Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 2298–2305
polymer
www.elsevier.com/locate/polymer

Entry in emulsion polymerization using a mixture of sodium polystyrene sulfonate and sodium dodecyl sulfate as the surfactant

Hou-Hsein Chu*, Yee-Shern Yeo, Kaun Shang Chuang

Department of Chemical Engineering, Feng Chia University, 100 Wen-Hwa Road, Seatwen, Taichung 407, Taiwan

Received 16 August 2006; received in revised form 5 February 2007; accepted 26 February 2007
Available online 28 February 2007

Abstract

A mixture of sodium polystyrene sulfonate (NaPSS) and anionic surfactant, sodium dodecyl sulfate (SDS), was used as the emulsifier in the emulsion polymerization of styrene at 60 °C. The latexes prepared were stable, bearing the better resistance to the addition of electrolyte, and have the larger values in particle size and the higher polymerization rates than those counterparts prepared using SDS only. The NaPSS was prepared by a series of process: a concentrated cyclohexane solution of an anionically polymerized polystyrene (PS) was sulfonated with sulfuric acid at 80 °C, and then neutralized and purified through dialysis. The data of average polymer number per particle (n_p) were found useful in investigating the surfactant content effect on the entry of radicals into particles, where the latex particle size plays an important role.

Keywords: Sodium polystyrene sulfonate; Sodium dodecyl sulfate; Emulsion polymerization

1. Introduction

The interfacial properties of sodium polystyrene sulfonate (NaPSS), an amphipathic molecule constituting of the hydrophobic polystyrene (PS) chain and the hydrophilic sodium sulfonate groups, attract an abundant attention.

The sulfonation of polystyrene can be performed either homogeneously [1–4] or heterogeneously [5,6].

It has been reported that poly(styrene sulfonic acid) (PSS), prepared from a narrowly molecular weight distributed polystyrene, had solubility and other characteristics significantly different from those of poly(vinyl sulfonic acid) [6], and the investigation also includes the influence of the aromatic group on local and long range interactions in solution.

The concentration dependence of radius of gyration (R_g) of NaPSS in aqueous solution without added salt has been investigated by small-angle neutron scattering measurements [7].

It has been suggested that NaPSS can form polyelectrolyte aggregates in solution at low ionic strength [8], where dynamic and static light scattering experiments in combination with light microscopy have been performed on solutions of NaPSS. Both the apparent fast and slow diffusion coefficients depend on the NaPSS concentration and on the ionic strength when semidilute solutions were investigated with dynamic light scattering over a wide NaPSS concentration range [9].

Increasing conductivity with time in NaPSS solution during dialysis against water in the dilute/semidilute region (0.1 g/L) was attributed to the aggregation of NaPSS in the aqueous solution [10]. Before that, the polyelectrolyte solutions with no or low added salt have been often regarded as a heterogeneous solution in the earlier reports [11–20].

The solution properties of poly(styrene sulfonate) ionomers (of narrow molecular weight distribution containing about 0.5 to about 4.7 mol% sulfonate group) in both a polar and a relatively nonpolar solvent have been studied [21].

The adsorption of NaPSS to the air surface of water as a function of polymer concentration was investigated with neutron and X-ray reflectivity and surface tension measurements [22]. Interesting segment profiles, such as trains, and loops

---

* Corresponding author. Tel.: +886 4 2451 3876; fax: +886 4 2451 0890.
E-mail address: hhchu@fcu.edu.tw (H.-H. Chu).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.02.057

and tails were related to different levels of polymer concentrations added.

A study has prepared a styrene–styrene sulfonate block copolymer and applied it in emulsion polymerization as stabilizer [23]. The block copolymer is expected to provide electrostatic stabilization, however, the initial result showed that it was not as effective as short-chain surfactants, since the solid content of the experiment is as low as 3%.

A delicate approach studying the entry of free radicals into latex particles in emulsion polymerization [24,25] has made the study of emulsion polymerization kinetics more consolidated. In the study, the styrene, a monomer, was commonly used since plenty of kinetic source data were available for comparison and comparatively less complicated nucleation mechanism was involved.

In this study, an anionically polymerized polystyrene (PS) with a narrow molecular weight distribution (MWD) was sulfonated and neutralized to obtain the NaPSS, which was used as a component-surfactant (in conjunction with SDS) in the emulsion polymerization of styrene. The latex prepared was stable with a narrow particle size distribution ($D_w/D_n < 1.05$). Stabilizing effect of the NaPSS was also investigated by carrying out experiments to determine the critical flocculation concentration of KCl on the latex sample, and the critical micelle concentration of NaPSS in water. Interestingly, by using the data of average polymer number per particle (n_p) and average radical number per particle ($\overline{n}$), we can examine the cases for the entry of z-mer (or oligomeric radical) into the particle when different surfactant contents are involved.

2. Experimental

2.1. Materials

Polystyrene was prepared by anionic polymerization technique and molecular weights were determined by GPC to be $M_w = 16\,300$ and $M_n = 12\,600$, respectively. A 5 wt% cyclohexane solution of PS was used at the later sulfonation process. Sulfuric acid (from SHOWA company, Japan, purity of 97%) was used as the sulfonating agent. Other chemicals are sodium hydroxide (from SHOWA company, Japan, purity>96%), and hydrochloric acid (concentration ~ 35%). All were used as received. Water was purified through a Reverse Osmosis System (Ultra-pure Water System, Model DI-S3, Kintech Co.) with a conductivity of 2 μmho.

For the emulsion polymerization, monomer styrene (from Lancaster Synthesis Ltd., UK, 99% pure) was purified by distillation under reduced pressure; initiator potassium persulfate ($K_2S_2O_8$, KPS, from Wako Company, Japan, 99% pure) and surfactant sodium dodecyl sulfate (SDS, from Sigma Company, 99% pure) were used as received.

2.2. Sulfonation of polystyrene

Cyclohexane solution of the anionically polymerized PS was concentrated to about 5.3 g of PS in 20 mL solution, and then mixed with 30 g of sulfuric acid (97%). The mixture was agitated with a magnetic stirrer (at around 700 rpm) in a 100 mL beaker, setting the temperature of the mixture at 80 °C for 2 h, then stop agitation and left the mixture cooling down to room temperature. The mixture was diluted with 100 g of extra pure water, and neutralized with NaOH aq. solution (25 g NaOH in 200 g of water) to pH of 8–9. After filtration, the filtrate was dialyzed with dialysis membrane tubings (Cellu. Sep T1, Membrane Filtration Products, Inc., USA, with nomial MWCO of 3500) for two days. After that, it was dried at 60 °C, under reduced pressure, until it reached a constant weight (i.e., taking about 24 h).

2.3. Characterization of NaPSS

The structure of the NaPSS was characterized using FTIR (Nicolet Avatar, 320 FTIR) and NMR (Varian, VRX-300/51). The surface tension of NaPSS aq. solution was determined with the surface tension meter (Du Nouy's Tensiometer, Uchida, 514-B).

2.4. Emulsion polymerization and product characterization

Emulsion polymerizations were performed at 60 °C, in 250 cm^3 four-necked round-bottomed flasks in a constant temperature bath, with a mechanical stirring rate of 150 rpm. Polymerization recipes are shown in Table 1. Surfactant(s) and initiator were dissolved in water in the flask first, then the monomer styrene was added, and the bath temperature was raised to the reaction temperature to start the polymerization. During the polymerization, samples for monomer conversion and for particle size measurements were withdrawn using a hypodermic needle and a syringe. The conversion of monomer to polymer was determined gravimetrically, i.e., by using hydroquinone as a shortstop and methanol as a coagulation agent. The sample latex was coagulated in the aluminum dish and it was then dried in an oven at 80 °C for overnight, and the solid content was computed. The polymerization rate was determined from the slope of the conversion–time curve in constant rate region (i.e., around the region between 20 and 60% conversions) as follows:

$$R_p = \left(\%\ \text{conversion change/time}\right)\left(M/W\right)d_w/\left(100M_0\right) \qquad (1)$$

Table 1
Emulsion polymerization recipes and emulsion polymerization rate (R_p) for each recipe

Recipe no.	Styrene (g)	Water (g)	$K_2S_2O_8$ (g)	Surfactants (g)		$R_p \times 10^7$ (mol/mL s)
				SDS	NaPSS	
S1	36	144	0.50	0.30	0	1.76
S2	36	144	0.50	0.50	0	2.02
S3	36	144	0.50	0.70	0	3.10
M1	36	144	0.50	0.30	1.0	4.18
M2	36	144	0.50	0.50	1.0	5.60
M3	36	144	0.50	0.70	1.0	7.05

Polymerization at 60 °C with a stirring rate of 150 rpm.

where (M/W) is the weight ratio of monomer to water in the recipe, d_w is the density of water (1.0 g/cm^3), and M_0 is the molecular weight of monomer (104.15 g/mol for styrene). The instantaneous polymerization rate was calculated based on the difference between the neighboring conversion data points.

The particle size was determined with a Photal DLS 3000/3100 dynamic light scattering (DLS) spectrophotometer. The determination of latex particle size and distribution by using DLS is referred from Ref. [26]. The number-average, volume-average and weight-average diameters (i.e., D_n, D_v and D_w, respectively), and the particle number per cm^3 of aq. phase (N) are defined as usual [27], and are shown as follows:

$$D_n = \left[\sum N_i D_i / \sum N_i\right] \tag{2}$$

$$D_v = \left[\sum N_i D_i^3 / \sum N_i\right]^{1/3} \tag{3}$$

$$D_w = \left[\sum N_i D_i^6 / \sum N_i D_i^3\right]^{1/3} \tag{4}$$

$$N = [6(M/W)(\%\,\text{conversion})d_w] / \left[100\pi d_p \left(D_v^3\right)\left(10^{-21}\right)\right] \tag{5}$$

where N_i particles of diameter D_i were counted; d_p is the density of polymer (1.053 g/cm^3 for PS); D_v is in nm; and N is in cm^{-3}.

The molecular weights and molecular weight distribution of polystyrene were determined with a gel-permeation chromatograph (GPC) (Jasco, PU-980 pump with Phenolgel columns (pore sizes of 10^3, 10^4, 10^5 and 10^6 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 ($\bar{n}$) [28] was calculated using the following equation:

$$R_p = k_p N \bar{n} [M] / A_v \tag{6}$$

where k_p is the propagation rate coefficient (=176 L/mol s at 60 °C), N the particle number per cm^3, A_v Avogadro's number, and $[M]$ the monomer concentration in particle. And the $[M]$ (mol/L) was determined as follows:

$$[M] = \frac{d_p}{(M_0/1000)\left[\left(d_p/d_m\right) + \left(1/\Phi_m\right) - 1\right]} \tag{7}$$

where d_m is the density of styrene (0.906 g/cm^3), and Φ_m is the weight fraction of monomer in the particle at the saturated condition(=0.60 at 60 °C). The $[M]$ value is 5.53 mol/L at 60 °C.

The critical flocculation concentration (CFC) of latex was determined as follows: a 10 cm^3 of latex with a concentration of about 19.0 wt% was titrated with 0.5 cm^3 of 50 mM KCl solution each time until flocculation happening, the particle size (D_w) was monitored using the DLS during the process, and the concentration of KCl in solution was then computed.

3. Results and discussion

3.1. Preparation and characterization of NaPSS

The initial trials showed that the sulfonation of PS powders had rather low degree of sulfonation, while the sulfonation of PS conducted homogeneously (i.e., using the cyclohexane solution of PS) at 80 °C, 97% sulfuric acid showed a better result. Therefore, the latter was adopted for the sulfonation process in this study. After sulfonation, the product was purified by neutralization and dialysis processes.

In the sulfonation process, the mixture turned from colorless and transparency to orange, and then to deep-brown. When the dialysis is over, the solution is pale-yellow.

The fraction of sulfonation was determined by using both the neutralization titration and the NMR. The deviation between two determination methods is within ±0.08, as shown in Table 2. The different batches of NaPSS were blended together to form a single batch, and the mixture having an average fraction of sulfonation of 0.714 as determined from NMR, was used as the surfactant in emulsion polymerization thereafter.

The dialysis process can reduce Na_2SO_4 to a pretty low level within 48 h. The initial solution has a solid of 11.7 wt%. The solids remaining in the dialysis tube were 2.7, 2.6, 2.4, and 2.2% after 12, 24, 48, and 144 h, respectively. This reflects that for an additional 96 h, there is only a further reduction of 0.2% in solid content, compared to that at 48 h.

Alternatively, the dialysis of pure Na_2SO_4 solution versus time also showed that the solid contents of 3.13 and 2.5% remained in the tubes after 48 and 144 h, respectively. The initial solution has a solid of 11.8 wt%.

The FTIR and NMR determinations of NaPSS have been conducted. NaPSS carries characteristic IR peaks at 1185, 1130, 1042, 1011, 668, and 639 cm^{-1} [29]; where peaks at 1185 and 1042 cm^{-1} can be assigned to the SO_3^- group antisymmetric and symmetric vibrational adsorption peaks, respectively, and 1130 and 1011 cm^{-1} to the in-plane skeleton vibration of benzene ring and in-plane bending vibration of benzene ring [30]. For ^{1}H NMR determination, the peaks at both 7.6 and 6.7 ppm reflect the connection of SO_3^- group on the phenyl ring [29]. The details of both FTIR and NMR spectra for PS and NaPSS bearing different sulfonation degrees can be referred from Ref. [29].

The surface tension measurement of aqueous solution of NaPSS has been performed. The data are shown in Fig. 1. The critical micelle concentration (CMC) was determined to be 0.49 g/100 mL of water, or 1.8×10^{-4} M, when the

Table 2
Values of the fraction of sulfonation determined by the neutralization titration and NMR 300 for different batches

Fraction of sulfonation	Neutralization titration	NMR 300
Mixed	0.648	0.714
Batch AB	0.633	0.683
Batch AE	0.790	0.714

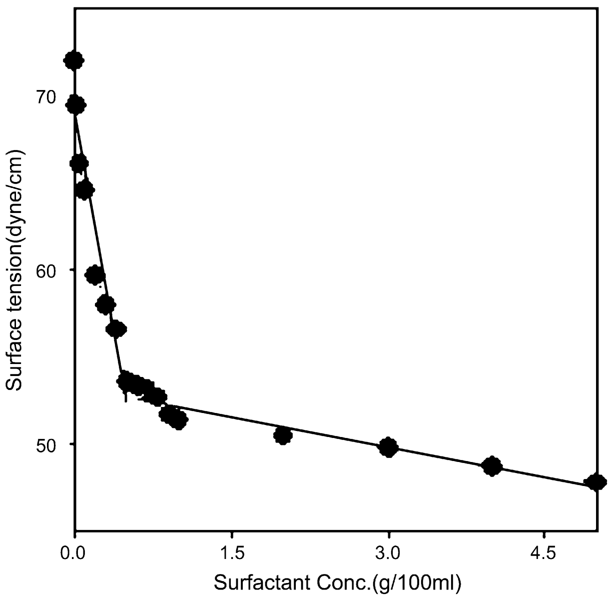

Fig. 1. The CMC of NaPSS in water was determined to be 0.49 g/100 mL or 1.8×10^{-4} M.

molecular weight of NaPSS was taken as 2.70×10^4 g/mol. In comparison, the CMC of sodium dodecyl sulfate (SDS) in water at 25 °C was determined to be 6.6×10^{-3} M (or 0.19 g/100 mL of water) in this study, and the value at 20 °C reported in literature for SDS is 7.4×10^{-3} M [31]. The deviation between our and the reported data may be attributed to the difference in taking the intercept of the correlation lines.

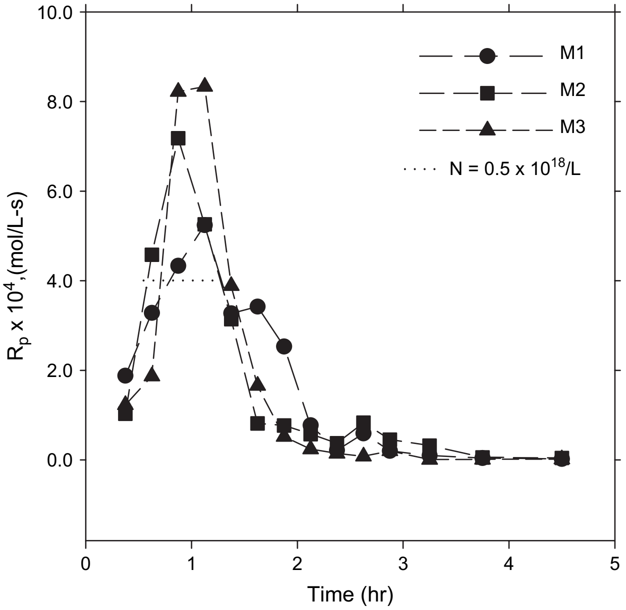

Fig. 2. Instantaneous polymerization rate versus time for emulsion polymerization runs using a fixed amount of NaPSS (1 g) and various amounts of SDS (i.e., recipes M1–M3). (The dotted line with an R_p of 4.04×10^{-4} (mol/L s) represents the line of theoretical prediction assuming a constant particle density of 0.5×10^{18}/L and $\bar{n} = 0.5$.)

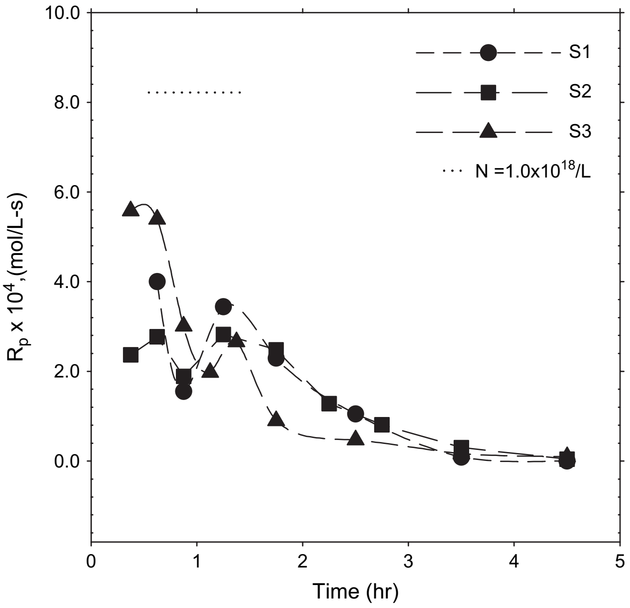

Fig. 3. Instantaneous polymerization rate versus time for emulsion polymerization runs using various amounts of SDS (i.e., recipes S1–S3). (The dotted line with an R_p of 8.08×10^{-4} (mol/L s) represents the line of theoretical prediction assuming a constant particle density of 1.0×10^{18}/L and $\bar{n} = 0.5$.)

3.2. *Stabilizing effect of NaPSS in the emulsion polymerization of styrene*

A pretest revealed that the polymerization of styrene in water using NaPSS only is close to a suspension polymerization, where the reaction time is more than 12 h to achieve a high conversion, and the particle sizes are large enough to be spotted by eyes. It's been reflected that even a block copolymer (PS-*b*-PSS) is not as effective as short-chain surfactant when used in emulsion polymerization as the stabilizer [23].

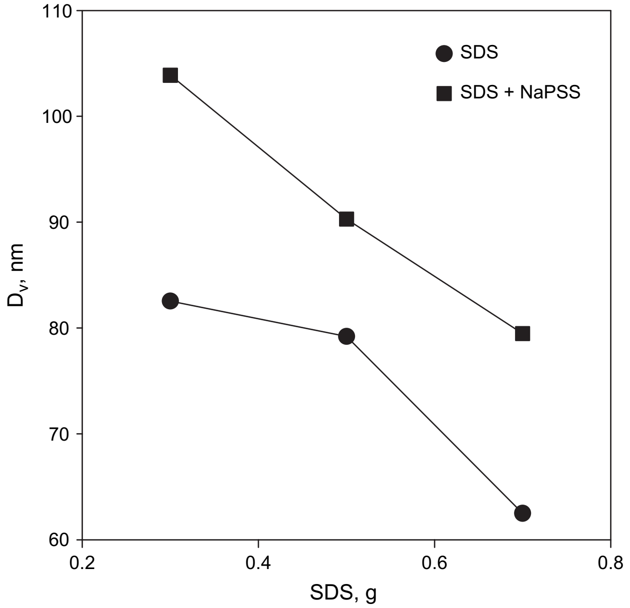

Fig. 4. Values of volume-average particle diameter of latex at final conversions (95–99%) for various emulsion polymerization runs.

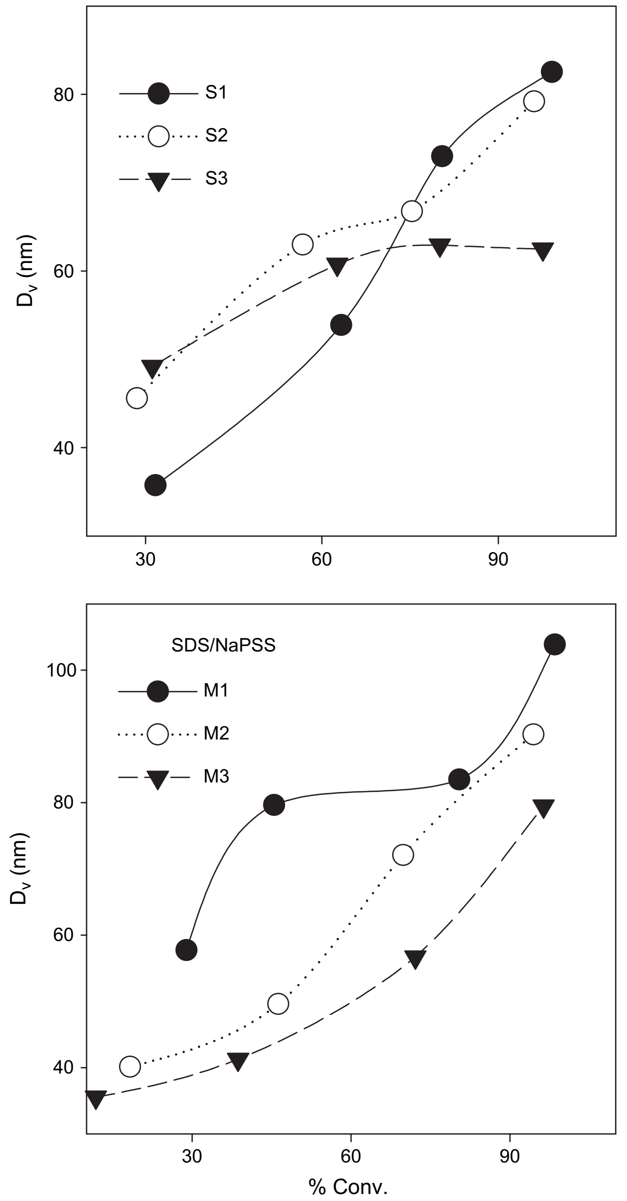

Fig. 5. Variations of volume-average diameter during the emulsion polymerization for different runs.

By using a mixture of 1.0 g of NaPSS and various amount of SDS as the emulsifier (recipes M1–M3, as shown in Table 1), the emulsion polymerizations led to stable latex. The instantaneous polymerization rate versus time curves are shown in Fig. 2, where the polymerization rate increases slightly by increasing the amount of SDS. Also, the polymerization rates are slightly faster than those without NaPSS (Fig. 3). The polymerization rate data are also shown in Table 1. Lines of theoretical prediction assuming a constant particle density (N) and ($\overline{n}$) of 0.5 were also indicated in Figs. 2 and 3. Obviously, the M series have rates faster than the theoretical prediction, while the S series have rates slower than the theoretical prediction. This can be attributed to the fact that the former has higher $\overline{n}$ values than the latter.

Table 3
Data of the volume-average diameter (D_v), particle size distribution (D_w/D_n), and particle number per cm^3 of aq. phase (N) of latex; and molecular weights of weight-average (M_w) and number-average (M_n), and polymer number per particle (n_p) of polystyrene prepared at final conversions

SDS (g)	NaPSS (g)	% Conv.	D_v (nm)	D_w/D_n	$N \times 10^{-15}$	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	n_p[a]
0.3	0	99.1	82.5	1.01	0.798	6.87	2.25	271
0.5	0	96.1	79.2	1.01	0.876	8.41	2.23	196
0.7	0	97.6	62.5	1.12	1.81	8.18	1.45	99.0
0.3	1.0	98.5	103	1.01	0.399	17.0	5.11	218
0.5	1.0	94.5	90.3	1.01	0.582	12.3	3.44	188
0.7	1.0	96.4	79.5	1.01	0.869	14.1	6.68	118

[a] Calculated from the relationship $6.02 \times 10^{23} \pi D_v^3 d_p / 6M_w$.

Table 4
Data of the volume-average diameter (D_v), particle number per cm^3 of aq. phase (N), molecular weights of weight-average (M_w) and number-average (M_n), and polymer number per particle (n_p) for each recipe at low conversions

SDS (g)	NaPSS (g)	% Conv.	D_v (nm)	$N \times 10^{-15}$	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	n_p[a]
0.3	0	31.7	35.7	3.14	8.16	3.85	18.6
0.5	0	28.5	45.6	1.37	8.23	4.23	38.1
0.7	0	31.2	49.2	1.19	12.0	4.84	32.8
0.3	1.0	28.9	57.7	0.682	11.8	6.68	53.9
0.5	1.0	18.2	40.1	1.28	10.7	5.52	19.9
0.7	1.0	11.8	35.5	1.19	9.7	4.51	15.3

[a] Calculated from the relationship $6.02 \times 10^{23} \pi D_v^3 d_p / 6M_w$.

The data of volume-average particle diameter (D_v) at final conversion are shown in Fig. 4. Note that the emulsion polymerizations using a mixture of surfactants (M series) have the larger particle diameters than the counterparts using a single surfactant of SDS (Table 3), though the previous ones have the faster polymerizations (Table 1). This may seem controversial since the M series have the smaller particle number density (N) (Table 5). However, by considering Eq. (6), we found that the average radical number per particle ($\overline{n}$) (Table 5) has the deciding role in polymerization rate.

Most of the values of average radical number per particle ($\overline{n}$) at middle conversions (see Table 5) are lower than 0.5 (i.e., $\overline{n} = 0.5$ for Case II of Smith–Ewart theory [32]), except recipe M1. This implies that the desorption of radicals from particles and termination in the aqueous phase are not negligible [33]. Recipe M1 has the highest $\overline{n}$ value, since it has the largest particle diameter, where more radicals can coexist in a particle without instantaneous termination [34].

Table 5
Data of the volume-average diameter (D_v), particle number per cm^3 of aq. phase (N), and average radical number per particle ($\overline{n}$) of latex; and molecular weights of weight-average (M_w) and number-average (M_n), and polymer number per particle (n_p) for each recipe at middle conversions

SDS (g)	NaPSS (g)	% Conv.	D_v (nm)	$N \times 10^{-15}$	$\overline{n}$	$M_w \times 10^{-5}$	$M_n \times 10^{-5}$	n_p[a]
0.3	0	63.3	53.9	1.83	0.059	9.33	5.19	55.6
0.5	0	56.8	63.0	1.03	0.12	11.4	5.16	72.7
0.7	0	62.6	60.7	1.27	0.15	11.3	5.57	65.5
0.3	1.0	45.5	79.6	0.408	0.63	13.5	6.48	124
0.5	1.0	46.3	49.6	1.72	0.20	14.5	9.11	27.8
0.7	1.0	38.7	41.2	2.49	0.17	11.8	1.23	19.8

[a] Calculated from the relationship $6.02 \times 10^{23} \pi D_v^3 d_p / 6M_w$.

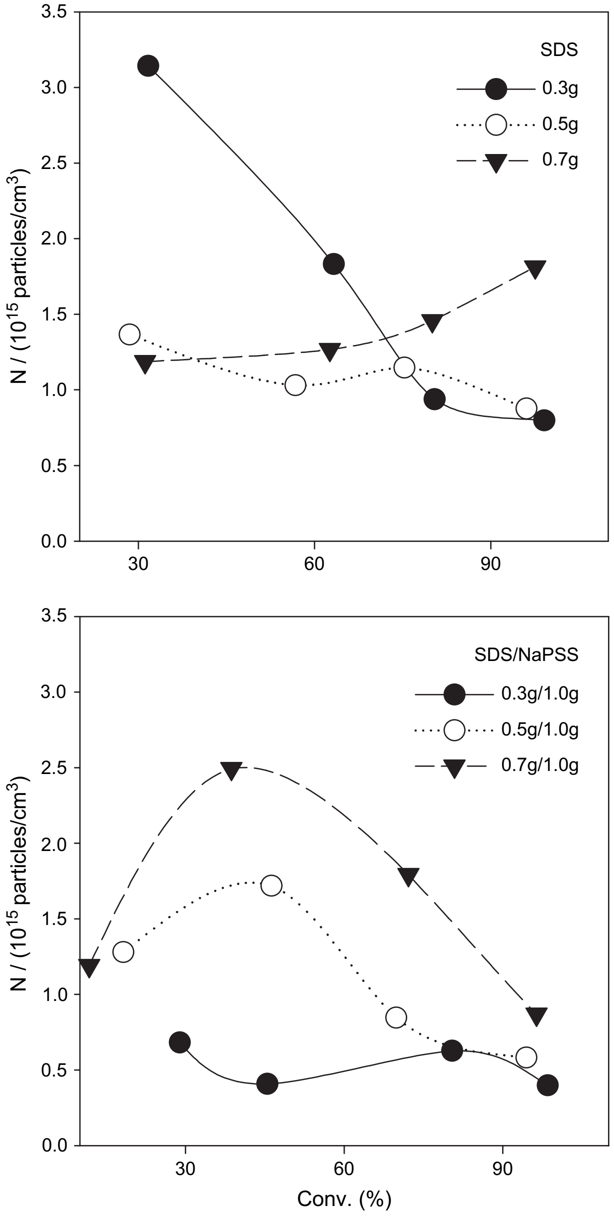

Fig. 6. Variations of particle number per cm^3 of aqueous phase during the emulsion polymerization for different runs.

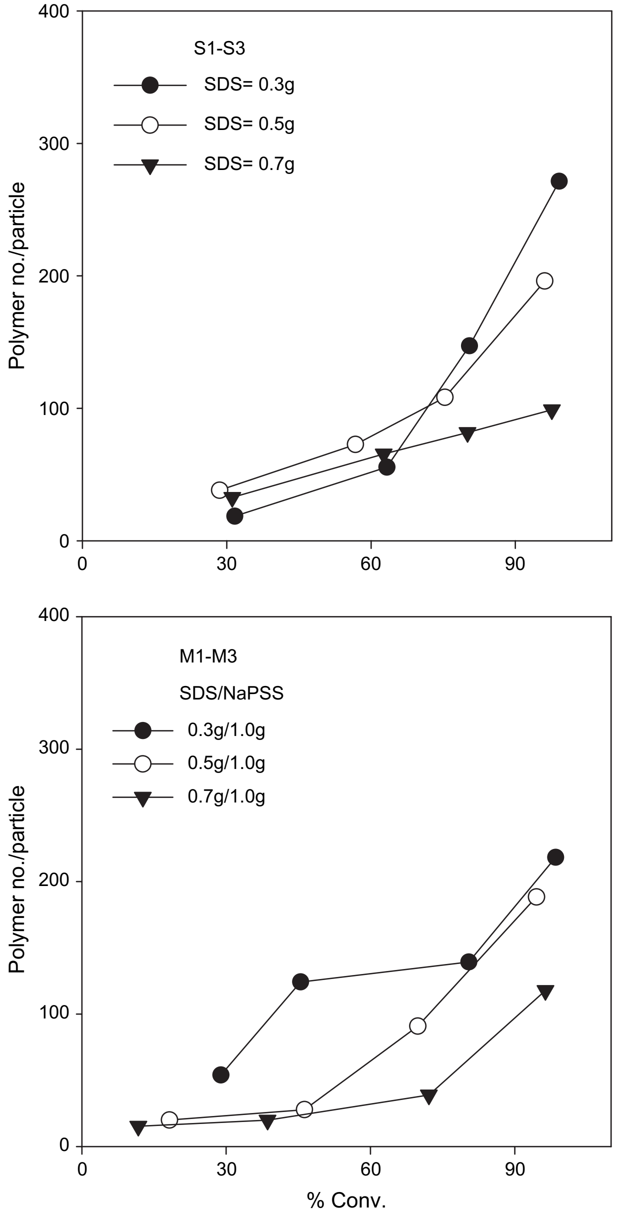

Fig. 7. Variations of polymer number per particle during the emulsion polymerization for both SDS system and (SDS/NaPSS) system.

Also, the recipe with the higher content of SDS has the smaller particle diameter in both the series.

The vigorous particle agglomeration occurs during the emulsion polymerization, especially for the recipe S1. The values of D_v increase with % conversion, as shown in Fig. 5 and Tables 3–5; while the values of particle number per cm^3 of aqueous phase (N) decrease rapidly at high conversions for recipes S1, M2 and M3 (see Fig. 6 and Tables 3–5). The S1 recipe also reveals substantial nucleation at low conversions.

Table 6
Values of the critical flocculation concentration of latexes prepared with different combinations of surfactants

SDS (g)	0.30	0.50	0.70	0.30	0.50	0.70
NaPSS (g)	–	–	–	1.0	1.0	1.0
CFC (KCl, mM)	84	84	140	470	500	470

The variation of particle number per unit volume of aqueous phase during the emulsion polymerization has been reported before [35], where a dynamic equilibrium between particle nucleation and particle coagulation during the polymerization was revealed. A similar idea has been proposed by Roe [36], Feeney et al. [37] and Lichti et al. [38]. In Chu's dissertation [35], surfactants of SDS and Emulphogene BC-840 ($C_{13}H_{27}(OC_2H_4)_{15}OH$) were used in the emulsion polymerization of styrene, and the average particle diameter was counted using TEM photos so that it can avoid miscounting of the cluster of aggregated particles as a large one that may occur in the dynamic light scattering method.

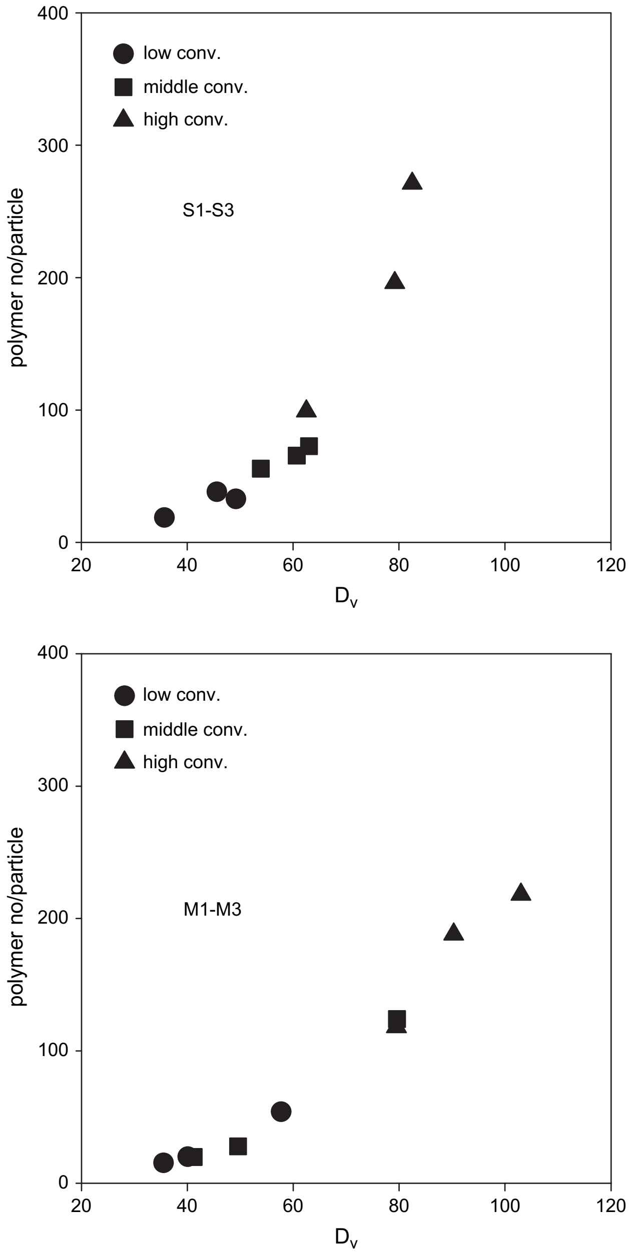

Fig. 8. Average polymer number per particle versus volume-average particle diameter for SDS system and (SDS/NaPSS) system.

The recipe S1 has a surfactant content below the critical micelle concentration (CMC), however, it has a much larger particle number than other recipes at low conversions and a continuous agglomeration until high conversions. In the presence of 1.0 g of NaPSS, the recipes M2 and M3 show continuous nucleation (i.e., the values of *N* increasing) until 40–45% conversion, and have limited agglomerations (i.e., the values of *N* decreasing) afterward, leading to maxima in *N*.

The NaPSS chains may attach to particle in a profile of "loops and tails", since the polystyrene backbone of NaPSS can attach to particle, while the hydrophilic sodium sulfonate groups on styrene point out to the aqueous phase. It's been reported that at high enough concentrations, the NaPSS molecules form a layer extending to larger depths into liquid, forming loops and tails at the air surface, when the adsorption of NaPSS to the air surface of water was studied [22]. Also, the NaPSS may exist as an extended moiety, since the distributed sodium sulfonate groups may hinder the chains to coil up. Therefore, the molecular chain length of NaPSS (the number-average degree of polymerization is around 121) may be about at least 10-fold as large as that of SDS, and in the presence of NaPSS, the system is prone to form large particles. In the presence of surfactant molecules having the relatively longer chains, it tends to form the larger particles, as the case of using a nonionic surfactant (Emulphogene BC-840) in the emulsion polymerization of styrene [39], where a number of TEM pictures are illustrated. This is consistent with the facts that the mixed-surfactant series (i.e., M series) have the larger particle diameters than the single-surfactant series (i.e., S series).

The mixed-surfactant system has the greater capability to cope with the flocculation when certain amounts of electrolyte (i.e., KCl) were added to latexes. This system endures the addition of much volume of KCl solution without flocculation. Values of the critical flocculation concentration (CFC) for the mixed-surfactant system are much higher than those for the single-surfactant system, as shown in Table 6.

In the presence of 1.0 g of NaPSS (mixed-surfactant system, or recipes M1–M3), the n_p values don't cross over each other, and the value decreases with increasing the SDS content, as shown in Fig. 7.

3.3. Entry of oligomeric radicals (or z-mers)

The entry of oligomeric radicals (or z-mers) into particles can be interesting [24,25]. In this study, both average particle diameter and molecular weight of polystyrene have been determined at low, middle and high conversions. This facilitates to compute the average polymer number per particle (n_p) at each instance. Data are shown in Tables 3–5.

The surfactant amount will affect the average particle diameter of latex, as shown in Fig. 4. In addition, it has been mentioned [34] that the larger the particle size, the radicals can coexist in a polymer particle without instantaneous termination, therefore, $\bar{n}$ will be larger than 0.5, like in the case of recipe M1, as shown in Table 5. Obviously, the content and combination of surfactants affect the particle size, which in turn, affects the entry of oligomeric radicals.

When plotted the n_p versus average particle diameter (D_v) (see Fig. 8), we found that the larger the D_v, the higher the n_p values. Both series are plotted, respectively, in Fig. 8. The result agrees with the idea mentioned in literature [34]. Therefore, the larger the particle size, the more chances for the oligomeric radicals to enter into particles, so that the n_p values are higher in each series.

In Fig. 8, the series S has the larger n_p values at smaller average particle diameters, compared to those for series M with the same SDS content. It is quite clear that radicals in the S series have the higher entry rates to particles and termination rates in particles, so that the S series have the higher n_p values at the similar D_v values corresponding to those in the M series. Note that S series have the smaller values in molecular weights than M series at final conversion (Table 3).

4. Conclusions

The NaPSS was prepared by sulfonating a narrowly distributed polystyrene. This surfactant has a critical micelle concentration of 0.49 g/dL of water. By using SDS as the cosurfactant in the emulsion polymerization of styrene, the polymerization rates are higher than those using SDS only, while the latexes have the average particle diameters larger than those prepared with the SDS surfactant only. The M series have also the better resistance to endure the addition of the electrolyte. Values of average polymer number per particle (n_p) at low, middle and high conversions decrease with increasing SDS content for both series of M and S, since the D_v values decrease accordingly. Values of average radical number per particle ($\overline{n}$) also decrease. Obviously, the content and combination of surfactants affect the particle size, which in turn, affects the entry of oligomer radicals, and the n_p values. The results agree with the report that the larger the particle size, the radicals can coexist in a polymer particle without instantaneous termination. Obviously, the radicals in S series have the higher entry rates to particles and termination rates in particles, compared to the M series.

Acknowledgements

This report was sponsored by the National Science Council of ROC (Taiwan) (Grant number: NSC-93-2216-E-035-007).

References

[1] Vink H. Macromol Chem 1981;182:279.
[2] Thaler WA. Macromolecules 1983;16:623.
[3] Turbak AF. Ind Eng Chem Prod Res Dev 1962;1:275.
[4] Kučera F, Jančář J. Chem Pap 1996;50(4):224.
[5] Carroll WR, Eisenberg GH. J Polym Sci 1966;4:599.
[6] Kim GY, Salovey R. Polym Bull [Berlin] 1990;23:543.
[7] Takahashi Y, Natsumoto N, Iio S, Kondo H, Noda I. Langmuir 1999; 15:4120.
[8] Tanahato JJ, Kuil ME. J Phys Chem B 1997;101:5905.
[9] Tanahato JJ, Kuil ME. J Phys Chem B 1997;101:10839.
[10] Lin KF, Yang SN, Cheng HL, Cheng YH. Macromolecules 1999;32:4602.
[11] Ise N. Angew Chem Int Ed Engl 1986;25:323; Matsuoka H, Ise N, Okubo T, Kunugi S, Tomiyama H, Yoshikawa Y. J Chem Phys 1985;83: 378; Sogami I, Ise N. J Chem Phys 1984;81:6320.
[12] Lin SC, Lee WI, Schurr JM. Biopolymers 1978;17:1041.
[13] Schmitz KS, Lu M, Gauntt J. J Chem Phys 1983;78:5059.
[14] Drifford M, Dalbiez JP. Biopolymers 1985;24:1501.
[15] Schmitz KS, Ramsay DJ. J Colloid Interface Sci 1985;105:389.
[16] Sedlak M, Konak C, Stepanek P, Jakes J. Polymer 1987;28:873.
[17] Forster S, Schmidt M, Antonietti M. Polymer 1990;31:781.
[18] Sedlak M, Amis EJ. J Chem Phys 1992;96:817.
[19] Walkenhorst R, Dorfmuller Th, Eimer E. Ber Bunsenges Phys Chem 1995;99:1137.
[20] Tanahato JJ, Kuil ME. J Phys Chem B 1997;101:9233.
[21] Lantman CW, MacKnight WJ, Peiffer DG, Sinha SK, Lunberg RD. Macromolecules 1987;20:1096.
[22] Yim H, Kent MS, Matheson A, Stevens MJ, Ivkov R, Satja S, et al. Macromolecules 2002;35:9737.
[23] Bouix M, Gouzi J, Charleux B, Vairon JP, Guinot P. Macromol Rapid Commun 1998;19:209.
[24] Van Berkel KY, Russell GT, Gilbert RG. Macromolecules 2003;36: 3921.
[25] Maxwell IA, Morrison BR, Napper DH, Gilbert RG. Macromolecules 1991;24:1629.
[26] Eshuis A, Harbers G, Doornink DJ, Mijnlieff PF. Langmuir 1985; 1(3):289.
[27] Chu H-H, Lin C-S. J Polym Res 2003;10:283.
[28] Chu H-H, Gau J-H. Macromol Chem Phys 1995;196:2251.
[29] Yang JC, Jablonsky MJ, Mays JW. Polymer 2002;43:5125.
[30] Zundel G. Hydration and intermolecular interaction. NY: Academic Press; 1969.
[31] Fonteuot K, Schork FJ. J Appl Polym Sci 1993;49:633.
[32] Smith WV, Ewart RH. J Chem Phys 1948;16:592.
[33] Hansen FK, Ugelstad J. J Polym Sci Polym Chem Ed 1979;17(10):3047.
[34] Stockmayer WH. J Polym Sci 1957;24:314.
[35] Chu H-H. PhD dissertation, University of Akron; 1988.
[36] Roe CP. Ind Eng Chem 1968;60(9):20.
[37] Feeney PJ, Napper DH, Gilbert RG. Macromolecules 1984;17:2520.
[38] Lichti G, Gilbert RG, Napper DH. J Polym Sci Polym Chem Ed 1983; 21:269.
[39] Piirma I, Chang M. J Polym Sci Polym Chem Ed 1982;20:489.