macromol. Res.*, **15**, 244 (2007).

(33) J. Lee, C. K. Hong, S. Choe, and S. E. Shim, *J. Colloid Interf. Sci.*, **310**, 112 (2007).

(34) K. E. J. Barrett, *Dispersion Polymerization in Organic Media*, Wiley, London, 1975.

(35) A. J. Paine, W. Luymes, and J. McNulty, *Macromolecules*, **23**, 3104 (1990).