

# A Study on the Synthesis and Characteristics of Acrylic Composite Particles

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**Abstract** : The core-shell latexes were synthesized by sequential emulsion polymerization of methyl methacrylate (MMA), styrene (St), and n-butyl acrylate (BA) in the presence of anionic surfactant, and the characteristics of these latexes were evaluated. The synthesis of core latex had to be performed carefully to avoid in the formation of secondary particles. The sequential polymerization method adopted in these synthesis took advantage of stabilizing particles grown during shell polymerization. In the core-shell latex polymerization, to suppress the generation of new particles and to minimize the gelation during the shell polymerization, amount of surfactant (sodium lauryl sulfate : SLS) should be reduced to the minimum, 0.01 wt% and 0.02 wt% of SLS to amount of monomer respectively when the polymethyl methacrylate (PMMA) and polystyrene (PSt) core latexes were prepared. In addition, monomer pre-emulsion method was 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.

*Keywords* : core-shell, acrylic composite particles, sequential emulsion polymerization.

## 1. Introduction

Latex materials in which a core of one polymer is surrounded by a shell of a second polymer are important in many industrial applications. For example, those with core and shell polymers differing in their glass transition temperatures ( $T_g$ ) 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[1,2]. All the earlier theoretical treatments of the emulsion polymerization of styrene were based on the assumptions that the particles were swollen homogeneously, i.e., there was no concentration difference through out the particles, because styrene weres miscible with polystyrene in all proportions. But Williams et al[3-5]. 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 brought controversial arguments.

The terminology of core-shell is straight forward 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[6] 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. 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 above showed various structure such as inverted core-shell, polymeric oil-in-oil, raspberry, confetti-like, etc [7-9]. Many researchers studying polymer colloids are concentrating their attention on the production micron-sized monodispersed core-shell polymer particle prepared by soap-free emulsion polymerization to apply biomedical field, microelectronics, etc [10]. Sarac studies that the use of a redox initiation system enables to perform polymerizations at lower temperature than possible with thermal reaction[11]. Lee studied

that effect of heating on the morphology and physical properties of PMMA/PS core-shell composite and the polymer blends[12]. He found that the behavior of the interpenetration layer was the same as compatibilizer that would be increase the degree of compatibility of polymer blend. Park et al. studied on the effect of surfactants in acrylic emulsion polymerization[13]. 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. 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 distributed on the surface of composite polymer latex[14]. 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. reported the thermomechanical properties of film from structured soft-core/hard-shell hydrophobic latexes[15]. 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.

## 2. Experimental

### 2.1. Materials

Reagent grade styrene (St), methyl methacrylate (MMA), n-butyl acrylate (BA) were distilled at reduced pressure under N<sub>2</sub> atmosphere. Potassium persulfate (PPS) as initiator was obtained from Aldrich. sodium lauryl sulfate (SLS) as an emulsifier was used without purification. All water was deionized.

### 2.2. Polymerization

The 1 liter 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 60rpm for core polymer and 80rpm for shell polymerization. Prior to polymerization, reaction mixture was purged with nitrogen for at least 30 minute and during the reaction a small positive pressure of nitrogen was maintained. SLS was dissolved in deionized water, monomers were then added to the SLS 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 shell polymerization step, core latexes (500g, 2wt%) 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 PPS 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 kinds of monomers for core and shell polymers. The experimental conditions are summarized in Table 1 and Table 2.

### 2.3. Latex characterization

#### 2.3.1. Hydrolysis of latex for alkali solution

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 (10g) diluted to 2 wt % and NaOH of N/200(65g) were weighed out and then mixed. This mixture was stirred at 65°C for 48 hours and pH was measured by pH meter.

Table 1. Polymerization Recipe of Core Polymers

(Unit:g)

	DW	SLS	MMA	St	BA	PPS	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
CB-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

where, DW : deionized water, St : styrene, SLS : sodium lauryl sulfate,  
BA : n-butyl acrylate, MMA : methyl methacrylate,  
PPS : potassium persulfate.

Table 2. Polymerization Recipe of Shell Polymers

	CM-2 (2.0%)	CM-3 (2.0%)	CB-4 (2.0%)	CS-6 (2.0%)	CS-7 (2.0%)	MMA	BA	St	PPS	DW	Conversion (%)
SMM-1	500					5			0.05	10	97.2
SMB-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
SBS-5			500					5	0.05	10	95.6
SBM-6			500			5			0.05	10	98.2
SSM-7				500		5			0.05	10	97.6
SSB-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

where, MMA : methyl methacrylate, BA : n-butyl acrylate,  
St : styrene, PPS : potassium persulfate, DW : deionized water.

### 2.3.2. 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.

### 2.3.3. Latex particle size

The average particle size was measured by a Particle Size Analyzer (Autosizer IIC, Malvern Instrument Ltd.). The latex typically diluted 1000 times in water.

### 2.3.4. Transmission Electron Microscopy

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

### 2.3.5. 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. Results and Discussion

PSt and PMMA core latexes were made at 5% solids content. This reaction was performed in the varied concentration of SLS to observe the effect of polymerization. Fig. 1 and 2 show the conversion in PSt-core polymerization and PMMA-core polymerization. As shown in Fig. 1 and 2, the percent of conversion was affected by concentration of SLS. The conversion of PSt-core polymer using 0.01 wt% of SLS to the monomer at CS-5 of Table 1 was 77.6%. However, at 0.02% and 0.03% concentration of SLS of CS-6, CS-7, the conversion was 95.5% and 96.1%, respectively. Fig. 2 show the conversion-time curves of PMMA-core polymer for effect of emulsifier concentration on the conversion at the same the initiator level. Also, the conversion of PMMA-core polymer in the same process of PS-core polymer seems to depend on the SLS concentration, where it is found to be 86.6%, 97.0%, and 98.0%, respectively, for 0.005 wt%, 0.01 wt%, and 0.02wt % of SLS to MMA with increasing the SLS content. It is known that the more micelles are formed in aqueous phase at the higher concentration of SLS and the micelles then, solubilized the

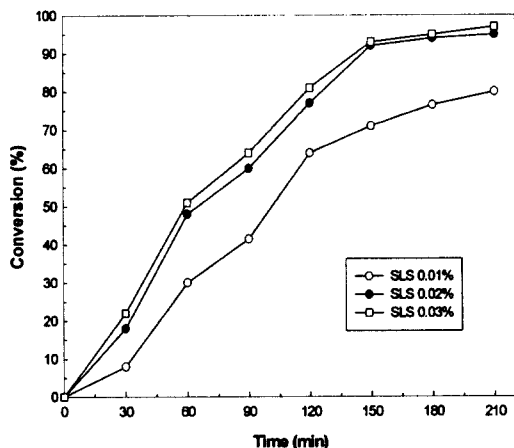


Fig. 1. Conversion-time curve of PSt core polymerization.

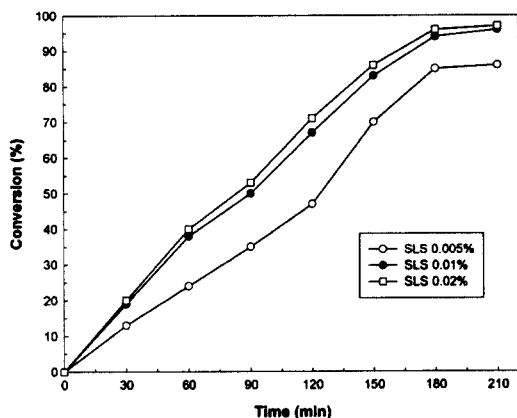


Fig. 2. Conversion-time curve of PMMA core polymerization.

more monomer 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 lead to rapid polymerization. The stung micelle becomes a growing particle with increasing surfactant requirement. The more monomer swollen micelles are formed at relative higher concentration of emulsifier, the more number of particles are generated with

same initiator concentration at the same time in seed polymerization. Therefore, the rate of polymerization depended on emulsifier concentration, because all subsequence 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 as 97% was higher than that of PSt-core polymer at the same concentration of SLS(0.01 wt% to monomer). Since MMA has a high solubility in water compared to St, the radicals generated in the aqueous phase initiate MMA solubilized in water as well as MMA swollen micelles for particle nucleation, thus the more number of particles generated in seed polymerization gave the more locus of polymerization in core growth stage than the case of St polymerization. Fig. 1 and 2 have shown that stabile PMMA and PSt latexes with no grits are obtained using 0.01 and 0.02 wt% of SLS to total monomer respectively, when the conversions of both PMMA and PSt latexes were higher than 95%. Table 3 show particle size ( $Z$  average) of core latex and core-shell latex. As shown in Table 3, the particle size of PMMA latexes of C-1 and C-2 prepared by

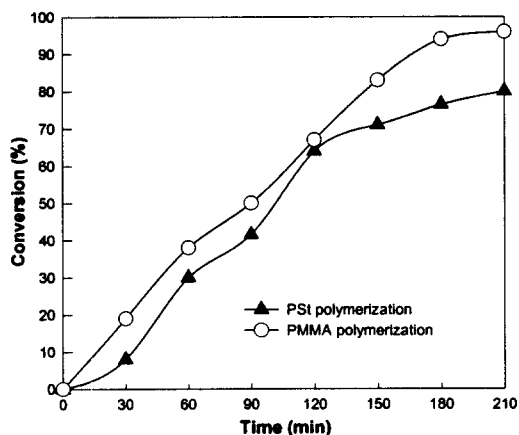


Fig. 3. Conversion comparison of PSt and PMMA core polymerization at the same SLS concentration(0.01wt% to monomer).

Table 3. Particle Size of Core Polymer(a) and Shell Polymer(b) with Surfactant Concentration

(a) Core polymer

(Unit:g)

Core	DW	SLS	MMA	St	PPS (%)	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

(b) Shell polymer

Shell	C-1 (2.0%)	C-2 (2.0%)	C-3 (2.0%)	C-4 (2.0%)	St	MMA	PPS (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

where, DW : deionized water, SLS : sodium lauryl sulfate,  
MMA : methyl methacrylate, St : styrene,  
PPS : potassium persulfate.

pre-emulsion method using SLS of 0.01 and 0.02wt% to total monomer were 276.5 nm and 175.4nm respectively. The particle size of PSt latexes of C-3 and C-4 prepared in same manner were 298.4nm and 229.4nm respectively and then the amount of SLS used to total monomer was 0.02wt%, 0.03wt%. The particle size of the core-shell latexes prepared using above these 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 0.02wt% and 0.03wt% of SLS 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 SLS 0.01wt% and 0.02wt% to monomer in the core polymerization. The results indicate that appropriate amount of SLS in the core polymerization were 0.01wt%/monomer for PMMA and 0.02wt%/monomer for PSt to obtain stable core-shell latex without g. The pH comparison of particles hydrolyzed with NaOH solution is given in Table 4. As a result, PSt/PSt, PMMA/PSt, PSt/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 an evidence of core-shell structure that the core was surrounded by the outside shell polymer in a

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%) : 10g, N/200 NaOH : 65g,  
Temp : 65°C, Time : 48hr.

particle. Fig. 4 show DSC curves of PSt/PBA (2/1) core-shell (a), PSt/PBA copolymer (b) prepared with the same ratio of monomer for the determination of glass transition temperature. Copolymer (b) involving a single copolymer of PSt-PBA compositional ratio of 2/1 by weight shows a single Tg, as expected. In contrast, the core-shell latex (a) show two glass transition temperature, namely, Tg of PBA around -60°C and PSt around 100°C, respectively. This analysis indicates that composition of copolymer particles are homogeneous over the particle radii in a particle and Tg of the polymer is one for that reason. The

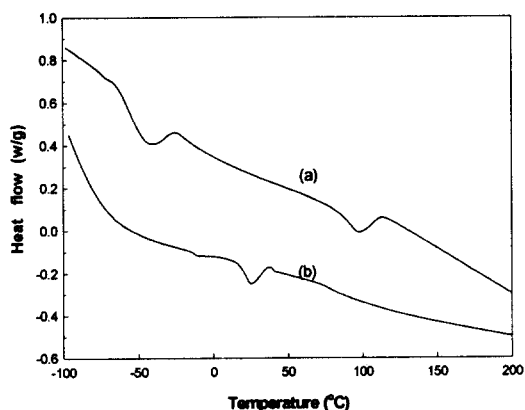


Fig. 4. DSC curves of PSt/PBA (2/1) core-shell polymer (a) and PSt/PBA (2/1) copolymer(b).

core-shell latex particles were, however, found to have a heterogeneous structure comprising of PSt core surrounded by a shell of PBA. It means that the core-shell latex composes of the inside core and the outside shell structure. Fig. 5 is the photography of films formatted for PSt/PBA (2/1) core-shell latex (a), PSt/PBA (2/1) copolymer (b), and PBA/PSt(2/1) core-shell latex(c) at 20°C. In comparison of the core-shell latex (a) and copolymer latex (b) with the same ratio of polymer, the sample (a) with shell composition containing PBA gave more clear film formation, as shown in Fig. 4, than the copolymer counterpart. Because PBA of shell in the PSt/PBA core-shell latex has a much lower Tg than PSt/PBA latex, it was expected that the minimum film formation temperature (MFFT) of PBA in the shell would decreases film. Fig. 6 shows TEM photographs of PMMA core particles (a) and PSt core particles.

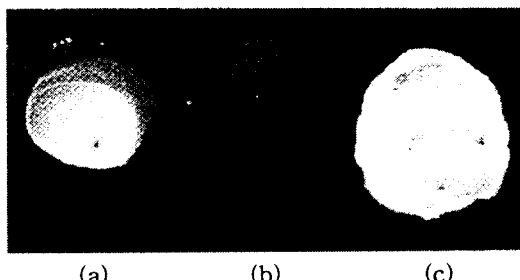


Fig. 5. Photograph of film formation at 20°C.  
(a) PSt/PBA (2/1) copolymer  
(b) PSt/PBA (2/1) core-shell polymer  
(c) PBA/PSt (2/1) core-shell polymer

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 0.02wt% to total monomer respectively when core polymerization was carried out. As shown in Fig. 6 and 7, PMMA core and PSt core-shell

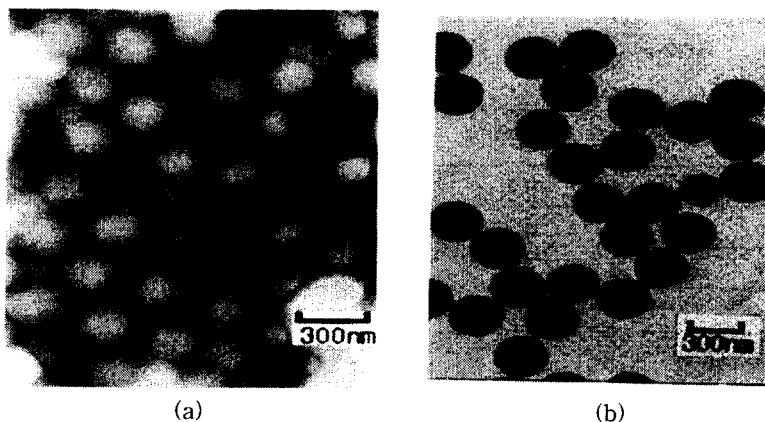


Fig. 6. TEM photographs of PMMA (a) and PSt (b).

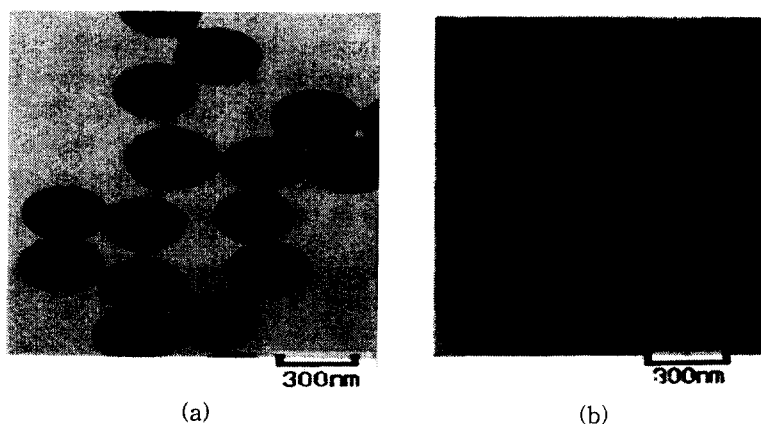


Fig. 7. TEM photographs of morphology for PMMA/PSt (2/1) (a) and PSt/PMMA core-shell polymer (2/1) (b).

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.

#### 4. 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 SLS in the core polymerization was 0.01wt%/monomer for PMMA and 0.02wt%/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 MFFT study etc. All results from above characterization show that shell polymers surrounded the core latexes and encapsulation took place during shell polymerization.

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