

# Emulsion Polymerization Using NaPSS-*b*-PS as a Cosurfactant

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**ABSTRACT:** A NaPSS-*b*-PS was prepared via a two-stage stable free-radical polymerization using a mixture of ethylene glycol and water as the medium. Styrene emulsion polymerization was conducted using a mixture of NaPSS-*b*-PS and SDS. Results showed that there is little aggregation among particles. Two other NaPSSs with different sulfonation fractions were also compared. Comparisons were made using relationships, such as  $\bar{n}$  versus

$D_v$ , chain growing time versus SDS content, and  $D_v$  versus SDS content. Characteristic behaviors of various NaPSSs on entry were revealed. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2883–2890, 2012

**Key words:** emulsion polymerization; living polymerization; block copolymers

## INTRODUCTION

The amphiphilic structure of surfactants plays a crucial role in emulsion polymerization.<sup>1</sup> Efforts have been exerted on the systematic study of polymeric stabilization of colloidal dispersion.<sup>2</sup> Di- and triblock copolymers are considered as effective stabilizers in heterophase polymerization.<sup>3,4</sup>

Stabilizers used in emulsion polymerization because of the multiple surface particle contact have also been reported like block copolymers, such as amphiphilic block copolymers consisting of a hydrophobic block of hydrogenated polybutadiene and a partly sulfonated polyelectrolyte block of poly(styrenesulfonate).<sup>5</sup> It is proposed that fully-sulfonated polymer systems presumably exhibit a molecular orientation perpendicular to the particle surface, whereas 50% sulfonated species take on a tail-like conformation along the surface.<sup>5</sup>

Emulsion polymerization of styrene using a sodium polystyrene sulfonate (NaPSS) has been reported that the NaPSS is synthesized through post-sulfonation of a narrow disperse polystyrene.<sup>6</sup>

The enhanced hydrophobic character of postsulfonated NaPSS over that of free radical polymerized NaPSS has been reported.<sup>7</sup> It is attributed to its intrinsically low configurational entropy that results from the formation of intramolecular sulfone link-

ages, whereas the latter gives only a linear structure. However, the principle is not clear yet, and quite ample space leaves us to exploit.

The preparation of NaPSS macroradicals by a living free radical polymerization technique has been reported elsewhere,<sup>8</sup> and this intrigues the interests on the preparation of a diblock copolymer of NaPSS and styrene as the surfactant.

Utilization various structures of NaPSS or NaPSS-*b*-PS in emulsion polymerization, the entry of oligomer radical into the latex particles may be varied.

There are different oligomer radical entry theories in emulsion polymerization.<sup>9–14</sup> The rate-controlling step for entry has been attributed to the aqueous-phase propagation to a critical degree of polymerization.<sup>9</sup> Other proposed theories include (a) the diffusion of the free radical to particle surface<sup>10–13</sup>; (b) the displacement of surfactant from the particle surface<sup>14</sup>; and (c) the entering species is a large oligomer, whose entry rate coefficient is decided by colloidal consideration.<sup>10,13</sup>

In this study, we prepared NaPSS-*b*-PS by using living-free-radical polymerization technique, and carried out emulsion polymerization of styrene using the NaPSS-*b*-PS as the cosurfactant. Other sources of data<sup>6,15</sup> for NaPSS with various sulfonation fractions were also compared to see some of the entry behavior of oligomer radicals.

## EXPERIMENTAL

### Materials

The following compounds were used as received: 4-styrene sulfonic acid sodium salt hydrate (NaSS,

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monomer, Aldrich Chemical Company), Ethylene glycol (EG, Tedia Company, 99.9%), benzoyl peroxide (BPO,  $C_6H_5COOOCOC_6H_5$ , Wako Pure Chemical Industries, reagent grade), 2,2,6,6-tetramethyl-piperidine 1-oxyl (TEMPO, Acros Organics, 98%), sodium dodecyl sulfate (SDS, Sigma Company, 99%), and hydroquinone (Showa Chemical, 99%). Water was purified through a Reverse Osmosis System (Ultra-pure Water System, Model DI-S3, Kintech) with a conductivity of 2  $\mu$ mho.

Monomer styrene (Acros Organics, 99%) was purified by distillation under reduced pressure.

### Preparation of NaPSS-*b*-PS diblock copolymer

Preparation uses the stable free-radical polymerization technique.<sup>8</sup> In the recipe, a mixture of BPO and TEMPO were used as the initiator, and a mixture of ethylene glycol (EG)/H<sub>2</sub>O (w/w = 6/1) was used as the medium. Both TEMPO (0.19 g) and BPO (1.18 g) were dissolved in a small amount of acetone and then added to (EG/H<sub>2</sub>O) (=60.0/10.0 g) solution, containing 10.0 g of sodium styrenesulfonate (NaSS). The solution was purged and stirred at 150 rpm. The temperature was set at 60°C for 1 h. After that, the temperature was raised to 120°C, and was kept at this temperature for 10 h to finish the reaction. The macro-initiators were dried to remove solvents and residual monomer. Four batches of NaPSS macro-initiators were mixed together for further uses. In the second stage, 3.0 g of macro-initiators were dissolved in a (EG/H<sub>2</sub>O) solution (60.0/10.0 g) at 60°C, 20.0 g of styrene was then added, and the mixture was purged. The reaction was then conducted at 120°C for 4 h to finish the reaction. Six batches of NaPSS-*b*-PS products were mixed together for further uses. The conversion was determined gravimetrically in both stages using hydroquinone as a shortstop and acetone as a coagulation agent. Filtration was needed in collecting the solid.

### Purifications and characterizations of NaPSS and NaPSS-*b*-PS

NaPSS was purified by procedures as following: dissolved in deion water, precipitated in methanol and filtrated; dissolved in acetone and decanted the supernate for 2–3 times; and dried in 80°C oven.

The residual polystyrene in NaPSS-*b*-PS has been removed by extracting the aqueous solution with toluene.

A thin layer chromatographic (TLC) technique has been used to qualitatively determine the purity in NaPSS-*b*-PS.

The purified sample of NaPSS or NaPSS-*b*-PS was pressed with KBr and was determined by using Fou-

rier Transform Infrared Spectrometer (Nicolet Avatar, 320FTIR).

Molecular weight and distribution were determined using a gel-permeation chromatographic (GPC) technique with an aqueous phase eluent. The Shimadzu GPC (LC-10AT pump, CTO-6AS oven, and RID-10A refractive index detector) with the Waters column (Ultrahydrogel linear 7.8 mm  $\times$  300 mm) was used. The oven temperature was set at 40°C and the elution rate was 0.80 mL/min. The molecular weight was calibrated using NaPSS molecular weight standards.

The surface tension of NaPSS-*b*-PS aqueous solution was determined with the surface tension meter (Du Nouy's Tensiometer, Uchida, 514-B).

### Emulsion polymerization and characterizations of product

Styrene emulsion polymerization using a mixture of SDS and NaPSS-*b*-PS as the surfactant was conducted at 60°C. The recipes are shown in Table II. The conversion of monomer to polymer was determined gravimetrically. The latex particle size and distribution were determined with a Photal DLS 3000/3100 dynamic light scattering (DLS) spectrophotometer. Some samples were double-checked using SEM (Cold Field Emission Scanning Electron Microscope, Hitachi, S-4800). The % conversion, polymerization rate ( $R_p$ ), number-average ( $D_n$ ), volume-average ( $D_v$ ), and weight-average diameters ( $D_w$ ), and the particle number per cm<sup>3</sup> of aqueous phase ( $N$ ) were determined in the same manner as shown in Ref. 6. The number-average and weight-average molecular weights ( $M_n$  and  $M_w$ ) of polystyrene were determined with a gel-permeation chromatograph (GPC) (Jasco, PU-980 pump with Phenogel columns (pore sizes of 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, and 10<sup>6</sup> Å, respectively) and refractive index detector (Jasco, RI-930), where the oven temperature was set at 40°C, and the flow rate of THF was 0.8 mL/min.

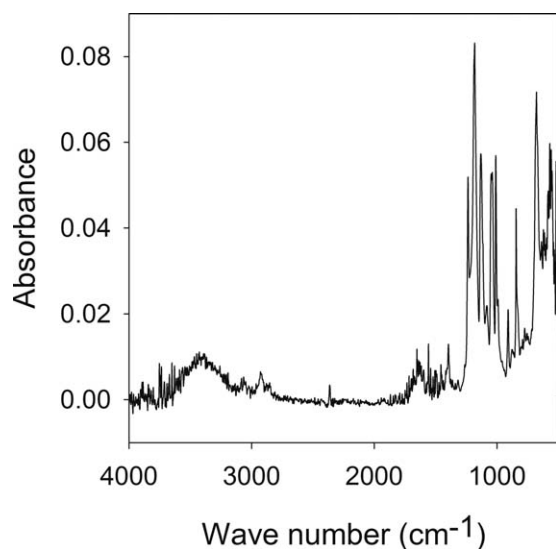
The average radical number per particle ( $\bar{n}$ ) was calculated using eq. (1).

$$R_p = k_p N \bar{n} [M] / N_A \quad (1)$$

where the propagation rate coefficient,  $k_p = 353$  L/mol/s at 60°C,<sup>16,17</sup>  $N_A$  is the Avogadro's constant,  $\bar{n}$  is the average radical number per particle, and the monomer concentration in particles,  $[M]$  (mol/L)<sup>6</sup> was determined as follows:

$$[M] = \frac{d_p}{(M_0/1000)[(d_p/d_m) + (1/\Phi_m) - 1]} \quad (2)$$

where  $M_0$  is the molecular weight of monomer (= 104.15 g/mol for styrene),  $d_m$  is the density of



**Figure 1** FTIR spectrum of NaPSS-*b*-PS (E) prepared in this study.

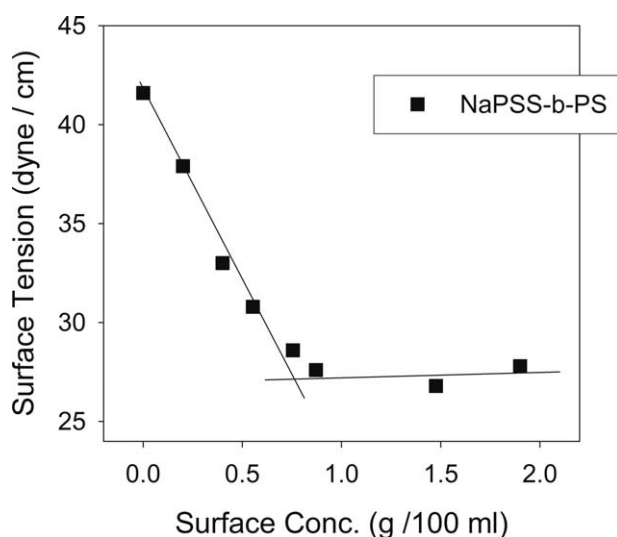
styrene ( $0.906 \text{ g/cm}^3$ ),  $d_p$  is the density of polymer ( $=1.053 \text{ g/cm}^3$  for polystyrene), and  $\Phi_m$  is the weight fraction of monomer in the particle at the saturated condition and calculated from the conversion that the transition of Interval II to Interval III occurs.

The average polymer number per particle ( $n_p$ ) can be calculated as:

$$n_p = N_A \pi (D_v \times 10^{-7})^3 d_p / 6 M_w \quad (3)$$

The chain growing time ( $t_c$ ) can be computed as the ratio of the number-average degree of polymerization ( $X_n$ ) and the rate of polymerization within a single micelle, as follows:

$$t_c = X_n / k_p [M] \quad (4)$$



**Figure 2** The critical micelle concentration of NaPSS-*b*-PS (E) in water was determined to be  $0.75 \text{ g/100 mL}$ .

**TABLE I**  
Comparison of Critical Micelle Concentration Among Different NaPSS Surfactants

Surfactants	NaSS fraction in polymer	CMC (g/100 mL)	CMC (mol/L)
NaPSS (MH)	1.00	0.41	$5.9 \times 10^{-5}$
NaPSS (M)	0.71	0.49	$1.8 \times 10^{-4}$
NaPSS- <i>b</i> -PS(E)	0.53	0.75	$7.8 \times 10^{-5}$

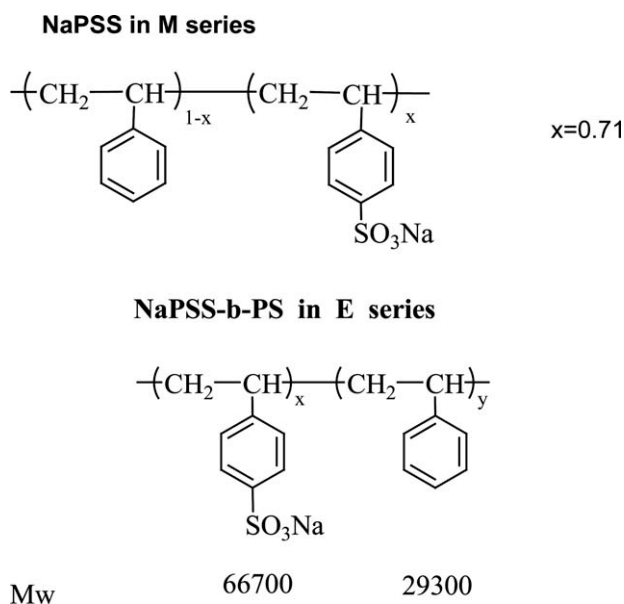
## RESULTS AND DISCUSSION

### Preparation and characterization of NaPSS-*b*-PS

Using a mixture of EG and water as the medium, we prepare the NaPSS-*b*-PS via the stable free-radical polymerization technique. The NaPSS macro-initiators were synthesized, the styrene polymerization was then conducted using the macro-initiators. The detailed of preparation, purification, and characterization were present in "Experimental" section.

Several batches of NaPSS-*b*-PS were prepared and mixed together to form a mixed batch. Using an aqueous phase GPC, the  $M_n$  and  $M_w$  for NaPSS-*b*-PS were determined to be 67,800 and 96,000, respectively; and the  $M_n$  and  $M_w$  for the first block (i.e., NaPSS) are 46,500 and 66,700, respectively. This diblock copolymer was designated as "NaPSS-*b*-PS" and used in E series in this study.

The IR spectrums of NaPSS and NaPSS-*b*-PS have been determined. The spectrum of NaPSS-*b*-PS was shown in Figure 1. The characteristic IR peaks of NaPSS are 1185, 1130, 1042, 1011, 668, and 639  $\text{cm}^{-1}$ <sup>18</sup>; where peaks at 1185 and 1042  $\text{cm}^{-1}$  can be



**Figure 3** Chemical structures for NaPSS in M series and NaPSS-*b*-PS in E series.

TABLE II  
Emulsion Polymerization Recipes and Polymerization Rate

Recipe no.	Styrene (g)	H <sub>2</sub> O (g)	Initiator K2S2O8 wt (g)	Surfactant wt (g)			$R_p \times 10^4$ (mol/L/s)	
				SDS	NaPSS- <i>b</i> -PS(E)	NaPSS (M)		NaPSS (MH)
D1	36	144	0.5	0.30			5.31	
D2				0.50			3.62	
D3				0.70			6.97	
E1				0.30	1.0		6.34	
E2				0.50	1.0		8.21	
E3				0.70	1.0		8.04	
M1 <sup>a</sup>				0.30		1.0	4.27	
M2 <sup>a</sup>				0.50		1.0	7.49	
M3 <sup>a</sup>				0.70		1.0	8.07	
MH1 <sup>b</sup>				0.30			1.0	1.95
MH2 <sup>b</sup>				0.50			1.0	4.31
MH3 <sup>b</sup>				0.70			1.0	9.56

<sup>a</sup> Data of M series are adopted from Ref. 6.

<sup>b</sup> Date of MH series are adopted from Ref. 15.

assigned to the SO<sub>3</sub><sup>-</sup> group antisymmetric and symmetric vibrational adsorption peaks, respectively, and 1130 and 1011 cm<sup>-1</sup> to the in-plane skeleton vibration of benzene ring and in-plane bending vibration of benzene ring.<sup>19</sup>

The surface tension of NaPSS-*b*-PS in water was measured. The critical micelle concentration (CMC) of NaPSS-*b*-PS in water was determined to be 0.75 g/100 mL. The titration curve is shown in Figure 2.

The NaPSS synthesized through postsulfonation of a narrow disperse polystyrene<sup>6</sup> with a NaSS fraction of 0.71 and a number-average molecular weight of 28,000, used in M series, has a CMC of 0.49 g/100 mL, while the NaPSS having an average molecular weight of 70,000 (polymerized from NaSS and available from Aldrich Chemical Company, used in MH series) has a CMC of 0.41 g/100 mL. Obviously, because of the presence of a PS block, the NaPSS-*b*-PS has the largest CMC value when the unit of g/100 mL is used. Table I has summarized the results. The chemical structures for NaPSS used in M series and NaPSS-*b*-PS in E series are shown in Figure 3.

#### Emulsion polymerization using NaPSS-*b*-PS as a cosurfactant

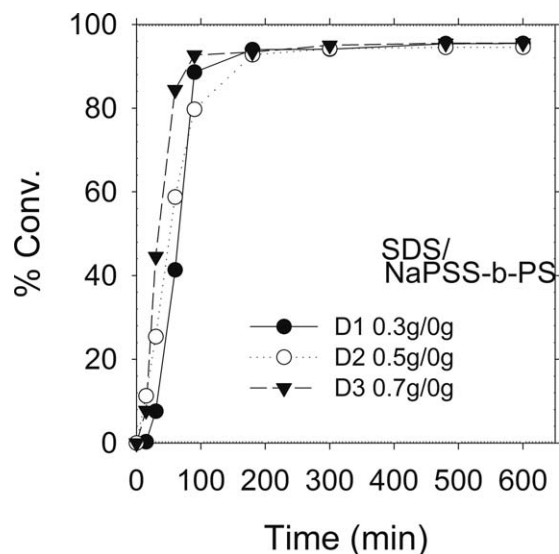
Two series of recipes were conducted for styrene emulsion polymerization using a single surfactant (SDS) (i.e., Series D) and a mixture of SDS and NaPSS-*b*-PS as the surfactant (i.e., Series E), as shown in Table II.

Rudimentary experimental results showed that using 1.0 g of NaPSS-*b*-PS in emulsion polymerization without using SDS, the reaction takes long hours (i.e., 16 h) to reach high conversion (i.e., 88%) and the weight-average particle diameter increases rapidly from around 50 nm at 1% conversion to 2780 nm at 88% conversion. The presence of small amount of SDS, or a further increase in the SDS content decreases the particle diameter tremendously, as shown in Table III.

The conversion-time curves for Series D and E are shown in Figures 4 and 5, respectively. Data of the polymerization rate ( $R_p$ ) of each recipe are shown in Table II. The data of  $R_p$  were plotted against average particle diameter in Figure 6. The  $R_p$  decreases with

TABLE III  
Data of (DLS Determined) Volume-Average Diameter ( $D_{v,DLS}$ ), Particle Size Distribution ( $D_w/D_n$ ), Particle Number per cm<sup>3</sup> of Aqueous Phase ( $N$ ) of Latex, Number-Average Molecular Weight ( $M_n$ ), Weight-Average Molecular Weight ( $M_w$ ), and Polymer Number per Particle ( $n_p$ ) of Polystyrene Prepared at Final Conversion

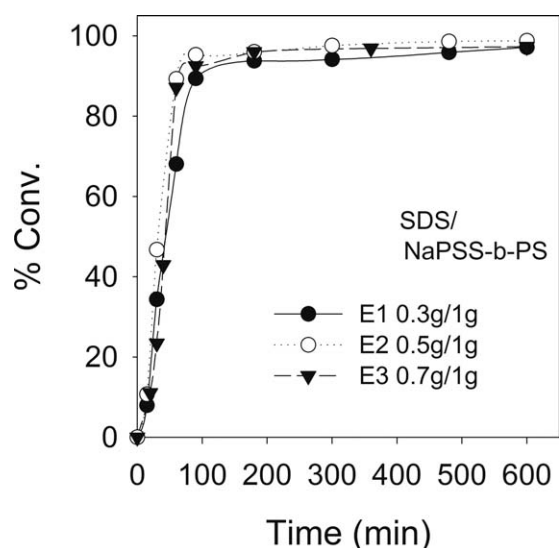
Recipe no.	% conv.	$D_{v,DLS}$ (nm)	$D_w/D_n$	$N \times 10^{-15}$ (1/cm <sup>3</sup> )	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$n_p$
D1	95.5	63.5	1.26	1.69	32	88	97
D2	94.6	59.6	1.29	2.02	8	24	290
D3	95.5	54.5	1.23	2.68	14	30	280
E1	97.1	79.9	1.12	0.86	11	20	850
E2	98.7	60.8	1.29	2.00	15	28	270
E3	97.3	48.9	1.28	3.78	28	56	70



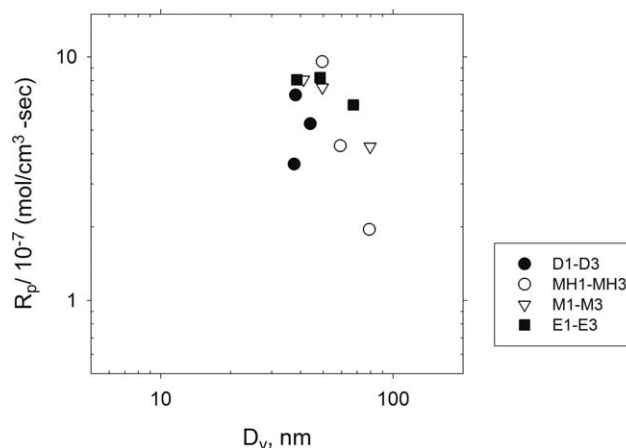
**Figure 4** Conversion-time curves for single-surfactant series (Series D).

increasing average particle diameter. Since the particle number per  $\text{cm}^3$  of aqueous phase ( $N$ ) is proportional to  $D_v^{-3}$ , the result is consistent with the relationship reflected by eq. (1). Data for Series M and MH are also included in Figure 6. Both Series M and MH have same recipes as those of Series E as shown in Table II, except that the different types of NaPSS were used instead.

The latex particle size data for both D and E series at final conversions and middle conversions are shown in Tables III and IV. The particle size decreases with increasing the SDS content. Data of the molecular weights ( $M_n$  and  $M_w$ ), and polymer number per particle ( $n_p$ ) for polystyrene are also



**Figure 5** Conversion-time curves for mixed-surfactant series (Series E).



**Figure 6** Polymerization rate decreases with increasing average particle diameter.

shown in Tables III and IV. A deviation from the usual trend was found in comparing recipe D2 with D1 that increasing the SDS content, the average particle size decreases but the average molecular weight decreases. Usually, the latex with the smaller average particle size tends to have the larger average molecular weight, since the smaller particles accommodate fewer radicals and less chance to terminate. Note that the SDS content in recipe D1 is barely close to and below the CMC (i.e.,  $7.4 \times 10^{-3} M^{20}$ ), while those in recipes D2 and D3 are larger than the CMC. The nucleation mechanism is different that D1 is due to the homogeneous nucleation<sup>21,22</sup> and D2 and D3 the micellar nucleation.<sup>23,24</sup>

The particle sizes are larger in E, M, and MH, compared to D series with the same amount of SDS. The surfactants, NaPSS and NaPSS-*b*-PS, have quite high molecular weights. Using mixtures of SDS and NaPSS (or NaPSS-*b*-PS) led to a situation similar to the miniemulsion polymerization,<sup>25-27</sup> and the formation of latices with the larger particle sizes. In miniemulsion polymerization, stable minidroplets form, becoming the important nucleation sites at some later stages.

The  $n_p$  value increases monotonously with the particle size at various conversions, as shown in Figure 7, for Series E. This reflects that the larger the particle size the latex has, the chain number can be accommodated in particle is higher.

The value  $\bar{n}$  increases with increasing the volume-average particle diameter ( $D_v$ ), as is shown in Figure 8, despite that the MH series show a decreasing trend. The NaPSS (with a sulfonation fraction of 1.0) used in MH series may have a molecular orientation perpendicular to particle surface<sup>5</sup> and it allows more charge-carrying chain radicals to pass through the stabilizer shell on particle surface. Therefore, it may enhance the exit effect of oligomer radicals. The SEM picture of MH2 (Fig. 9) show some aggregation

**TABLE IV**  
**Data for (DLS Determined) Volume-Average Diameter ( $D_{v,DLS}$ ), Particle Size Distribution ( $D_w/D_n$ ), Particle Number per  $\text{cm}^3$  of Aqueous Phase ( $N$ ), Number-Average Molecular Weight ( $M_n$ ), Number-Average Kinetic Chain Length ( $\bar{X}_n$ ), Average Radical Number per Particle ( $\bar{n}$ ), and Chain Growing Time ( $t_c$ ) at Middle Conversion**

Recipe no.	% Conv.	$D_{v,DLS}$ (nm)	$D_w/D_n$	$N \times 10^{-15}$ ( $1/\text{cm}^3$ )	$M_n \times 10^{-5}$	$\bar{X}_n$	$\bar{n}$	$t_c$ (s)
D1	41.3	44.0	1.35	2.20	1.90	1830	0.19	2.4
D2	58.7	37.5	1.37	5.03	1.00	962	0.051	1.1
D3	44.5	38.0	1.36	3.69	2.60	2500	0.15	3.2
E1	68.0	67.5	1.19	1.00	2.70	2600	0.39	2.6
E2	46.7	48.5	1.24	1.85	1.60	1540	0.40	2.3
E3	42.9	38.5	1.32	3.40	4.80	4620	0.13	4.2

among particles but this does not lead to the higher  $\bar{n}$  value at the higher  $D_v$  value.

Note that most of the  $\bar{n}$  values are below 0.50 (i.e., follows Smith-Ewert Case 1), except that of recipe M1. This reflects that the exit mode<sup>28,29</sup> of oligomer radicals occurs.

Data of the entry rate coefficient ( $\rho = \bar{n}/t_c$ ) versus the  $D_v$  were shown in Figure 10. The  $\rho$  values increase rapidly with  $D_v$  and level-off at  $D_v > 50$  nm. The leveling-off trend seems consistent with the report<sup>9</sup> that "all other things being equal, there should be no effect of latex particle size on the entry rate coefficient."

Both chain growing time ( $t_c$ ) and entry rate coefficient ( $\rho$ ) may affect the emulsion polymerization rate. The  $t_c$  values are rather close to one another, except data for recipes M1 and M2, as shown in Figure 11, where values of  $t_c$  are plotted against the SDS content.

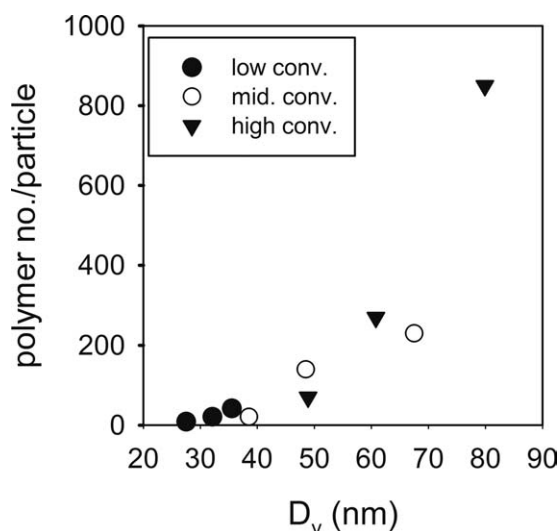
For recipes M1 and M2, a partially sulfonated NaPSS (with a sulfonation fraction of 0.71) was used in emulsion polymerization, and the NaPSS chain may adsorb onto several latex particles leading to

limited aggregation through interparticular bridging as a case observed in literature using not an exact kind of surfactant.<sup>5</sup> The limited aggregation leads to the largest particle sizes (Fig. 12) and the largest  $t_c$  values (Fig. 11).

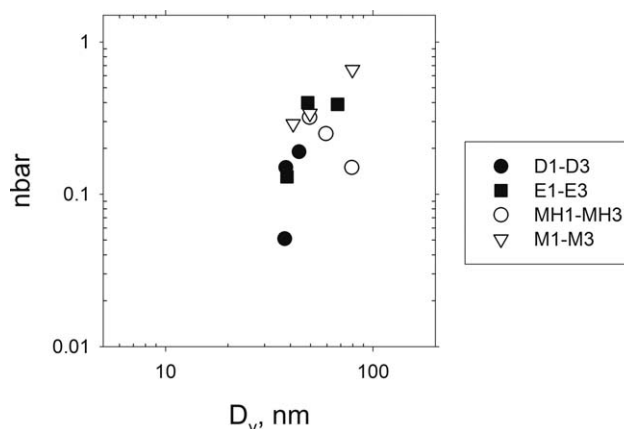
The MH recipe series have the second largest  $D_v$  values (Fig. 12), but have the comparatively low  $t_c$  values (Fig. 11). This implies that the MH series allow more charge-carrying chain radicals to pass through stabilizer shell, thus more chain radicals exit from particles, and the chain growing times ( $t_c$ ) are thus lower.

The polymerization rate ( $R_p$ ) increases with the chain growing time ( $t_c$ ) and then somewhat levels-off at a certain  $t_c$  value, as is shown in Figure 13. This reflects that  $t_c$  can affect the polymerization rate.

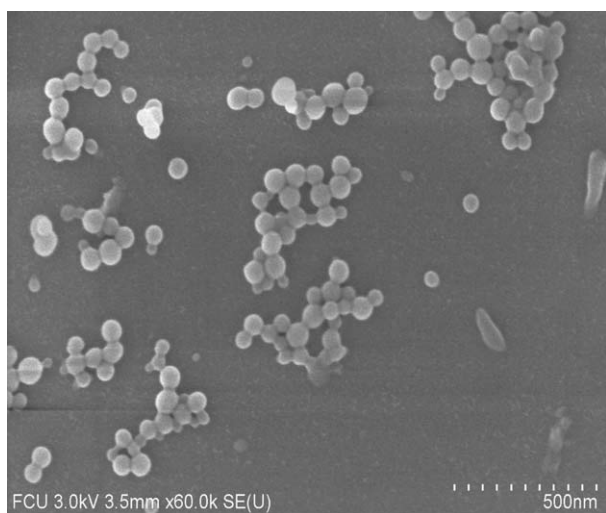
Images of some samples were taken in SEM, as shown in Figure 14. Comparisons between the particle size data from DLS and those from SEM for the E2 recipe are shown in Table V. It is evident that the deviations of average particle diameter data are not large. In Figure 14, particles are not stuck together to form flocks. Limited aggregation did not occur in this case. The percentage of the block copolymer to monomer weight is only 2.78%, lower than the



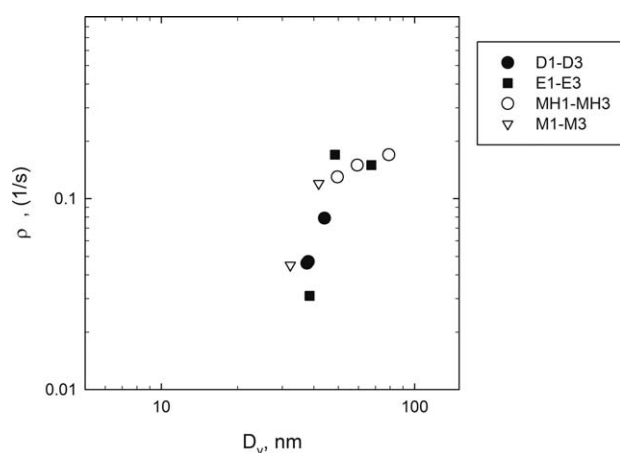
**Figure 7** Data of  $n_p$  versus  $D_v$  from low to high conversions for mixed-surfactant series (Series E).



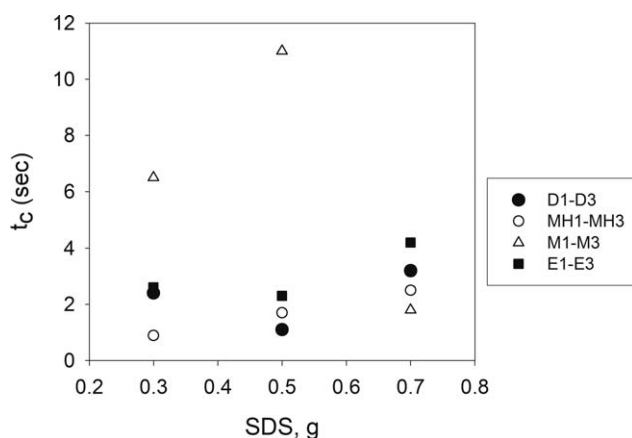
**Figure 8**  $\bar{n}$  increases with increasing  $D_v$  (Data at middle conversions).



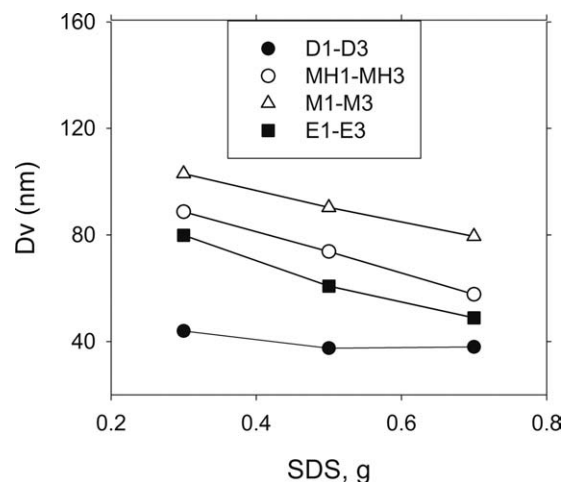
**Figure 9** SEM image for MH2 latex particles at 92.0% conversion.



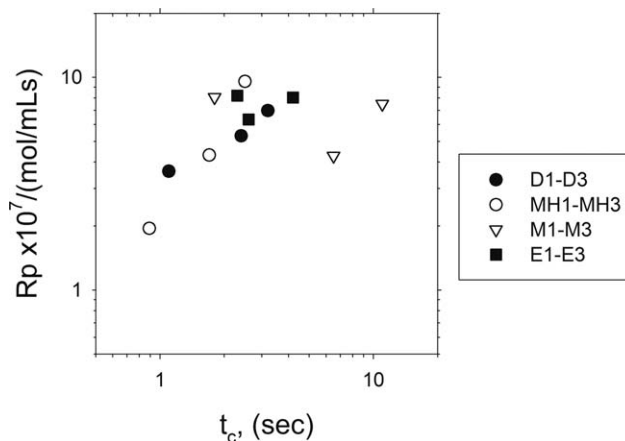
**Figure 10** The entry rate coefficient increases rapidly at smaller particle diameter and levels-off at  $D_v$  larger than 45 nm.



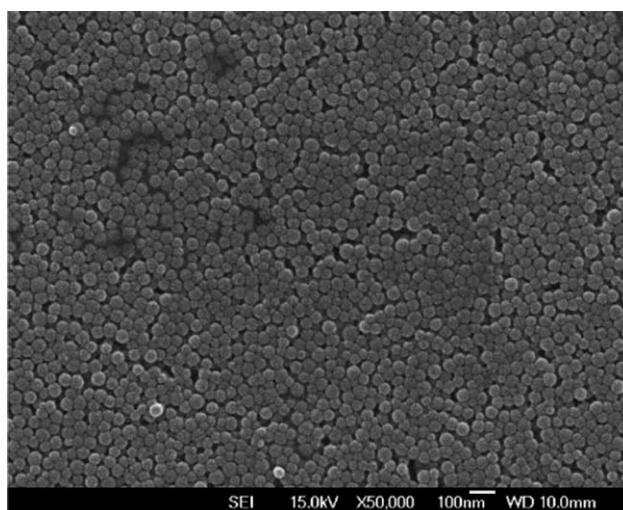
**Figure 11** Chain growing time versus SDS content for each recipe series.



**Figure 12** Volume-average particle diameter versus SDS content for each recipe series.



**Figure 13** The polymerization rate increases with increasing the chain growing time and levels-off when the chain growing time larger than a certain value.



**Figure 14** SEM image for E3 latex particles at 97.3% conversion.

**TABLE V**  
**Comparison of Particle Size Data from DLS with**  
**Those from SEM**

	E3	DLS	SEM	Deviation (%)
42.9% Conv.	$D_w$	60.2	53.2	13.2
	$D_n$	49.2	45.5	7.99
97.3% Conv.	$D_w$	59.7	63.5	5.92
	$D_n$	46.5	53.0	12.2

lowest limit for limited aggregation (i.e., 5%) as reported in Ref. 5. Beside, we used extra surfactant of SDS may alleviate the chance to aggregate in our study.

### CONCLUSIONS

Using a mixture of ethylene glycol and water as the medium, the NaPSS-*b*-PS was prepared via a two-stage stable free-radical polymerization. Mixtures of NaPSS-*b*-PS and SDS were used in styrene emulsion polymerization. The particle size data of polystyrene latex determined by using DLS and SEM do not deviate much from each other. The SEM image also reveals that there is little aggregation among particles. Most of the  $\bar{n}$  values are below 0.50 (i.e., follows Smith-Ewert Case 1). Comparisons among systems using different structures of NaPSSs were made using relationships, such as  $\bar{n}$  versus  $D_w$ , chain growing time versus SDS content, and  $D_w$  versus SDS content. Characteristics on entry for various NaPSSs were revealed.

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