

Core-Shell Poly(Styrene/Sulfonated *N*-hydroxy Ethyl Aniline) Latex Particles Prepared by Chemical Oxidative Polymerization in Emulsion Polymerization

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Abstract: The kinetic behavior of emulsion polymerizations of styrene in the presence of sulfonated *N*-hydroxy ethyl aniline (SHEA) was investigated with two initiators: 2,2'-azobisisobutyronitrile (AIBN) and potassium persulfate (KPS). SHEA was synthesized using a stepwise polyurethane reaction method from 3-hydroxy-1-propane sulfonic acid sodium salt, isophorone diisocyanate (IPDI), and *N*-(2-hydroxyethyl) aniline. Stable core-shell poly(styrene/sulfonated *N*-hydroxy ethyl aniline, St/SHEA) latex particles were successfully prepared by using an appropriate amount of AIBN, in which SHEA plays the role of 'surfmmer', i.e., acting as both a surfactant in the emulsion polymerization and a monomer in the chemical oxidative polymerization. The kinetic behavior was dissimilar to that of typical emulsion polymerization systems. A long inhibition period and low rate of polymerization were observed due to radical loss by the oxidative polymerization of SHEA. It was concluded, due to the low water-solubility of AIBN and retardation reaction by SHEA, that the initial loci of polymerization were monomer droplets. However, growing polymer particles as polymerization loci became predominant as polymerization proceeded. It was suggested that AIBN was more effective than KPS in the preparation of the core-shell type poly(St/SHEA) latex particles. With KPS, no substantial polymerization was observed in any of the samples.

Keywords: core-shell, conductive polymers, emulsion polymerization, oxidative polymerization, surfmmer.

Introduction

A lot of researches have focused on improving the processability of conductive polymers.¹⁻⁶ Often the solubilization of conductive polymers can be achieved through functionalization of the starting material with a suitable side chain prior to polymerization.⁷⁻⁹ To enhance the processability of poly(aniline), PANi, ring substituted PANi,^{10,11} and *N*-substituted PANi^{6,12-15} have been studied extensively. These substituted PANis, however, possess a lower conductivity than PANis. These substituted PANis are copolymerized with aniline in order to enhance the processability and their dielectric,^{6,12} corrosive,¹⁴ cathode activity¹⁵ properties have

been studied. Recently, many other methods have been examined with regard to their poor processability. For example, sterically stabilized poly(pyrrole), PPy, colloids can be easily synthesized in aqueous media by chemically polymerizing pyrrole in the presence of a suitable water-soluble polymer, such as methyl cellulose or poly(vinyl alcohol).^{16,17} Similarly, PANi particles can be synthesized using suitable surfactants (or steric stabilizers), such as poly(ethylene oxide),¹⁸ poly(vinyl alcohol),¹⁹ poly(vinyl alcohol coacetate),²⁰ and poly(vinyl pyridine).^{21,22}

An alternate route for the preparation of colloidal conductive polymers involves coated latex particles with a thin layer of conjugate polymer to form conductive composites with core-shell morphology.²³⁻²⁶ This is due to the expected improvement of polymer processability and the unique intrinsic properties in dispersed nanometer or micrometer-sized materials. If the conductive polymer overlayer is continuous, this can lead to a relatively high conductivity, even at

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very low conducting polymer loading. Yassar *et al.* reported that sulfonic and carboxylic acid (dopants for the growing conducting polymer) coated polystyrene latexes (ca. 130 nm in diameter) could be coated with PPy overlayers using FeCl_3 .²⁷ Beadle *et al.* prepared a range of PANi-chlorinated latex composites and showed that PANi loading could be easily controlled by varying the latex concentration in the syntheses.²⁸ Xie *et al.* prepared poly(butadiene-*co*-styrene-*co*-2-vinylpyridine)/PANi composite particles in the presence of 0.1 μm -sized poly(butadiene-*co*-styrene-*co*-2-vinylpyridine) particles.²⁹ The DSM group utilized several low T_g , film-forming colloidal substrates such as polyurethane latexes or alkyd resins. Particle diameters were in the 50–500 nm range, and the commercial potential of these water-borne anti-static or anti-corrosion coatings (ConQuest[®]) has been explored.³⁰ Lascelles *et al.* adapted this DSM protocol in order to coat micrometer-sized poly(*N*-vinylpyrrolidone) (PVP)-stabilized polystyrene latexes with PPy.^{23,24,26} Conductivity measurements on the dried PSt-PPy latexes indicated an unexpectedly low percolation threshold of 1–2 vol%. Barthet *et al.* synthesized micrometer-sized PANi-coated-PSt latexes and characterized the morphology and uniformity of the PANi over-layer by SEM and X-ray photoelectron spectroscopy.^{31,32} Okubo *et al.*³³ prepared the PANi/PSt composite particles in the presence of poly(vinyl alcohol) and Wang *et al.*³⁴ prepared the PANi/PSt composite particles in the presence of sodium dodecyl sulfate (SLS).

As mentioned above, although sulfonated PANis have hydrophilic moieties and can be used as water-soluble agents, they have never been introduced into emulsion polymerizations as emulsifiers and/or stabilizers. If they have adequate hydrophilic/hydrophobic balance, they could play a role in a surfactant in emulsion polymerization and could form a conductive coating layer on the shell of the particles. It is, however, difficult for them to be used due to the rigidity of their backbone and very strong reactivity with radical initiators such as potassium persulfate (KPS) and ammonium persulfate (APS).^{35,36} Therefore, the oxidation potential of the initiator is believed to be a crucial factor in this preparation method.

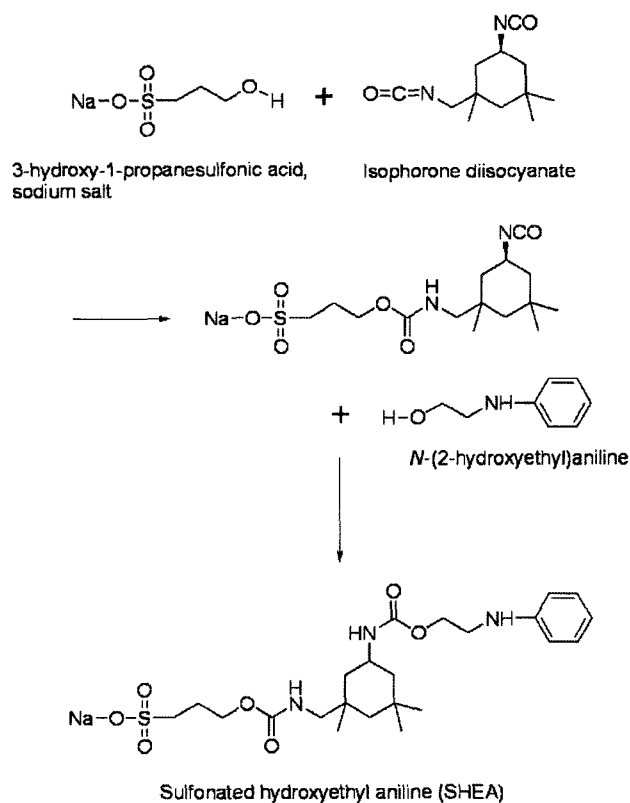
In this work, sulfonated *N*-hydroxy ethyl aniline (SHEA) was synthesized by using a stepwise polyurethane reaction in order to impart surface activity like that of a surfactant. SHEA was also used as a co-monomer in the chemical oxidative polymerization of aniline. The kinetic behavior of the emulsion polymerization of styrene, in the presence of SHEA as a 'surfmmer', was investigated by using KPS and 2,2'-azobis-isobutyronitrile (AIBN) for the chemical oxidative polymerization of SHEA.

Experimental

Materials. 3-Hydroxy-1-propane sulfonic acid, sodium salt (Aldrich, 98%), isophorone diisocyanate (IPDI, Aldrich,

98%), and *N*-(2-hydroxyethyl) aniline (Aldrich, 98%) were used as received. Impurities such as water in dimethyl sulfoxide (DMSO) were removed by molecular sieves (pore size: 5 Å). Styrene (Wako Chemicals) and butyl methacrylate (BMA, Junsei Chemicals) were purified by distillation under reduced pressure at 40°C. KPS and AIBN (Kanto Chemicals) were used as received. All aqueous solutions were prepared with deionized (DI) water.

Synthesis of Sulfonated *N*-hydroxy Ethyl Aniline. Synthesis of the SHEA was shown in Scheme I and can be summarized as follows: 3-hydroxy-1-propanesulfonic acid, sodium salt (8.11 g, 50 mmol), was dissolved in 80 mL of DMSO and heated to 80°C for 0.5 hrs under N_2 atmosphere. IPDI (11.17 g, 50 mmol) was added to the mixture and kept at the same temperature. The remaining isocyanate (NCO) concentration was monitored by *in-situ* FTIR (Mettler Toledo ReactIR 4000, USA). When a half of the initial isocyanate remained, *N*-(2-hydroxyethyl) aniline was added to the mixture. When the NCO peak disappeared, the reaction was terminated. After cooling the mixture to room temperature, a solid product formed by the evaporation of DMSO using a vacuum drying oven was dissolved with DI water and filtered with a 0.2 μm filter. Then, the final SHEA product as brown powder was obtained after the removal of water. The yield of SHEA was ca. 95%.



Scheme I. Schematic presentation for the synthetic process of sulfonated *N*-(2-hydroxy ethyl)aniline (SHEA).

Table I. Basic Recipe for the Preparation of Poly(St/SHEA) Latex Particles with Different SHEA Concentrations

Sample ID	PS- <i>h</i> -PSHEA10	PS- <i>h</i> -PSHEA20	PS- <i>h</i> -PSHEA40
Ingredient	Amount (g)	Amount (g)	Amount (g)
Styrene	7.00	7.00	7.00
SHEA	0.70	1.40	2.80
AIBN	0.42	0.42	0.42
DI Water	100	100	100

Emulsion Polymerization of Styrene in the Presence of SHEA. Styrene monomer and SHEA (10, 20, and 40 wt% based on styrene, respectively) aqueous solutions were added to a 3-neck round-bottom flask fitted with a condenser and a mechanical stirrer. The reaction vessel was then heated to 60 °C under a N₂ blanket and purged with N₂ for 1 hr in order to remove all traces of oxygen. Styrene monomer in the presence of AIBN was added to the reaction mixture, and then emulsion polymerization proceeded with mechanical stirring at 400 rpm. The time-conversion curves were obtained by the gravimetric method using 100 ppm of hydroquinone methanol as a short-stop solution. For a comparative study, the same molar concentration of KPS was used with the above mentioned method, except for the separate injection of a KPS aqueous solution at the beginning of polymerization. The basic recipe for the emulsion polymerization of styrene was given in Table I.

Characterizations

The ¹³C-NMR spectra of SHEA that dissolved in DMSO-*d*₆ were recorded using a FT-NMR spectrometer (AMX 500, Bruker, Germany). Tetramethylsilane (TMS) was used as an external standard material. In order to confirm the surface activity of SHEA, the surface tension and pyrene solubility of SHEA aqueous solutions were measured with different SHEA concentration levels.³⁷ The surface tension of these solutions was measured by using a surface tensiometer (Surface Tensiomat 21, Fisher Sci., USA) at room temperature.

The particle size and particle size distribution of the latexes were analyzed by capillary hydrodynamic fractionation (CHDF-2000, Matec Applied Science) and transmission electron microscopy (TEM, CM200, Philips). For better contrast, the latex sample was stained with a 1 wt% RuO₄ aq. solution at room temperature. Molecular weight and molecular weight distribution were determined by using a gel permeation chromatography (GPC, Waters Co., USA) equipped with a series of Waters® columns (HR4, HR3, HR2) at 40 °C. Molecular weights were determined from the refractive index data, which were analyzed with Waters Breeze® System. The eluent was tetrahydrofuran (THF) with a flow rate of 1.0 mL/min. The raw data were calibrated using polystyrene standard samples.

Results and Discussion

Characteristics of SHEA. SHEA was prepared by a stepwise reaction using IPDI, in which a large difference in the reactivity between primary and secondary isocyanates was applied. Figure 1(a) shows the ¹³C-NMR spectra of the intermediates.³⁸ The primary urethane bond, which was formed by a reaction between primary isocyanate in IPDI and hydroxy group in 3-hydroxy-1-propanesulfonic, acid sodium salt, was observed at 155.6 ppm. The secondary isocyanate that shows a lower reactivity than primary isocyanate, was observed at 121.4 ppm as well. After adding *N*-(2-hydroxyethyl) aniline, the secondary isocyanate peak at 121.4 ppm disappeared and the secondary urethane bond appeared at 157.0 ppm, as shown in Figure 1(b). This indicated that SHEA was successfully synthesized.

SHEA is amphiphilic and forms micelles in an aqueous solution to provide polymerization loci in emulsion polymerization. As in Figure 2, the critical micelle concentration (CMC) of SHEA was 0.6 wt% of water, as determined by surface tension analysis based on DuNouy ring method.³⁹ Pyrene was an aromatic hydrocarbon that exhibited very low solubility in pure water ($[Py]_w = 7 \times 10^{-7}$ M) and it was largely used as a probe for the study of micelles and other hydrophobic aggregates in water. Pyrene absorbance intensity increased as the SHEA concentration increased, which indicates the solubilization ability for hydrophobic materials

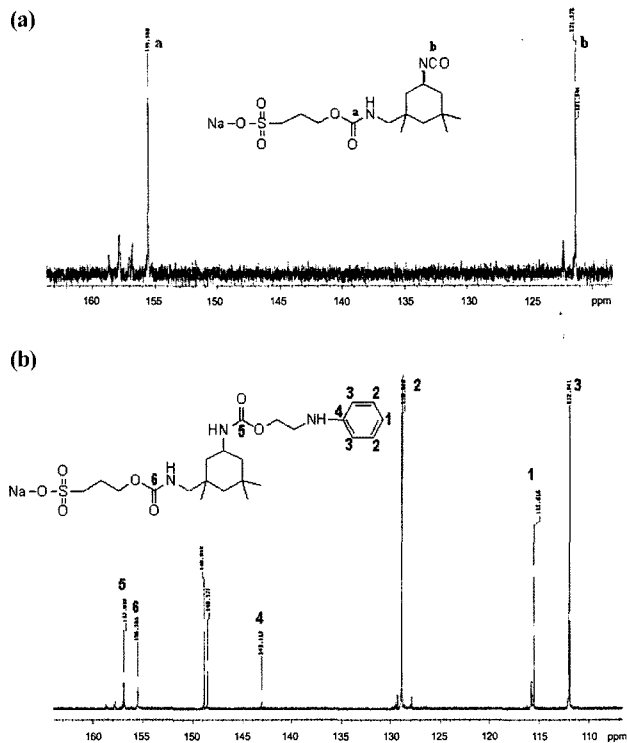


Figure 1. The ¹³C-NMR spectrum of SHEA in DMSO-*d*₆; (a) after 1st step and (b) 2nd step reaction.

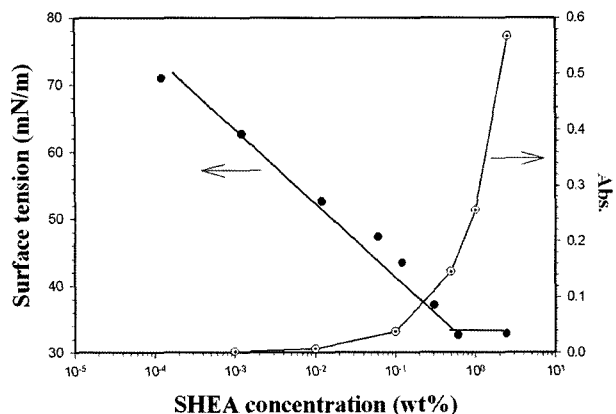


Figure 2. Surface tension data (by Dunouy ring method) and UV absorbance data of pyrene at 338 nm, as a function of SHEA concentration (wt% based on the DI water).

increases due to the formation of micelles in an aqueous solution. An increase in the solubility of pyrene is attributed to an increase in the number of the micelles, and therefore, SHEA can be used as a surfactant in emulsion polymerization because of its amphiphilic nature as mentioned before.

Morphology of the Poly(BMA-SHEA) Latex Particles Emulsion. For a feasibility of the use of SHEA in the emulsion polymerization, emulsion polymerization of butyl methacrylate (BMA) was carried out, since poly(St) and poly(SHEA) phases could not be discernible in the TEM image of poly(St/SHEA) particles. The hydrophobicity (i.e., saturation value of water-solubility) and propagation rate coefficient of BMA monomer are $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ and $587 \text{ L mol}^{-1} \text{ s}^{-1}$ (50°C), which are comparable with those of styrene, $4.3 \times 10^{-3} \text{ mol dm}^{-3}$ and $390 \text{ L mol}^{-1} \text{ s}^{-1}$ at 50°C , respectively.^{40,41} One can expect that poly(BMA) and poly(SHEA) would form core and shell parts, respectively. The reaction was done at 60°C in the presence of 20 wt% of SHEA and 6 wt% of AIBN, based on the BMA monomer. The TEM photo in Figure 3 shows the poly(BMA/SHEA) core-shell nanoparticles. The average particle size of the latex (\overline{D}_n) was around 45 nm. With KPS, however, no substantial polymerization of BMA monomer was observed with varying the SHEA concentration levels (from 10 to 40 wt%). The reason for this result originates from the high oxidation potential and water-solubility of KPS. The use of ordinary oxidative water-soluble initiators, such as KPS, leads to tremendous radical loss in the presence of SHEA due to the oxidation reaction of the aniline group of SHEA as well as destabilization of polymer particles by a high electrolyte concentration level from KPS. Scheme II shows a reaction mechanism of the chemical oxidative polymerization of aniline using persulfate species.^{35,36,42}

Retardation by SHEA in the Presence of KPS. In order to investigate the retardation effect by SHEA, SHEA was added in the middle of soap-free emulsion polymerizations

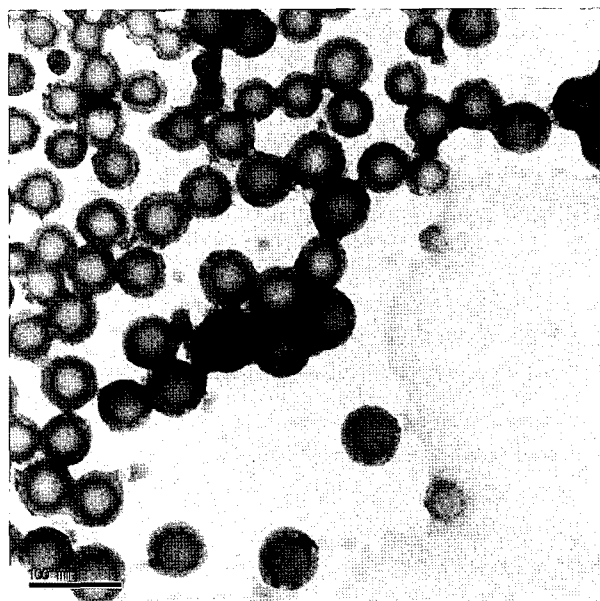
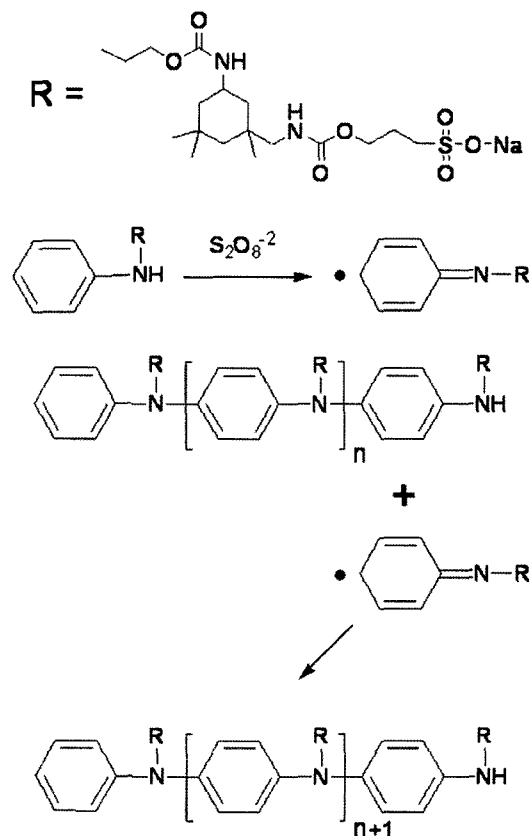


Figure 3. TEM photo of core-shell poly(BMA-SHEA) latex particles stained with RuO_4 prepared by emulsion polymerization, in the presence of 20 wt% SHEA based on the BMA monomer by AIBN (scale bar = 100 nm).



Scheme II. Schematic for the mechanism of oxidative polymerization of SHEA by using KPS.

of styrene with different reaction time. In the soap-free emulsion polymerizations, 10 g of styrene, 0.6 g of KPS, and 100 g of DI water were used. The injected amount of SHEA was 0.1 g. Figure 4 shows the time-conversion curves of styrene monomer with the addition of 1 wt% (based on initial styrene monomer) SHEA at different reaction time. When SHEA was injected at 79% conversion, the time-conversion curve showed a sort of retardation period. With 47% conversion, however, the rate of emulsion polymerization was dramatically retarded as compared with that of emulsion polymerization without SHEA. The rate of emulsion polymerization ($dx/dt=0.72\times 10^{-4} \text{ s}^{-1}$) in the presence of SHEA decreased below one fourth of that of emulsion polymerization ($dx/dt=2.69\times 10^{-4} \text{ s}^{-1}$) without SHEA as shown in Table II. One may expect that there should be secondary particle nucleation, since SHEA is a kind of surface active material. However, no secondary nucleation was observed after the addition of SHEA whilst ζ -potential values of the latexes slightly increased as compared with that of PSt latex without SHEA. In addition, the \overline{D}_n s with SHEA were comparable to those of the PSt latexes without SHEA. Table II

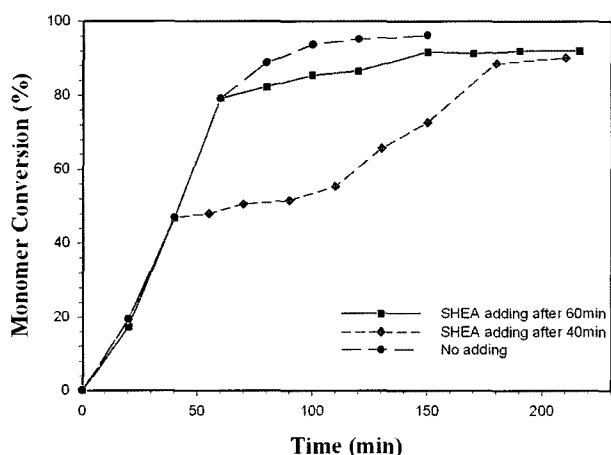


Figure 4. Effects of SHEA injection on the time-conversion curves for the soap-free emulsion polymerizations of styrene with the different injection time. The concentrations of SHEA and KPS were 1 and 6 wt%, respectively, based on styrene monomer.

shows the \overline{D}_n , ζ -potential, dx/dt , and so on, were listed.

Emulsion Polymerization Kinetics in the Presence of SHEA Using AIBN. Figure 5 shows the time-conversion curves of styrene with varying the SHEA concentration at 6 wt% of AIBN concentration. At a low SHEA concentration of 10 wt%, the maximum rate of polymerization ($R_{p,max}$) was extremely low ($2.1\times 10^{-5} \text{ molL}^{-1}\text{s}^{-1}$) while no induction period was observed. A large amount of unreacted monomer was, however, observed after polymerization, and which might be from the small number of monomer-swollen SHEA micelles or the low surface activity of SHEA. As the SHEA concentration increased from 20 to 40 wt%, $R_{p,max}$ increased from 6.5×10^{-5} to $89.1\times 10^{-5} \text{ molL}^{-1}\text{s}^{-1}$. This was attributed to the increase in the number of particles from 5.9×10^{17} to $8.2\times 10^{17} \text{ L}^{-1}$ of water, like common emulsion polymerizations. The \overline{D}_n decreased with increase of SHEA and the size distributions were broad as shown in Figure 6. However, as the SHEA concentration increased, the induction period increased. This seemed to be due to the fact that the consumption of AIBN by the oxidation with SHEA, which might be from the poly(SHEA) in aqueous phase or

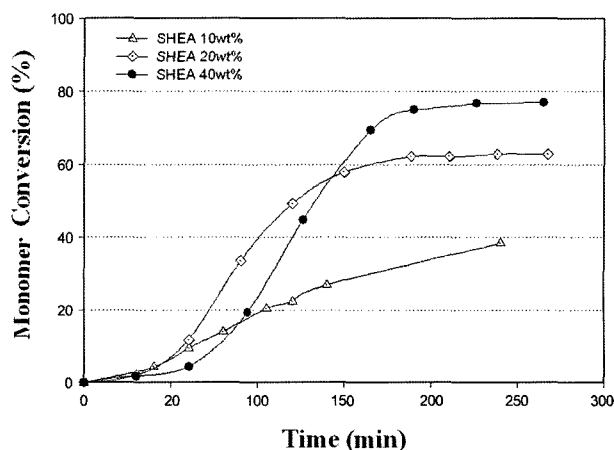


Figure 5. Time-conversion curves for the emulsion polymerizations of styrene using 6 wt% of AIBN with different SHEA concentrations (10, 20, and 40 wt% SHEA, based on the styrene monomer).

Table II. Effects of the Injection Time of SHEA on the Kinetic and Wet Properties of the PS Latexes

Sample	\overline{D}_n (nm)	PDI ^a	Final Conversion (%)	N_p (10^{18}L^{-1})	dx/dt^b ($\times 10^4 \text{ s}^{-1}$)	ζ -Potential (mV) ^c
PSt latex without SHEA	113.2	1.008	96	1.83	2.69	-15.8
SHEA-added PSt Latex ^d	Before	115.2	79	1.88		-23.5
	After (Final)	120.4	92	1.92		
SHEA-added PSt Latex ^e	Before	88.7	47	1.86	0.72	-21.4
	After (Final)	109.8	90	1.88		

^aPolydispersity Index (PDI) = D_w/D_n . ^bwas measured in the range of conversion between 50 and 80%. ^cfor the final latexes.

^dat 79% conversion. ^eat 47% conversion.

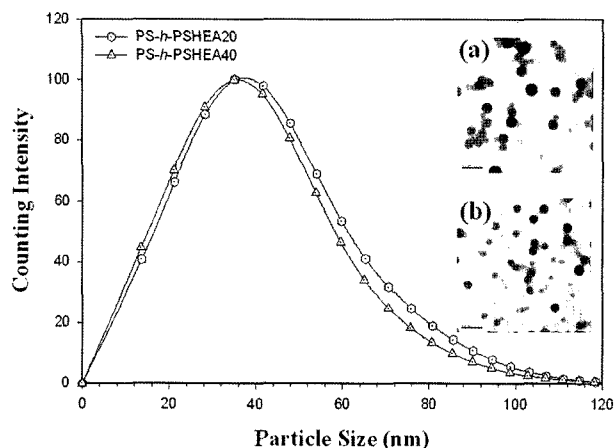


Figure 6. Particle size distribution of the core-shell poly(St/SHEA) particles prepared by emulsion polymerization with AIBN and different SHEA amounts. Insets show TEM photos of the particles (a) 20 wt% SHEA and (b) 40 wt% SHEA, based on the styrene monomer (scale bar = 100 nm).

the poly(SHEA) shell of particles, was expedited due to the increase of the SHEA concentration. Color change of the latex was observed from white to pinkish white in the beginning of polymerization. AIBN showed a reasonable polymerization rates were observed at the same initiator concentration compared with KPS. As mentioned above, the use of ordinary water-soluble initiator such as KPS, led tremendous radical loss in the presence of SHEA as a surfactant because of the oxidation reaction of aniline group in SHEA by KPS. Therefore, the use of AIBN would be more effective than KPS. AIBN is an oil-soluble initiator thus, it can be located in the inner part of latex and it can efficiently acts as a radical initiator in a competitive reaction between the radical polymerization of styrene and the oxidation reaction of SHEA. In addition, KPS is water-soluble and its oxidation potential is high enough to readily react with SHEA, which is dominantly located on the surface of the monomer-swollen micelles or the pre-matured growing latex particles. On the other hand, the polymerization of styrene in the presence of AIBN was believed to have taken place in both the formed polymer particles and monomer droplets since AIBN is an oil-soluble initiator. This explanation would be further corroborated by the GPC elution data in Figure 7 for the molecular weight and weight distribution measurement.

Molecular Weights. Figure 7 shows the GPC elution curves of PSt obtained from the poly(St/SHEA) particles with 20 wt% of SHEA concentration as a function of polymerization time. At the initial stage of polymerization, the number-average molecular weight (\overline{M}_n) of poly(St) was rather small (between 30,000 and 50,000 gmol^{-1}), and which is probably due to the bulk polymerization of styrene in the monomer droplets in the beginning; afterwards, the \overline{M}_n

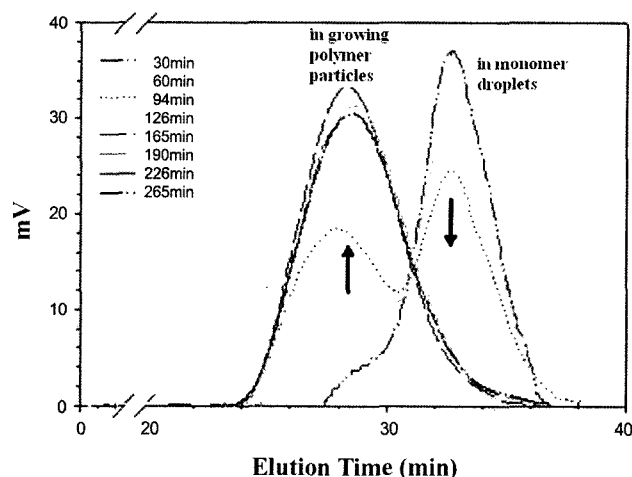


Figure 7. The GPC elution curves of the polystyrene produced in emulsion polymerization with 20 wt% SHEA, based on the styrene monomer.

increased in the range of between 300,000 and 600,000 gmol^{-1} . This is due to the substantial emulsion polymerization in the particles. This result is evident that the polymerization of styrene, in the case of AIBN, has taken place in both the formed polymer particles and monomer droplets. This result could be explained as follows: The polymerization in the monomer droplets would be important in the beginning, however, the partition of AIBN reaches equilibrium among monomer-swollen micelles, monomer droplets, and water phases as the reaction progresses, whilst the polymerization is inhibited or retarded by the radical losses of AIBN with oxidation reaction of SHEA in the aqueous phase. Polymerization in the growing polymer particles, however, become dominant as the polymerization proceeds because of nucleation of the particles for the polymerization 'loci' and the decrease of the unreacted SHEA in the aqueous phase, or in the interfaces of the droplets and particles, by the polymerization of SHEA.

Conclusions

From the emulsion polymerization of styrene in the presence of SHEA, it was found that core-shell poly(St/SHEA) latex particles (ca. 45 nm in diameter) were successfully prepared with AIBN, even though the time-conversion curves showed a retardation behavior. In the case of KPS initiation system, however, it was not possible to obtain an appropriate conversion. Since KPS has strong oxidation ability, it oxidizes SHEA rather than initiates polymerization. This was explained by the low $R_{p,max}$ and the long inhibition period of the emulsion polymerization of styrene with different amounts of SHEA. Retardation in the emulsion polymerization of styrene, with AIBN at the initial stage, can be explained by the consumptive oxidation reaction between SHEA and AIBN.

The mean particle size of the core-shell poly(St/SHEA) particles decreased and $R_{p,max}$ increased with the increase in SHEA concentration after the initial retardation stage. From the molecular weights of poly(St/SHEA), it was observed that the initial loci of polymerization were monomer droplets due to the low water-solubility of AIBN and retardation reaction by SHEA; however, growing polymer particles as polymerization loci became predominant as polymerization proceeded. Therefore, it can be suggested that AIBN is more effective, as compared with KPS, in the preparation of the core-shell type poly(St/SHEA) latex particles.

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