Korean J. Chem. Eng., 19(2), 318-323 (2002)

A Study on the Synthesis of Acrylic Composite Particles and Investigation of their Characterization

Sun-Ryong Lee and Soo-Duk Seul†

Department of Chemical Engineering, Dong-A University, 840, Hadan-dong, Saha-gu, Busan 604-714, Korea

(Received 12 February 2001 • accepted 15 September 2001)

Abstract−Core-shell latexes were synthesized by sequential emulsion polymerization of methyl methacrylate (MMA), styrene (St), and ethyl acrylate (EA) in the presence of anionic surfactant, and the characteristics of these latexes were evaluated. The core latex had to be synthesized carefully to avoid the formation of secondary particles. The sequential polymerization method adopted for this synthesis took advantage of stabilizing particles grown during shell polymerization. In core-shell latex polymerization, to suppress the generation of new particles and to minimize the gelation during the shell polymerization, the amount of surfactant (Sodium dodecyl benzene sulfonate: SDBS) should be reduced to the minimum, 0.01 wt% and 0.02 wt% of SDBS to amount of monomer, respectively, when the Polymethyl methacrylate (PMMA) and Polystyrene (PSt) core latexes are prepared. In addition, the monomer pre-emulsion method is better than monomer-add method. The core-shell structure for composite latex synthesized was demonstrated by Particle Size Analysis (PSA), Differential Scanning Calorimeter (DSC), Transmission Electron Microscope (TEM), formability of film, and hydrolysis under NaOH solution.

Key words: Core-shell, Latex, Polymethyl Methacrylate, Polystyrene, Sequential Emulsion Polymerization

INTRODUCTION

Latex materials in which a core of one polymer is surrounded by a shell of a second polymer are important in many different industrial applications. For example, those with core and shell polymers differing in their glass transition temperatures (Tg) may be used to modify the properties of latex paint. The core-shell latexes with polymer phases differing in pH sensitivity have been made to manufacture void-containing particles that can be used as opaquifiers in coatings [Devon et al., 1990; Blankenship, 1986].

All the earlier theoretical treatments of the emulsion polymerization of styrene [Kim et al., 1999, 2000; Park et al., 2000; Song et al., 1999] were based on the assumption that the particles were swollen homogeneously, i.e., there was no concentration difference throughout the particles, because styrene is miscible with polystyrene in all proportions.

But Williams et al. [1970, 1973, 1974] postulated that the polymerization occurred at near the surface of the monomer-swollen particle as the result of a monomer concentration gradient comprising a polymer-rich 'core' surrounded by a monomer-rich 'shell'. This core-shell polymerization morphology has been well known in systems that are inherently incompatible. However, in compatible systems this polymerization hypothesis has created controversial arguments.

Core-shell terminology is straightforward, indicating the locus for polymerization in a homopolymerization. In the composite pair system it is confusing since core-shell particle morphologies may be obtained during the polymerization by phase separation, in which case the morphology may be independent of the locus of polymerization.

Paxton [1969] investigated the soap adsorption characteristics of the surface of the PS-PMMA (polystyrene/poly methyl methacrylate) composite latex that was made by St-MMA emulsion polymerization using semi-batch technique.

Devon et al. [1990] studied the physical properties of two latexes that were the hard-core/soft-shell and the soft-core/hard-shell type composite polymer particles. In these systems the hard polymer was PMMA and the soft polymer was Polybuthyl acrylate (PBA). The observed properties also supported the core-shell morphology. In the above two systems the seed polymers became cores and the monomers were polymerized over the seed particle surfaces.

Also, Morgan [1982] studied multifeed emulsion polymerization with soft-hard and hard-soft polymer pair systems. He used MMA, EA, styrene, Buthyl acrylate (BA) as monomers and sequential batch addition. His hypotheses and experimental results showed core-first and shell-second composite latex particles.

A core-shell particle is roughly divided into organic-organic (polymer-core, polymer-shell) and inorganic-organic (inorganic surrounded by polymer) composite latexes. The core-shell composite particle is varied from a core-shell structure to a complete phase separation with various two phase structure in between, depending on polymerization sequence, polymerization methods, reaction condition, polymer compatibility, molecular weight of polymer, polymer phase ratio, etc. The shape of the core-shell composite particles in the above showed various structure such as inverted core-shell, polymeric oil-in-oil, raspberry, confetti-like, etc. [Lee and Ishikawa, 1983; Mastsumoto et al., 1976; Okubo et al., 1980, 1982]. Many researchers studying polymer colloids are concentrating their attention on the production of micron-sized monodispersed core-shell polymer particles prepared by soap-free emulsion polymerization to apply to the biomedical field, microelectronics, etc. [Okubo et al., 1999]. Sarac [1999] showed that the use of a redox initiation system enables polymerizations to be performed at lower temperature than possible with

---

†To whom correspondence should be addressed.
E-mail: Sdseol@daunet.donga.ac.kr

a thermal reaction. Lee [2000] studied the effect of heating on the morphology and physical properties of PMMA/PS core-shell composites and the polymer blends. He found that the behavior of the interpenetration layer was the same as compatibilizer that would increase the degree of compatibility of polymer blends. Park et al. [1999] studied the effect of surfactants in acrylic emulsion polymerization. He realized that the overall conversion of the polymerization reaction in a mixed surfactant system was found to be higher than that in a single nonionic surfactant system. Emulsion particle size decreased as surfactant content increased. Lee et al. [2000] examined that the morphology of the composite polymer latex was core-shell structure, the core was PMMA and shell was PMMA-PMAA copolymer. The carboxylic acid functional groups (COOH) of MAA were distributed on the surface of composite polymer latex. The concentration of carboxylic acid groups distributed on the surface of composite polymer latex could be controlled by the amount of MAA.

Fabre and Meunier et al. [2000] reported the thermomechanical properties of film from structured soft-core/hard-shell hydrophobic latexes. These films were formed at room temperature, that is, 70 °C lower than the Tg of the PMMA that built the shell. The latexes were characterized and exhibited a soft-core/hard-shell structure. They found that the mechanical properties of these films were closely related to their very particular organization.

In this article, we describe the formulation of acrylic core-shell latex polymerization employed to build core-shell structure. The structures of these composite particles were observed by studying with respect to film formation, hydrolysis by NaOH, glass transition temperature by DSC, particle size analysis, and micrological observation by TEM photograph.

EXPERIMENTAL

1. Materials

Reagent grade Styrene (St), Methyl methacrylate (MMA), Ethyl acrylate (EA) was distilled at reduced pressure under N_2 atmosphere. Ammonium persulfate (APS) as initiator was obtained from Aldrich. Sodium dodecyl benzene sulfonate (SDBS) as an emulsifier was used without purification. All water was deionized.

2. Polymerization

The 1 litter reactor vessel that was equipped with ports for nitrogen, a condenser, a paddle-type stirrer, dropping funnel, and thermometer was kept in a water bath maintained at 85 °C. Agitation speeds were 60 rpm for core polymer and 80 rpm for shell polymerization. Prior to polymerization, the reaction mixture was purged with nitrogen for at least 30 minutes, and during the reaction a small positive pressure of nitrogen was maintained. SDBS was dissolved in deionized water, and monomers were then added to the SDBS solution with agitation to prepare pre-emulsion. Initial seed was prepared with parts of pre-emulsion. The remainder monomer pre-emulsified and initiator solution was added via dropping funnels to grow this seed. The grown seed was used as the core polymer in the next emulsion polymerization. In the shell polymerization step, core latexes (500 g, 2 wt%) were placed in the reactor vessel in a water bath at 85 °C. After nitrogen degassing, monomer and initiator solution were added in the reactor for 5 hours. After monomer and APS solution addition was completed, the reaction was allowed to post react for 2 hours to remove residual monomers and the polymers were filtered with 120-mesh filter to remove grits.

In this manner, several core-shell polymers were prepared by changing the kinds of monomers for core and shell polymers. The experimental conditions are summarized in Table 1 and Table 2.

3. Latex Characterization

3-1. Hydrolysis of Latex for Alkali Solution

Table 1. Polymerization recipe of core polymers

(unit: g)

	DW	SDBS	MMA	St	EA	APS	Conversion (%)
CM-1	830	0.0021	42.1			0.31	86.6
CM-2	830	0.0042	42.1			0.31	97.0
CM-3	830	0.0084	42.1			0.31	98.0
CE-4	830	0.0042			42.1	0.31	97.5
CS-5	830	0.0042		42.1		0.31	77.6
CS-6	830	0.0084		42.1		0.31	95.5
CS-7	830	0.0120		42.1		0.31	96.1

DW: deionized water. St: styrene. SDBS: sodium dodecyl benzene sulfonate. EA: ethyl acrylate. MMA: methyl methacrylate. APS: ammonium persulfate

Table 2. Polymerization recipe of shell polymers

(unit: g)

	CM-2 (2.0%)	CM-3 (2.0%)	CE-4 (2.0%)	CS-6 (2.0%)	CS-7 (2.0%)	MMA	EA	St	APS	DW	Conversion (%)
SMM-1	500					5			0.05	10	97.2
SME-2	500						5		0.05	10	97.0
SMS-3	500							5	0.05	10	97.5
SMS-4		500						5	0.05	10	97.4
SES-5			500					5	0.05	10	95.6
SEM-6			500			5			0.05	10	98.2
SSM-7				500		5			0.05	10	97.6
SSE-8				500			5		0.05	10	97.3
SSS-9				500				5	0.05	10	96.3
SSM-10					500	5			0.05	10	97.8

MMA: methyl methacrylate. EA: ethyl acrylate. St: styrene. APS: ammonium persulfate. DW: deionized water

For identification of latex particle structure, hydrolysis of the latex with N/200 NaOH solution was employed and the results of final pH were mutually compared. The latexes (10 g) diluted to 2 wt% and NaOH of N/200 (65 g) were weighed out and then mixed. This mixture was stirred at 65 °C for 48 hours and pH was measured by pH meter.

3-2. Film Formation

Latexes were placed on the glass plate in round shape and then, the latexes were dried at 20 °C. After the latex had dried, the film formation comparison was taken where a clear film had formed. This usually occurred 2 to 3 hours after the latexes were placed on the plate.

3-3. Latex Particle Size

The average particle size was measured by a Particle Size Analyzer (Autosizer IIC, Malvern instrument LTD.). The latex typically diluted 1,000 times in water.

3-4. Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) was used to observe the morphology of the core-shell particle synthesized (TEM: JEM-200CX, JEOL, Japan).

3-5. Differential Scanning Calorimeter

A Dupont Instruments General V4.1C Dupont 2100 Differential Scanning Calorimeter was used for glass transition temperature measurement of the latex. The samples were dried completely in a vacuum oven at 25 °C. The scanning range used in these experiments was from −50 °C to 100 °C, with a scanning rate of 2 °C per minute.

3-6. Measurement of Conversion

The time-monomer conversion to polymer was calculated by measuring solid content. At appropriate intervals aliquots were withdrawn, of about 1 g by using a syringe, and quenched with methanol containing a small amount of hydroquinone, to prevent further polymerization. About 1 g of latex was weighed into an aluminum dish and left 1 hour at 130 °C. The dried polymer was then weighed and the solids content calculated from the following equation. The average of two samples was taken.

$$\text{Conversion }(\%)=100W_d/(W_t\cdot T_s)$$

W_t : sample weight
W_d: sample weight after drying
T_S : principal value of solid content in 100% conversion

RESULTS AND DISCUSSION

PS and PMMA core latexes were made at 5% solids content. This reaction was performed in the varied concentration of SDBS to observe the effect of polymerization. Figs. 1 and 2 show the conversion in PSt-core polymerization and PMMA-core polymerization. As shown in Figs. 1 and 2, the percent of conversion was affected by concentration of SDBS. The conversion of PSt-core polymer using 0.01 wt% of SDBS to the monomer at CS-5 of Table 1 was 77.6%. However, at 0.02% and 0.03% concentration of SDBS of CS-6, CS-7, the conversion was 95.5 %and 96.1% respectively. Fig. 2 shows the conversion-time curves of PMMA-core polymer for effect of emulsifier concentration on the conversion at same initiator level. Also, the conversion of PMMA-core polymer in the same process of PS-core polymer seems to depend on the SDBS concentration, where it is found to be 86.6%, 97.0%, and 98.0%, respectively, for 0.005 wt%, 0.01 wt%, and 0.02 wt% of SDBS to MMA with increasing the SDBS content. It is known that the more micelles are formed in aqueous phase at the higher concentration of SDBS and the micelles then, the more monomer solubilized during pre-emulsion. The radicals generated by thermal decomposition initiate the polymerization and the nucleation period by entering a monomer-swollen micelle and reacting with the monomer contained there in. Upon radical entry into a micelle, the higher concentration of monomer swollen micelles leads to rapid polymerization. The stung micelle becomes a growing particle with increasing surfactant requirement. The more monomer-swollen micelles are formed at relatively higher concentration of emulsifier, the greater number of particles are generated with same initiator concentration at same time in seed polymerization. Therefore, the rate of polymerization depends on emulsifier concentration, because all subsequent polymerization will take place in the seed particles that will continue to grow particles. The value of conversion, as plotted in Fig. 3 was selected at time equivalent to a residence time. It can be seen in Fig. 3 that the conversion of PMMA-core polymer as 97% was higher than that of PSt-core polymer at the same concentration of SDBS (0.01 wt% to monomer). Since MMA has a high solubility in water compared to St, the radicals generated in the aque-

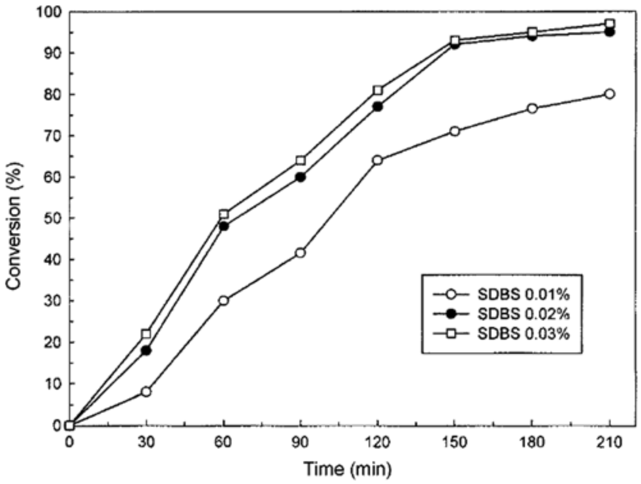

Fig. 1. Conversion-time curve of PSt core polymerization.

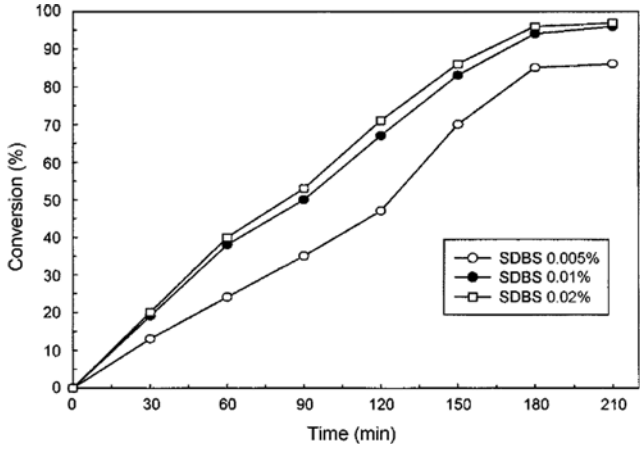

Fig. 2. Conversion-time curve of PMMA core polymerization.

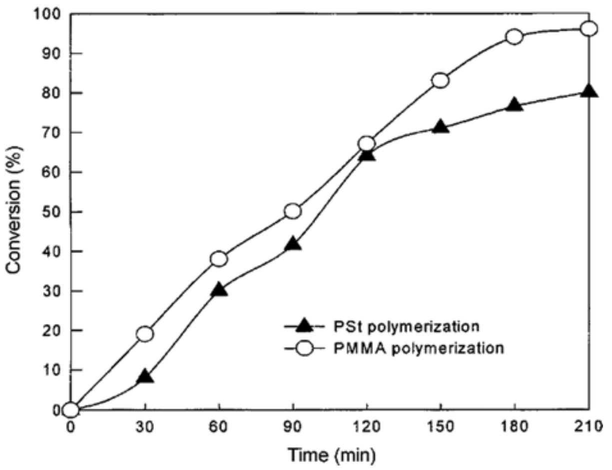

Fig. 3. Conversion comparison of PSt and PMMA core polymerization at same SDBS concentration (0.01 wt% to monomer).

ous phase initiate MMA solubilized in water as well as MMA swollen micelles for particle nucleation; thus the greater number of particles generated in seed polymerization gave more locus of polymerization in core growth stage than the case of St polymerization. Figs. 1 and 2 show that stabile PMMA and PSt latexes with no grits are obtained by using 0.01 and 0.02 wt% of SDBS to total monomer, respectively, when the conversions of both PMMA and PSt latexes were higher than 95%. Table 3 shows particle size (Z average) of core latex and core-shell latex. As shown in Table 3, the particle sizes of PMMA latexes of C-1 and C-2 prepared by pre-emulsion method using SDBS of 0.01 and 0.02 wt% to total monomer were 276.5 nm and 175.4 nm, respectively. The particle sizes of PSt latexes of C-3 and C-4 prepared in same manner were 298.4 nm and 229.4 nm, respectively, and then the amount of SDBS used to total monomer was 0.02 wt%, 0.03 wt%. The particle size of the core-shell latexes prepared using the above latexes as cores, namely, the S-1 (PMMA/PSt, 2/1), S-2 (PMMA/PSt, 2/1), S-3 (PSt/PMMA, 2/1) and S-4 (PSt/PMMA, 2/1) were found to be 310.0 nm, 189.4 nm, 330.8 nm and 240.2 nm, respectively. The differences of particle size in these core-shell latexes suggest that new particles in the shell polymerization of the S-2 and S-4 using C-2 of PMMA and C-4 of PSt core latexes stabilized by 0.02 wt% and 0.03 wt% of SDBS to monomer respectively were generated more than in the shell polymerization of the corresponding S-1 and S-3 polymerizing in the presence of the core latex C-1 and C-3, which were used SDBS 0.01 wt% and 0.02 wt% to monomer in the core polymerization. The results indicate that the appropriate amount of SDBS in the core polymerization was 0.01 wt%/monomer for PMMA and 0.02 wt%/monomer for PS to obtain stable core-shell latex without grits in shell polymerization.

Table 4. Final pH of core-shell polymer after hydrolysis by NaOH solution

Core/Shell	PH
PMMA/PMMA (2/1)	9.4
PMMA/PSt (2/1)	10.1
PSt/PMMA (2/1)	9.5
PSt/PSt (2/1)	10.7

* Hydrolysis conditions. Sample (2%): 10 g. N/200 NaOH: 65 g. Temp.: 65 °C. Time: 48 hr

The pH comparison of particles hydrolyzed with NaOH solution is given in Table 4. As a result, PS/PS, PMMA/PS, PS/PMMA and PMMA/PMMA were 10.7, 10.1, 9.5, and 9.4, respectively. The final pH was measured after hydrolysis at 65 °C for 48 hours. In comparison, the PSt/PSt and PMMA/PSt surrounded by shell of hydrophobic polymer PSt were found to be higher pH than PMMA/PMMA and PSt/PMMA shelled hydrophilic polymer PMMA. The pH change trend according to hydrolysis of outside shell polymers by sodium hydroxide is evidence of core-shell structure that the core was surrounded by the outside shell polymer in a particle. Fig. 4 shows DSC curves of PSt/PEA (2/1) core-shell (a), PSt/PEA copolymer (b) prepared with same ratio of monomer for the determination of glass transition temperature. Copolymer (b) involving a single copolymer of PSt-PEA compositional ratio of 2/1 by weight shows a single Tg, as expected. In contrast, the core-shell latex (a) shows two glass transition temperatures, namely, Tg of PEA around −25 °C and PSt around 100 °C respectively. This analysis indicates that composition of copolymer particles is homogeneous over the particle radii in a particle and Tg of the polymer is one for that reason. The core-shell latex particles were, however, found to have a heterogeneous structure consisting of PS core surrounded by a shell of PEA. It means that the core-shell latex is composed of the inside core

Table 3. Particle size of core polymer and shell polymer with surfactant concentration (unit: g)

Core	DW	SDBS	MMA	St	APS (%)	Conversion (%)	Z Average (nm)
C-1	800	0.0042	42.1		30.31	97.0	276.5
C-2	800	0.0082	42.1		30.31	98.0	175.4
C-3	800	0.0082		42.1	30.31	95.5	298.4
C-4	800	0.0126		42.1	30.31	96.1	229.2

Shell	C-1 (2.0%)	C-2 (2.0%)	C-3 (2.0%)	C-4 (2.0%)	St	MMA	APS (0.5%)	Conversion (%)	Z Average (nm)
S-1	500				5		10.05	97.5	310.0
S-2		500			5		10.05	97.4	180.4
S-3			500			5	10.05	97.6	330.8
S-4				500		5	10.05	97.8	240.2

DW: deinized water. SDBS: sodium persulfate. MMA: methyl methacrylate. St: styrene. APS: ammonium persulfate

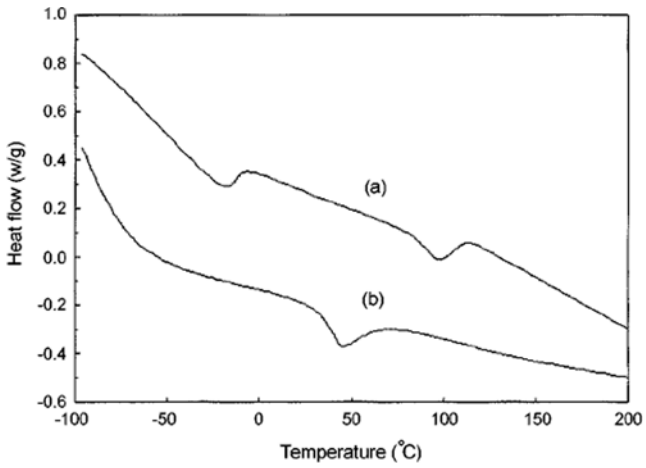

Fig. 4. DSC curves of PSt/PEA (2/1) core-shell polymer (a) and PSt/ PEA (2/1) copolymer (b).

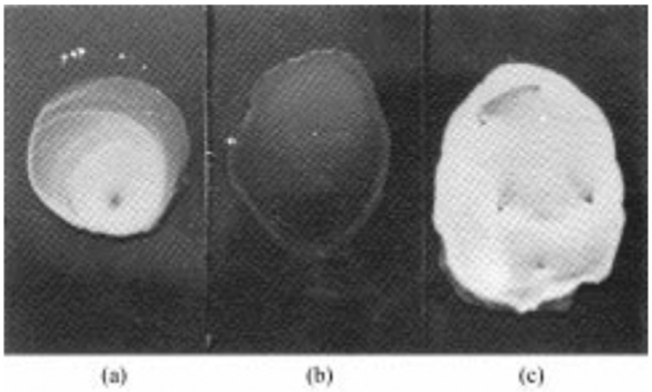

Fig. 5. Photograph of film formation at 20 °C.
(a) PSt/PEA (2/1) copolymer
(b) PSt/PEA (2/1) core-shell polymer
(c) PEA/PSt (2/1) core-shell polymer

and the outside shell structure. Fig. 5 is the photograph of films formatted for PSt/PEA (2/1) core-shell latex (a), PSt/PEA (2/1) copolymer (b), and PEA/PSt (2/1) core-shell latex(c) at 20 °C. In comparison of the core-shell latex (a) and copolymer latex (b) with same ratio of polymer, the sample (a) with shell composition containing PEA gave more clear film formation, as shown in Fig. 4, than the copolymer counterpart. Because PEA of shell in the PSt/PEA core-shell latex has a much lower Tg than PS/PEA latex, it was expected that the film formation temperature (MFT) of PEA in the shell would decrease film formation temperature and then make better film at 20 °C compared to sample (b) and sample (c). The core-shell latex (c) surrounded by PS shell shows that MFT was raised by the shell of PSt having higher Tg than PS/PEA and the appearance of the formatted film was not clear and had a just-dried appearance. These differences in film formation suggest that the homopolymer core was surrounded by homopolymer shell in the core-shell particles. Fig. 6 shows TEM photographs of PMMA core particles (a) and PSt core particles.

Fig. 7 shows TEM photographs of PMMA/PSt (2/1) core-shell particles (a) and PSt/PMMA (2/1) core-shell particles (b) produced by emulsion polymerizing with St and MMA in the presence of PMMA and PSt core containing 0.01 and 0.02 wt% to total monomer, respectively, when core polymerization was carried out. As shown in Figs. 6 and 7, PMMA core and PSt core-shell particles have slightly deformed shape. PSt core and PMMA/PSt core-shell latex show relatively non-deformed spherical structure. These differences seem to be based on the difference of existence of polymer in particle surface and composition variation with their radii.

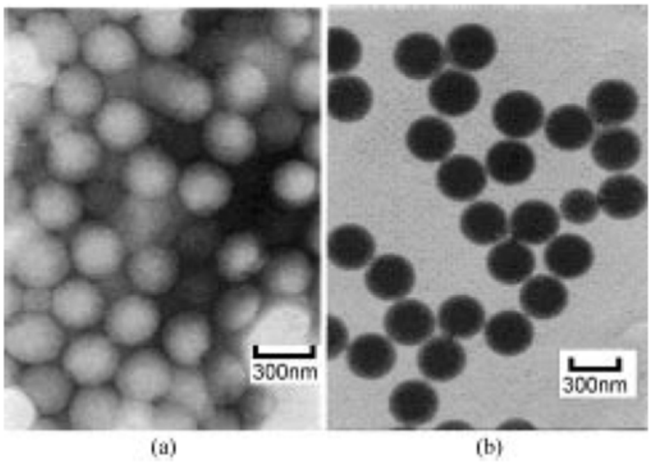

Fig. 6. TEM photographs of PMMA (a) and PSt (b).

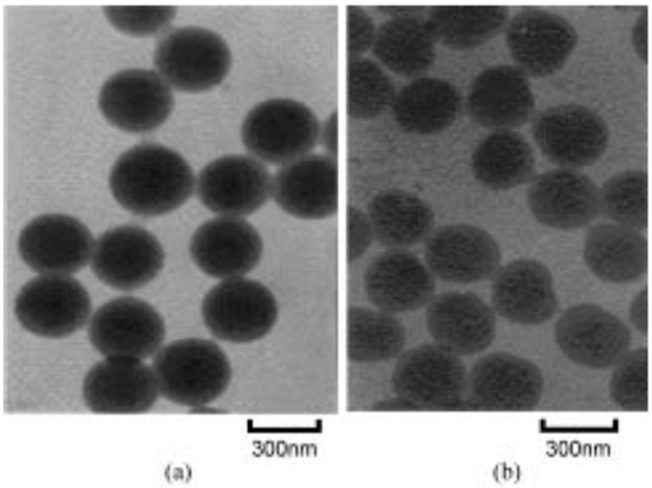

Fig. 7. TEM photographs of morphology for PMMA/PSt (2/1) (a) and PSt/PMMA core-shell polymer (2/1) (b).

CONCLUSION

Acrylic composite particles were successfully prepared by sequential emulsion polymerization of the corresponding monomers in the presence of core latexes. When PMMA and PSt core latexes were polymerized, the appropriate amount of SDBS in the core polymerization was 0.01 wt%/monomer for PMMA and 0.02 wt%/monomer for PSt to suppress the generation of new particles and to minimize the gelation during the shell polymerization in the presence of these core latexes. Moreover, a series of sequential seeded growth emulsion polymerization by adding monomers pre-emulsified were used to obtain high conversion latexes.

The structure of the core-shell composite particles synthesized was confirmed by DSC, hydrolysis under sodium hydroxide, TEM, particle size analyzer, and MFT study etc. All results from the above characterization show that shell polymers surrounded the core latexes and encapsulation took place during shell polymerization.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of Dong-A University for this work.

REFERENCES

Blankenship, R. and Kowalski, A., "Production of Core-sheath Polymer Particles Containing Voids, Resulting Product and Use," U.S. Patent, **4**, 594,363 (1986).

Devon, Michael J., "Effects of Core-shell Latex Morphology on Film Forming Behavior," *J. Appl. Polym. Sci.*, **39**, 2119 (1990).

Fabre, P., Drujon, X., Meunier, G. and Leibler, L., "Films from Soft-Core/Hard-Shell Hydrophobic Latexes: Structure and Thermomechanical Properties," *J. Polymer Science*, **38**, 2989 (2000).

Grancio, M. R. and Williams, D. J., "Molecular Weight Development in Constant-Rate Styrene Emulsion Polymerization," *J. Polym. Sci.*, **8**, 2733 (1970).

Grancio, M. R. and Williams, D. J., "The Morphology of the Monomer-polymer Particle in Styrene Emulsion Polymerization," *J. Polym. Sci.*, **8**, 2617 (1970).

Keusch, P. and Williams, D. J., "Equilibrium Encapsulation of Polystyrene Latex Particles," *J. Polym. Sci.*, **11**, 143 (1973).

Kim, S. S., Chun, B. H., Park, C. J. and Yoon, W. K., "Pyrolysis Characteristics of Polystyrene on Stirred Batch Reactor," *HWAHAK KONGHAK*, **38**, 732 (2000).

Kim, Y. S., Hwang, G. C., Bae, S. Y. and Yi, S. C., "Pyrolysis of Polystyrene in a Batch-Type Stirred Vessel," *Korean J. Chem. Eng.*, **16**, 161 (1999).

Lee, C.-F., "Synthesis and Properties of Polymer Latex with Carboxylic Acid Functional Groups for Immunological Studies," *J. Polymer*, **41**, 8565 (2000).

Lee, C.-F., "The Properties of Core-shell Composite Particles," *Polymer*, **41**, 1337 (2000).

Lee, D. I. and Ishikawa, T., "The Formation of "Inverted" Core-Shell latex," *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 147 (1983).

Morgan, L. W., Johnson, S. C. and Son, "Multifeed Emulsion Polymer: The Effects of Monomer Feed Sequence and the Use of Seed Emulsion Polymers," *J. Appl. Polym. Sci.*, **27**, 2033 (1982).

Okubo, M. and Izumi, J., "Synthesis of Micron-sized Monodispersed, Core-shell Composite Polymer," *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, **153**, 297 (1999).

Okubo, M., Katsuta, Y. and Matsumoto, T., "Studies on Suspension and Emulsion. LI. Peculiar Morphology of Composite Polymer Particles Produced by Seeded Emulsion Polymerization," *J. Polym. Sci. Polym. Letter Ed.*, **20**, 45 (1982).

Okubo, M., Katsuta, Y., Inoue, K., Nakamae, K. and Matsumoto, T., "Dynamic Viscoelastic Behavior of Composite Polymer Emulsion Film," **16**(7), 278 (1980).

Park, J. Y., Kwon, M. H., Lee, Y. S. and Park, O. O., "Effects of Nucleating Agent on Nonisothermal Crystallization of Syndiotactic Polystyrene," *Korean J. Chem. Eng.*, **17**, 262 (2000).

Park, S. J., "A Study on the Effect of Surfactants in Acrylic Emulsion Polymerization," *J. Korean Ind. Eng. Chem.*, **10**(4), 523 (1999).

Paxton, T. R., "Adsorption of Emulsifier on Polystyrene and Poly(Methyl Methacrylate) Latex Particle," *J. Colloid Interface. Sci.*, **31**(1), 19 (1969).

Sarac, A. S., "Redox Polymerization," *Prog. Polym. Sci.*, **24**, 1149 (1999).

Song, H. S. and Hyun, J. C., "An Optimization Study on the Pyrolysis of Polystyrene in a Batch Reactor," *Korean J. Chem. Eng.*, **16**, 316 (1999).

Williams, D. J. and Keusch, P., "Latex Particle Morphology during Polymerization and at Saturation Equilibrium," *J. Polym. Sci. Chem. Ed.*, **12**, 2123 (1974).