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ORIGINAL CONTRIBUTION

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Preparation and size control of monodispersed surface charged polystyrene nanoparticles by reversible addition fragmentation transfer reaction

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Abstract Highly monodispersed polystyrene (PS) nanoparticles were prepared via reversible addition fragmentation transfer (RAFT) living radical emulsion polymerization technique. Two types of novel sur-iniferters with different hydrophilic lipophilic balance (HLB) values, 4-diethythiocarbonylsulfanylmethyl-benzoic acid and 4-(2-hydroxyethyl) piperazine-1-carbodithioicacid benylether, were synthesized for the PS RAFT reaction and their chemical synthesis was identified using nuclear magnetic resonance spectroscopy. Scanning electron microscope and dynamic light scattering experiments showed that the size distribution of the particles prepared was highly monodispersed. The average particle size was affected by the type and concentration of sur-iniferters. It increased with decreasing sur-iniferter concentrations, and the use of sur-iniferters with higher HLB values led to increases of particle sizes, as the particles were growing from, initially, much larger monomer droplets. The surfaces of the nano particles prepared were ionically charged. The surface charge measured was −50 mV, which enabled particles to be stably dispersed in aqueous medium.

Keywords Mnodisperse · Particle · Emulsion · RAFT · Nano

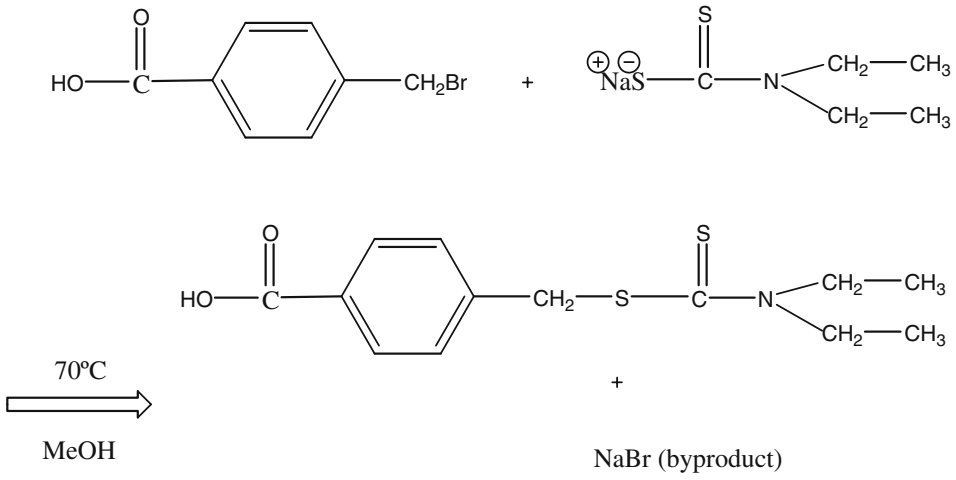
Introduction

Polymeric particles have been widely used as coating, adhesive, ink, and painting materials. The applications of Nano- to microscaled polymeric particles with monodispersed distributions are expanding to not only information and electronic industries manufacturing TFT-LCD, digital toner, e-paper, etc., but to biochemical and biomedical industries manufacturing drug delivery systems, chromatographic columns, diagnostic sensors, etc. [1–3].

Polymeric particles are usually prepared by the free radical polymerization method either in emulsion, dispersion, or suspension state [4, 5]. Highly monodispersed particle size distribution, however, is not easily achieved by this technique, simply because the molecular weight distribution of polymer chains comprising each particle is not easily controlled. In the conventional free radical polymerization [6], the reaction kinetics in initiation, propagation, and termination steps are different from one another. All polymeric chains do not grow at the same time in the initial stage, as the chain growth (propagation) rate is usually much higher than the radical formation rate. Similarly, all growing chains do not terminate at the same time in the final stage because of the difference between the propagation and termination rates. The surfactant or dispersing stabilizer is one of prerequisites in the production of polymeric particles when heterogeneous polymerization techniques, such as emulsion, dispersion, and suspension methods, are used. Thus, the use of surfactant is another cause for polydispersity, as the particle growing reaction occurs not only inside but also outside micelles and even in monomer droplets when surfactants are used.

Living radical polymerizations are characterized by their unique reaction mechanisms where radicals are reversibly detached from, and combined to, the polymeric chain ends [7]. Living radical polymerizations are categorized into three types according to their mechanisms: nitroxide-mediated polymerization (NMP) [8–13], atom transfer radical polymerization (ATRP) [14–17], and reversible addition fragmentation transfer (RAFT). While NMP and

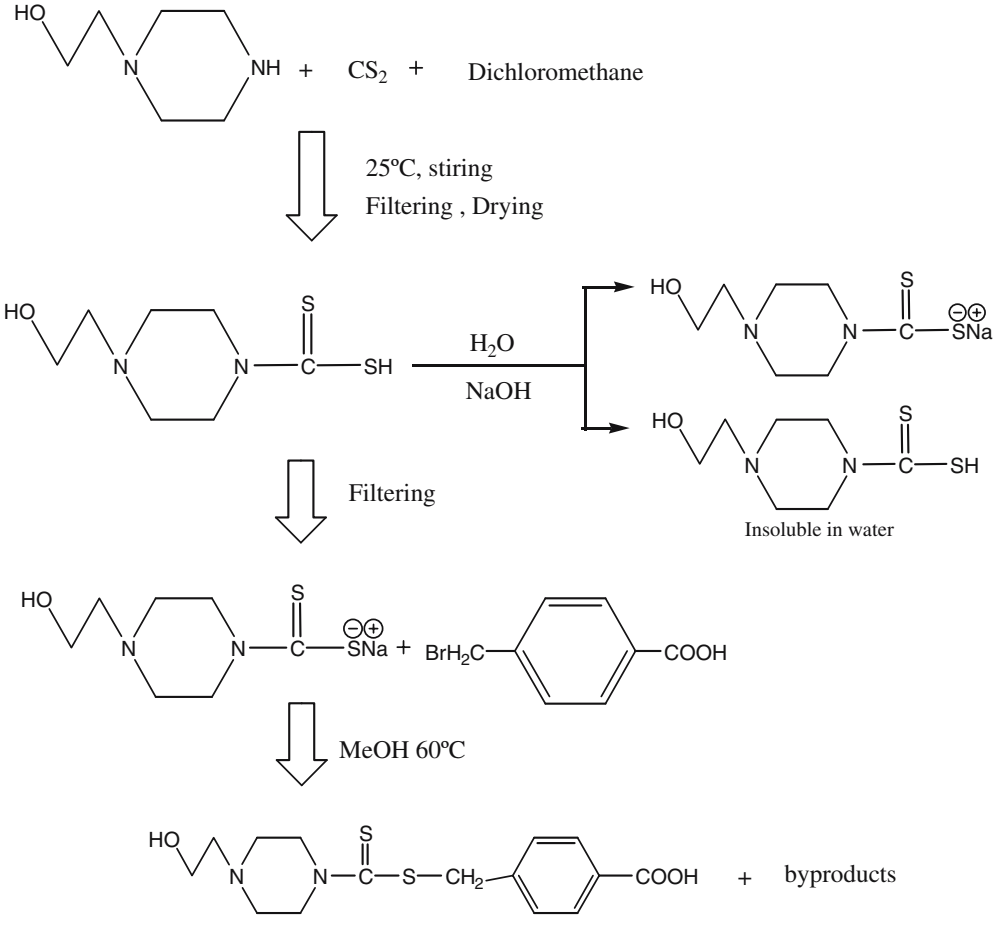
Scheme 1 Synthesis of 4-diethyl thiocarbonyl sulfanyl-methyl-benzoic acid (DTBA)



ATRP use 4-oxy 2,2,6,6-tetramethylpiperidyl-1-oxyl and metal catalysts in addition to their own initiators, respectively, RAFT does not use any independent additives besides the RAFT agent, iniferter [18–23].

In the RAFT reaction system, the iniferter is a key reagent that enables living radical polymerization to be successfully conducted, because living radical polymerization possesses all the roles as an initiator, chain transfer agent, and terminator [24–27]. If the role of surfactant is combined with that of iniferter, polymeric particles can be produced via the emulsion method without using any specific surfactant. When the RAFT mechanism is applied to the emulsion polymerization using this iniferter, the so-called sur-iniferter, ionic charges are provided on the

Scheme 2 Synthesis of 4-(2-hydroxy-ehtyl)-piperazine-1-carbodithioic acid (HPCB)



growing polymeric particle surfaces. As initiation, chain transfer reaction, termination, and emulsification are simultaneously provided by a reagent, the polymeric particles produced are highly monodispersed and no further separation or purification processes are required.

A number of studies have reported on the synthesis of polystyrene (PS) via the RAFT method in bulk state, but few have reported on emulsion or dispersion state. In this contribution, monodispersed PS nanoparticles were prepared via RAFT emulsion polymerization method. Anionic charges were provided on particle surfaces by novel sur-iniferters. Effects of the concentration and hydrophilic lipophilic balance (HLB) of sur-iniferters on the ultimate particle size and its distribution were investigated.

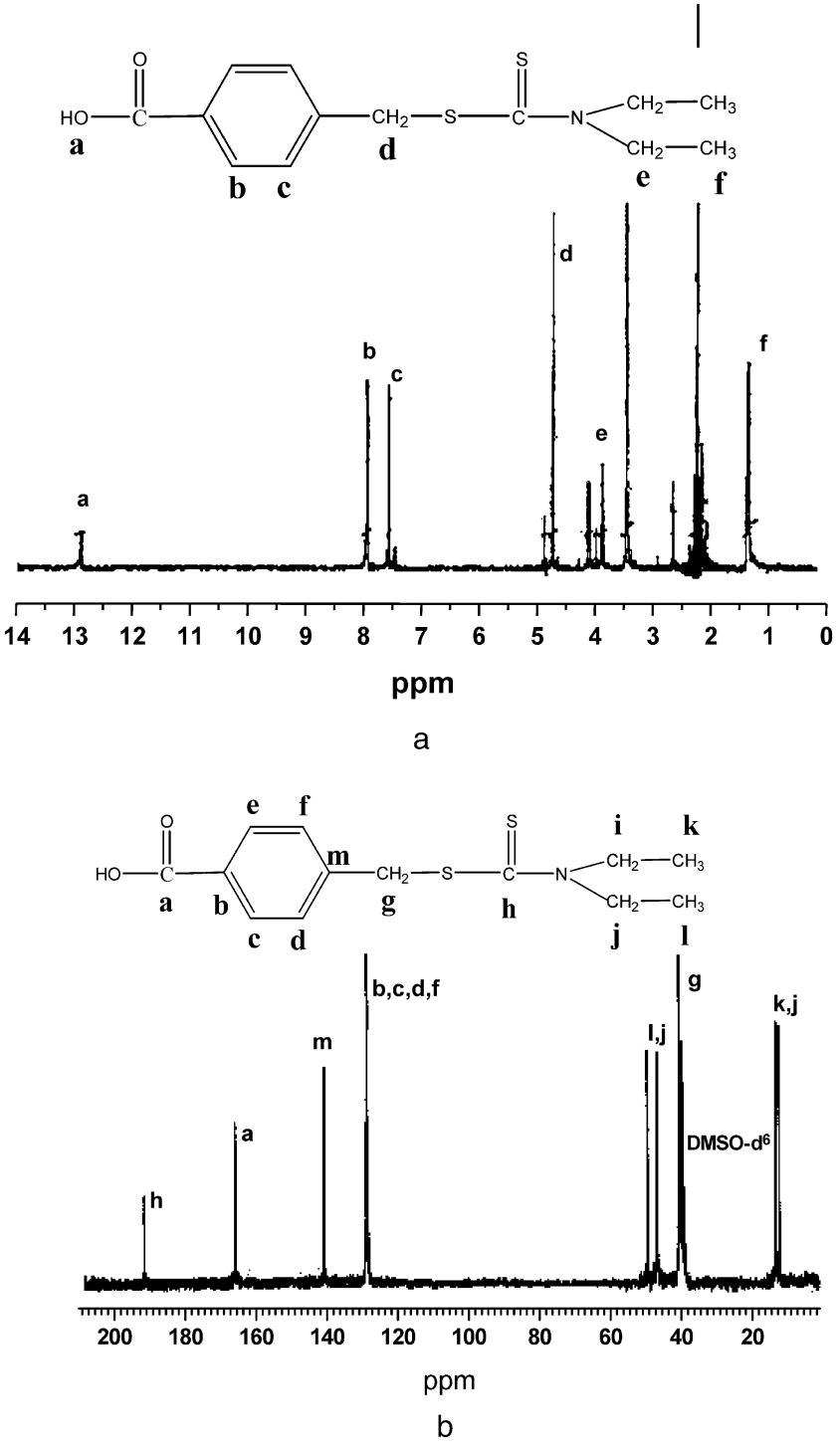


Fig. 1 ^{1}H-NMR (**a**) and ^{13}C-NMR (**b**) spectra of DTBA

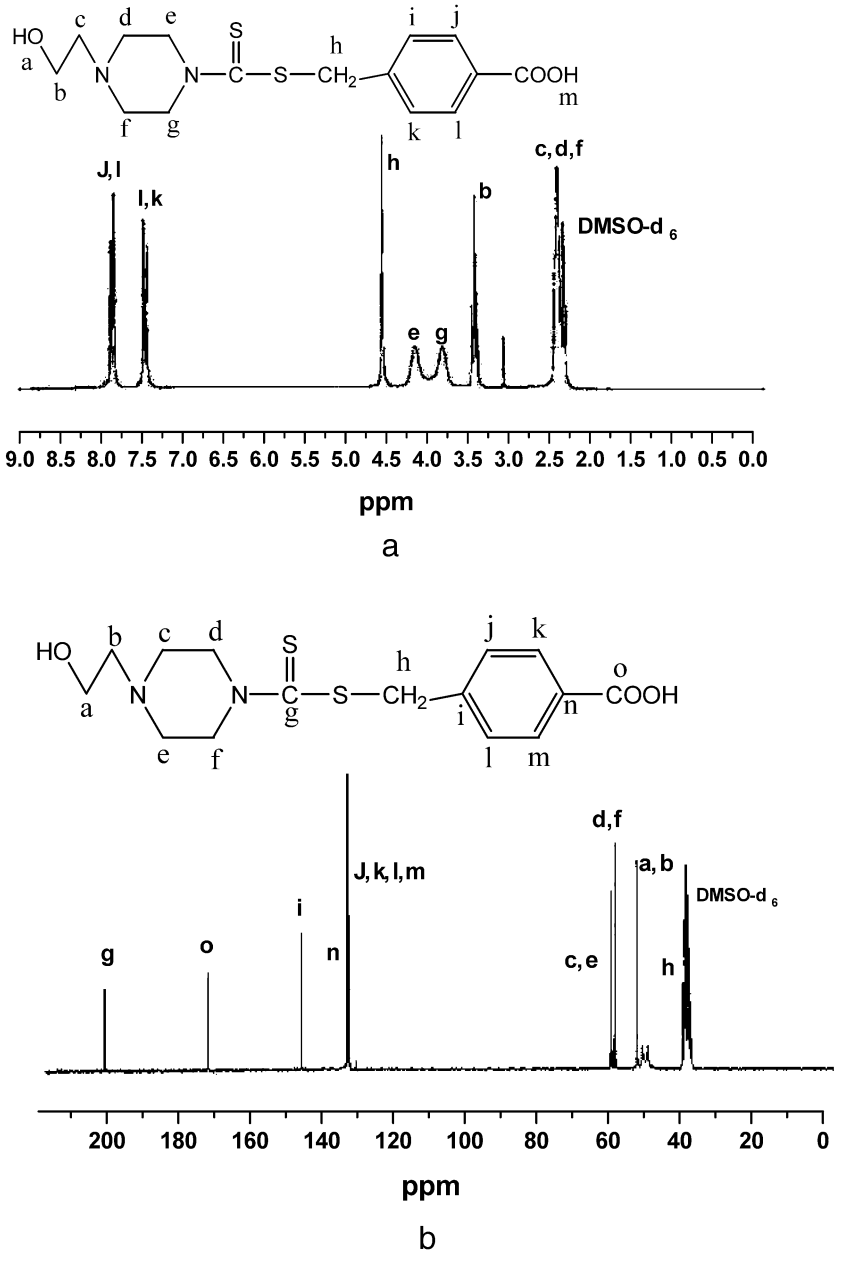


Fig. 2 ^{1}H-NMR (**a**) and ^{13}C-NMR (**b**) spectra of HPCB

Experimental section

Materials

Styrene monomer (St, Aldrich Chemical, Milwaukee WI, USA) was purified using a butyl carbitol inhibitor-removing column. 4-bromomethyl benzoic acid (Tokyo Chemical, Tokyo, Japan), sodium diethydithiocarbamate trihydrate (Aldrich Chemical), 4-hydroxy-ethyl piperazine, carbondisulfide (CS_2), 4-bromoethyl benzoic acid (Tokyo Chemical), and benzyl bromide (Aldrich Chemical) were reactants for the synthesis of sur-iniferters. Methanol (Daejung, Korea) and dichloromethane as solvent were dehumidified and vacuum distilled in the presence of CaH_2 (Tokyo Chemical) before use. Water, the dispersing medium, was purified at least twice before use by a water ultrapurification system (Aquamax, Younglin, Korea).

Table 1 Elemental analysis of 4-diethyl thiocarbonyl sulfanyl-methyl-benzoic acid (DTBA)

Anionic sur-iniferter (DTBA)					
Element	C	H	O	S	N
Calculation	55.09%	6.05%	11.29%	22.63%	4.94%
Analysis	54.98%	6.46%	11.30%	22.64%	4.61%

Table 2 Elemental analysis of 4-(2-hydroxy-ehtyl)-piperazine-1-carbodithioic acid (HPCB)

Anionic sur-iniferter (HPCB)					
Element	C	H	O	S	N
Calculation	52.92%	5.92%	14.10%	18.83%	8.22%
Analysis	53.11%	6.31%	13.27%	18.57%	7.73%

Synthesis of sur-iniferters

The synthetic route of the first sur-iniferter, 4-diethythiocarbonylsulfanylmethyl-benzoic acid (DTBA), was already reported by Kwak et al., and is illustrated in reaction Scheme 1 [28]. 4-bromomethyl benzoic acid, 0.1 mol, and sodium diethydithiocarbamate trihydrate, 0.1 mol, were dissolved in 250 ml methanol, and the mixture was reacted at 70°C for 24 h. The product, DTBA, was cooled to 4°C, and then the residual solvent (methanol) was removed using a rotary evaporator at room temperature. The unreacted substrates and other impurities were completely eliminated by washing in distilled water. The product was dissolved in NaOH solution, and then recrystallized in HCl solution. This purification process was conducted three times.

The other sur-iniferter, 4-(2-hydroxyethyl)piperazine-1-carbodithioicacid benylether (HPCB), was synthesized by a similar method to that used for DTBA. 4-hydroxy ethyl piperazine, 0.1 mol, was dispersed in 300 ml dichloromethane. CS_2, 0.1 mol was continuously dropped to the dispersant using a dropping funnel at room temperature. After reaction for 8 h, the product was filtrated at reduced pressure and then dried at 40°C in a vacuum oven. The dried product was placed in 100 ml, 1 M NaOH aqueous solution, and the mixture was stirred for 2 h at 40°C with a magnetic bar. The mixture was reacted with 0.1 mol 4-bromoethylbenzoic acid in 600 ml methanol for 8 h at 60°C. The final product, HPCB, was washed in ethyl ether. Other purification steps were the same as those for DTBA. The synthetic procedure of HPCB is illustrated in reaction Scheme 2.

Preparation of PS nanoparticles

Two kinds of sur-iniferters, DTBA and HPCB, synthesized as above, were used for the preparation of PS particles. Styrene monomer was dispersed in 150 ml water placed in a 250-ml flask. The monomer concentration was 10 wt.%, and the stirring speed was 700 rpm. Photopolymerization reaction was conducted by radiation of UV light at room temperature. Concentrations of sur-iniferter added were 0.90, 0.45, and 0.30 wt.% to control the molecular weights of polymer products. Reaction times were from 24 to 36 h.

Characterization

Chemical structures of the sur-iniferters synthesized, DTBA and HPCB, were identified using ^{1}H and ^{13}C-Fourier transform nuclear magnetic resonance spectroscopy [^{1}H and ^{13}C-Fourier transform nuclear magnetic resonance (FTNMR), Varian, Unit Inova 500, USA]. Each sur-iniferter was dissolved in $DMSO_4$-d_6 for this identification. The atoms comprising each sur-iniferter were quantified using the elemental analyzer (EA1100, CE Instruments, USA). A scanning electron microscope (SEM, Hitachi, S-2400, Japan) and dynamic light scattering (DLS, Brookhaven, BI-200SM, USA) were used to analyze the shape and size distribution of PS particles, respectively. Each sample was coated with platinum for SEM measurement. Gel permeation chromatography (Waters 515, USA) was used to measure the molecular weights of the PS products using tetrahydrofuran as a solvent at the injection flow rate of 1 ml/min. Zeta-potential analyzer (ELS-8000, Otsuka Electronics, Japan) was used to measure electric potentials of polymer particles.

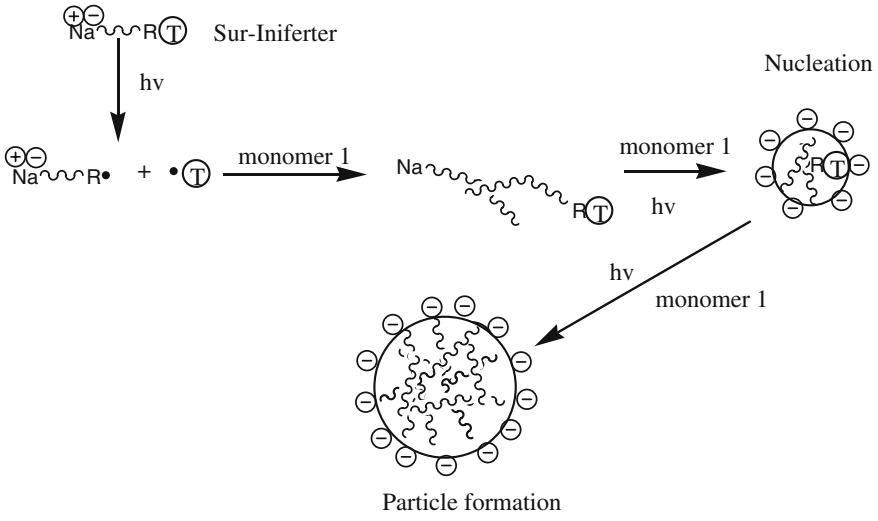


Fig. 3 Particle growth mechanism via RAFT living radical emulsion polymerization using sur-iniferters

Results and discussion

Identification of sur-iniferters

Reaction Schemes 1 and 2 show the schematics of synthetic routes of the sur-iniferters DTBA and HPCB, respectively. Both DTBA and HPCB have living radical functions associated with their reversible reactivity attributed to the weak interaction between dithio- and benzyl-ether groups. NaBr, a by-product, was released during their synthesis. While DTBA has a hydrophilic group, a carboxylic acid group, at the end of a polymer chain, HPCB has two hydrophilic groups, a carboxylic acid group and a hydroxyl group, at chain ends; thus, the latter can provide

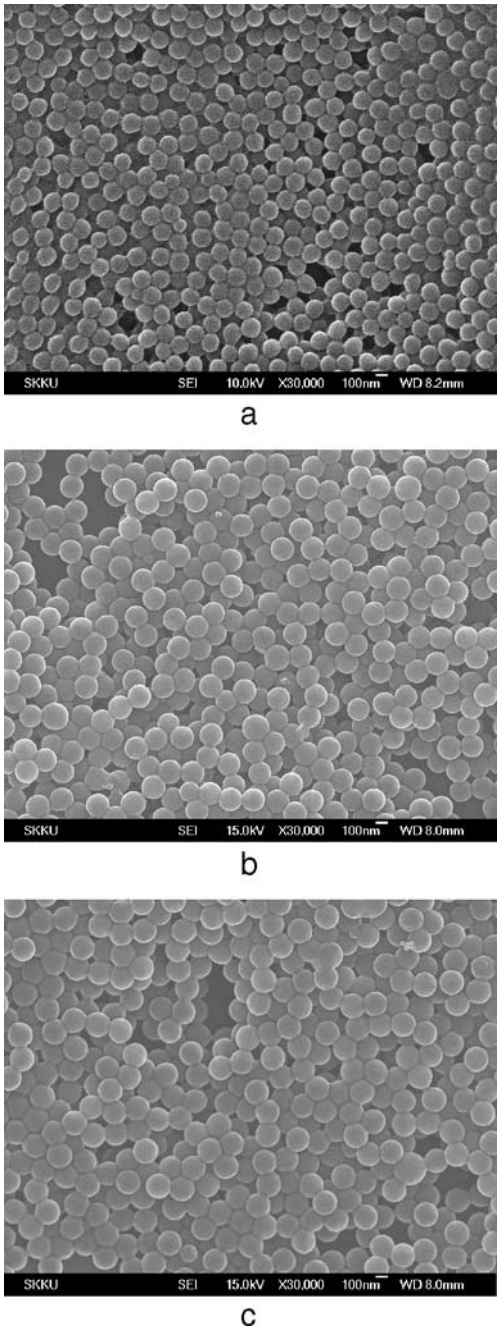


Fig. 4 Microphotographs of PS particles prepared using different concentrations of DTBA of **a** 0.90, **b** 0.45, and **c** 0.30 wt.%

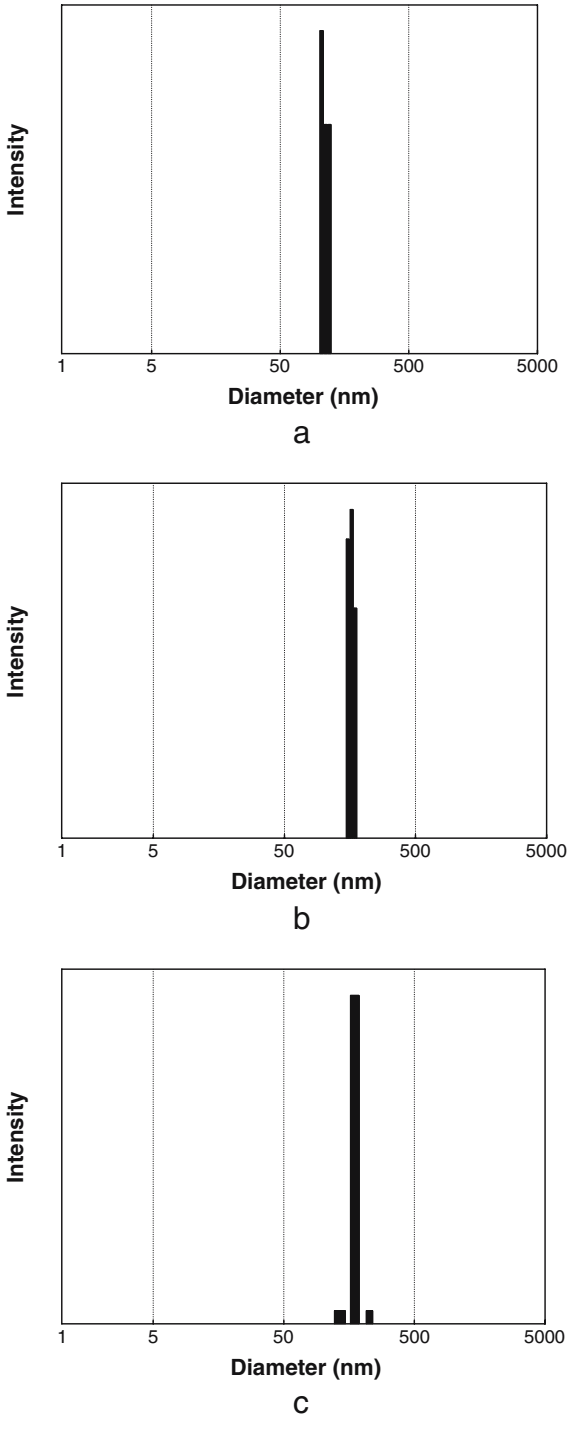


Fig. 5 Size distribution of PS particles prepared using different concentrations of DTBA of **a** 0.90, **b** 0.45, and **c** 0.30 wt.%

either anionic or cationic surfactant function by the addition of NaOH or HCl. Figures 1 and 2 show chemical identification results for DTBA and HPCB from FTNMR measurement, respectively. All protons in DTBA and HPCB molecules were possibly identified, assigning and analyzing their corresponding peak positions and integration areas as shown in the ^{1}H-NMR of Figs. 1a and 2a, respectively. The presence of CS_2 groups in DTBA and HPCB was examined from the occurrence of its characteristic peak at 190 ppm of ^{13}C-NMR spectra in Figs. 1b and 2b, respectively. Tables 1 and 2 show the elemental analysis results of the two sur-iniferters. Experimental results on their atomic compositions were in accordance with theoretical results.

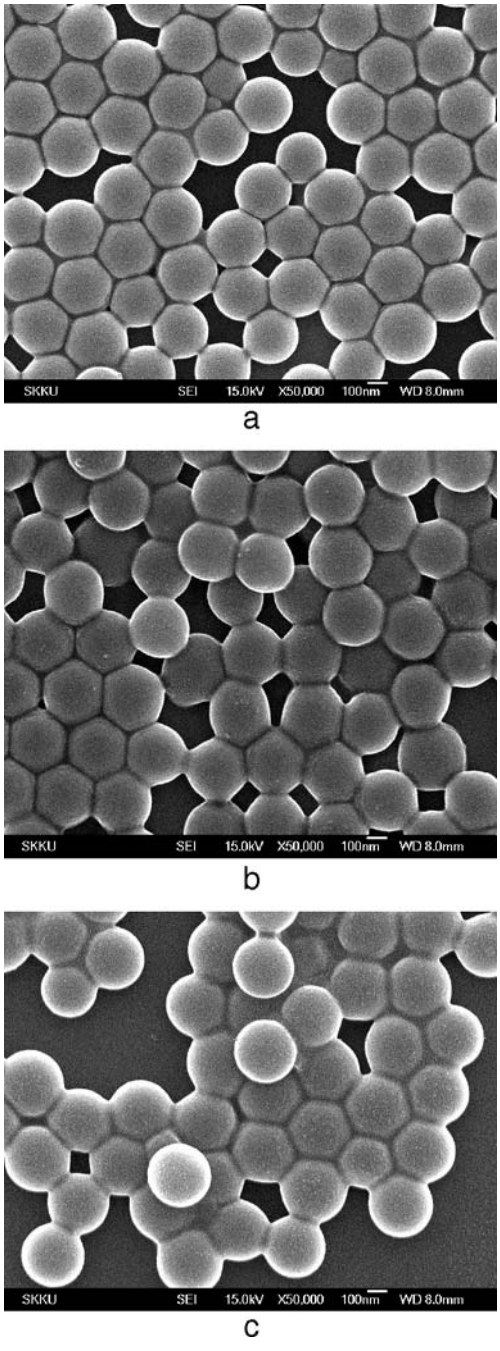


Fig. 6 Microphotographs of PS particles prepared using different concentrations of HPCB of **a** 0.90, **b** 0.45, and **c** 0.30 wt.%

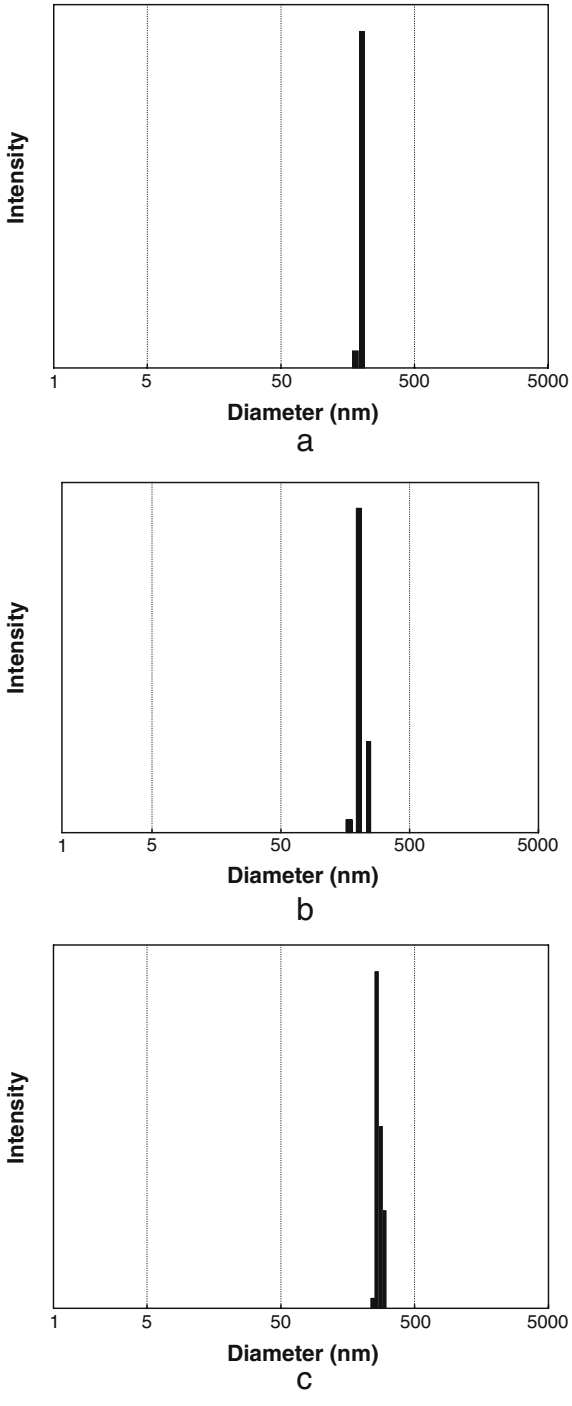


Fig. 7 Size distribution of PS particles prepared using different concentrations of HPCB of **a** 0.90, **b** 0.45, and **c** 0.30 wt.%

Sur-iniferter concentration effect

Figure 3 shows a scheme of particle growth mechanism in this RAFT living radical emulsion polymerization using sur-iniferters. The initiation reaction proceeds continuously at the same rate as the termination reaction until all monomers are consumed [7]. When the concentration and reactivity of living radicals are invariant regardless of monomer concentration, a linear increase of chain growth with very narrow distribution is expected. Being different from free radical emulsion polymerization, the chain growing sites are confined to inside the micelles, as the sur-iniferter itself has a surfactant function at its end molecular position. As the nucleation occurs only inside the micelles, the radiation of radical generation energy eventually induces the growth of particles with the ions present at their surfaces. Much more stable and monodispersed particles are obtained by the prevention of particle coagulations attributed to ionic repulsion associated with the surface charges.

Figure 4 shows SEM microphotographs of PS particles prepared using a sur-iniferter of DTBA. Particle sizes decreased with increasing sur-iniferter concentration. In conventional free radical emulsion or suspension polymerization, particle sizes are affected mostly by surfactant concentration, while molecular weight distribution is affected mostly by initiator concentration. In this living radical polymerization method, however, both are affected by the same parameter, sur-iniferter concentration, because it possesses both surfactant and initiation functions. In this study, the number average molecular weights of the prepared polymer particles were 110,000 (Fig. 4a), 121,000 (Fig. 4b), and 172,000 g/gmol (Fig. 4c), depending on DTBA concentrations from 0.90 to 0.30 wt.%. Polydispersity indices of polymer particles were 1.31, 1.24, and 1.22, respectively.

Figure 5 shows the particle size distribution of the synthesized PS nanoparticles measured by DLS. Highly monodispersed size distributions are shown for all systems. Comparison of Fig. 5a–c reveals that the average particle diameters increase from 110 to 200 nm with decreasing DTBA concentrations from 0.90 to 0.30 wt.%, as observed in SEM microphotographs.

HLB effect

Figures 6 and 7 show SEM microphotographs and DLS data, respectively, for PS nanoparticles prepared using the sur-iniferter of HPCB that has a higher HLB value than DTBA. The size of particles obtained using HPCB was much higher than that obtained using DTBA at the same sur-iniferter concentration. It is because the particles were growing from much larger monomer droplets in the initial emulsion state as the hydrophilicity that HPCB was higher than DTBA. Particle size increased with decreasing sur-iniferter concentrations for the same reason as DTBA. In this study, HLB values of sur-iniferters were determined according to the Griffin equation [Eq. (1)] as follows:

$$\mathrm{HLB} = 20(1 - \mathrm{M}_0/\mathrm{M}) \tag{1}$$

Here, M_0 and M are the molecular weights of hydrophobic and total chemical segments, respectively [29].

Surface zeta potential

The particles prepared in this study have ionic charges at the particle surfaces. Zeta potential is a parameter indicating the dispersion stability of particles in dispersant. Figure 8 shows the zeta potential behavior for PS particles prepared using DTBA in aqueous medium. The surface charge measured was −50 mV, and this value assures one that the particles were well dispersed in the aqueous medium, as it was reported that repulsion forces are enough for stabilization when zeta potential is higher than −25 mV.

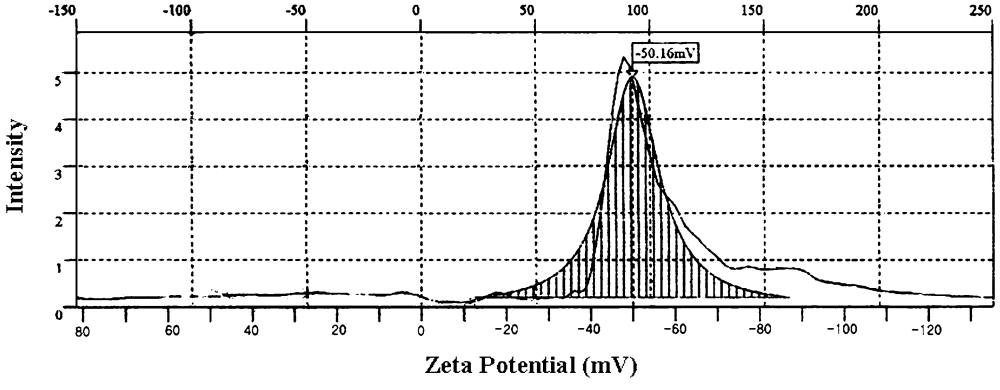


Fig. 8 Zeta-potential of PS particles prepared using DTBA concentration of 0.45 wt.% in aqueous medium

Conclusion

Preparation of highly monodispersed PS nanoparticles by RAFT living radical emulsion polymerization technique using novel sur-iniferters was discussed. Sur-iniferters were synthesized and their chemical structures were identified using FTNMR and elemental analyzer. Both particle size and polymer molecular weight increased with decreasing sur-iniferter concentrations. The particle size distribution was highly monodispersed from DLS analysis. Higher HLB values of sur-iniferters led to an increase of particle size, as the particles were growing from initially much larger monomer droplets. The surfaces of nano particles prepared were ionically charged. As the value of zeta potential was −50 mV, it was assured that the particles were well dispersed in the aqueous medium.

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