

PREPARATION OF SULPHONATE-CONTAINING POLYMER PARTICLES VIA SEMI-CONTINUOUS EMULSION COPOLYMERIZATION OF STYRENE AND SODIUM STYRENE SULPHONATE*

Ji-shuai Wang, Yun-shen Chen, Wei Deng and Cheng-you Kan**

Department of Chemical Engineering and Key Laboratory of Advanced Materials of Ministry of Education,
Tsinghua University, Beijing 100084, China

Abstract Submicron-sized P(St-NaSS) latexes were prepared via a semi-continuous emulsion copolymerization of styrene (St) and sodium styrene sulphonate (NaSS) in the presence of anionic surfactant, in which NaSS aqueous solution and St were separately dropwise charged into the polymerization system at the same time. The hydrodynamic diameter of the latex particles was measured by dynamic light scattering (DSL) method, and the NaSS unit content of the purified copolymer by water extraction was calculated based on the elementary analysis. Results showed that the copolymerization could be performed smoothly with the monomer conversion more than 96% in the absence of crosslinker, and PNaSS homopolymer could be removed from the latex product by water extraction for 28 h. The weight loss in the water extraction tended to decrease and the NaSS unit content of the purified copolymer tended to increase with the increase of monomer feeding time, and both of them increased with the increase of NaSS/St mole ratio in the charge. The introduction of divinyl benzene (DVB) could decrease the weight loss in the water extraction and increase the NaSS unit content of the purified copolymer. When 25/75 mole ratio of NaSS/St and 11 mol% DVB of total NaSS and St were used in the recipe, and the monomer feeding time was 3 h in copolymerization, the NaSS unit content of the purified copolymer reached 7.31 mol%.

Keywords: Emulsion polymerization; Sulphonate-containing polymer particles; Crosslinking; Poly(styrene-sodium styrene sulphonate).

INTRODUCTION

Since the polymers with sulphonate groups have some special properties such as good stability towards hydrolysis, oxidation and thermal degradation, and high proton conductivity even at extremes of pH^[1, 2], many researches have been focused on sulphonate-containing polymers particularly on their particles for more than 40 years, and a number of applications have been found in diverse fields such as catalysts, carrier materials, separation, medicament, etc^[3–8]. Previous studies showed that poly(styrene-co-sodium styrene sulphonate), P(St-NaSS), presented different behaviors from ionomer, polymeric surfactant to polyelectrolyte according to its sulphonate content^[9, 10]. Recently, as a proton conductivity component, P(St-NaSS) copolymers have been used successfully to prepare composite polymer electrolyte membranes for the full cell fabrication^[2, 11–13].

Emulsion copolymerization is one of the important techniques to synthesize functional polymeric particles, and the solubility or polarity of monomers plays a vital role in the polymerization process, the reaction kinetics as well as the copolymer properties. Different emulsion copolymerization approaches have been investigated to synthesize P(St-NaSS) latex particles, and some mechanisms have been proposed^[6, 7, 14–19]. Because the

* This work was financially supported by Hitachi Chemical Co. Ltd.

** Corresponding author: Cheng-you Kan (阚成友), E-mail: kancy@tsinghua.edu.cn

Received January 20, 2010; Revised March 3, 2010; Accepted March 8, 2010

doi: 10.1007/s10118-011-1001-6

properties of the sulphonate-containing polymer particles are strongly influenced by their sulphonate content, how to increase NaSS unit content is a key problem in the preparation of P(St-NaSS) latex. However, since NaSS is highly water soluble and St is typical oil soluble, their incompatibility makes the emulsion copolymerization more complicated^[17]. NaSS molecules prefer to homopolymerize in aqueous phase to form PNaSS polyelectrolyte, and to copolymerize with St to initiate the homogeneous nucleation when NaSS units in the copolymer reach certain content; whereas St molecules prefer to micellar nucleation. Thus, the concurrence of the homopolymerization of water soluble NaSS and the generation of secondary particles makes the conventional emulsion copolymerization approaches impossible to prepare highly sulphonated P(St-NaSS) latexes^[17]. For example, Kim and his coworkers^[16, 17] have synthesized P(St-NaSS) latexes *via* conventional batch, seeded batch and semi-continuous emulsion copolymerization, respectively, and found that the content of NaSS units in the final latex copolymer could not be increased beyond 2.6 wt%, no matter how much NaSS was charged in the polymerization recipe.

In our previous study, P(St-NaSS) latex with 4.53 mol% of NaSS units in the copolymer has been synthesized *via* batch emulsion copolymerization in the presence of anion/nonionic composite emulsifiers^[20]. In this work, in order to meet the requirement of the latex particles with highly proton conductivity, water-insoluble P(St-NaSS) particles with more NaSS units were prepared *via* semi-continuous emulsion copolymerization, and the influences of the monomer feeding time, NaSS/St mole ratio as well as crosslinker on the polymerization process, the particle size and the copolymer composition were investigated.

EXPERIMENTAL

Materials

All chemicals were of analytical grade from Alfa Aesar Co. and used as received unless noted. Styrene (St) was distilled under reduced pressure. Sodium styrene sulfonate (NaSS) and ammonium persulfate (APS) were recrystallized in water before use. Sodium dodecyl sulfate (SDS), NaHCO₃ and divinyl benzene (DVB) were purchased from Fluka Co. Double distilled and deionized water was used throughout.

Emulsion Copolymerization

Emulsion copolymerization was carried out in a 250 mL flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and two pressure-equalizing funnels in nitrogen atmosphere. A typical recipe is listed in Table 1. The total amount of St and NaSS was the same but the mole ratio of NaSS/St was variable for different polymerization systems. The reactor was first immersed in a water bath and initially charged with 100 g of water, SDS and NaHCO₃ under stirring with 300 r/min. When the temperature of the system was elevated to 75°C, half of the APS aqueous solution, which was previously prepared by dissolving APS in 10 g water, was introduced into the reactor. Then, the aqueous solution of NaSS (dissolved in 20 g water) and the mixture of St and DVB were dropwise introduced into the system simultaneously from two funnels. After the monomers were added in a prescribed time, 1/4 of APS solution was then added. 1 h later, the rest of APS solution was added and the reaction continued for another 1 h at the same temperature. Then, the polymerization was continued at 80°C for 0.5 h, and the system was then cooled down to the room temperature to obtain the expected latex.

Table 1. Typical emulsion copolymerization recipes of St and NaSS

Component	Total amount of St and NaSS	DVB	SDS	APS	NaHCO ₃	H ₂ O*
Weight (g)	20.0	Variable	0.600	0.200	0.200	130

* For the recipes with DVB, additional amount of water was added to maintain the theoretical solid content of the system unchanged.

Homopolymer Preparation

Poly(sodium styrene sulphonate)

20 g of NaSS was dissolved in 100 g of water which was previous charged into a 150 mL flask equipped with a mechanical stirrer, a thermometer and a reflux condense. When the reactor was immersed in a water bath and

heated to 80°C, 0.2 g APS dissolved in 20 mL water was added into the system to initiate polymerization, and the reaction was maintained at 80°C for 6 h to obtain aqueous PNaSS solution. Under gently stirring, the solution was dropwise added into 250 mL of methanol which was previously cooled down to 4°C, and the precipitate was filtered and washed with methanol, and the solid PNaSS with yield of 96% was obtained by drying in a vacuum oven.

Polystyrene

PSt latex was prepared *via* batch emulsion polymerization according to the recipe in Table 1 except no DVB was used. Solid PSt sample was obtained by first dropwise adding the latex into methanol, and then filtrating, washing the precipitate with methanol and drying the solid in a vacuum oven.

Removal of Water-soluble Substances

About 20 mL copolymer latexes were dried first at 80°C for 5 h and then at 120°C for 2 h, and the obtained solid was extracted with water in a Soxhlet extractor.

In order to confirm the feasibility of the purifying process, control experiments were designed and conducted as follows: (a) Certain amounts of NaSS, NaHCO₃, SDS, PSt and PNaSS were extracted with methanol in a Soxhlet extractor for different time, and then the weight loss in this process was calculated, respectively; (b) PSt latex and PNaSS aqueous solution were mixed with the equal mole of St and NaSS units, and the aqueous mixture was dried as above to obtain PSt/PNaSS mixture. The PSt/PNaSS mixture was extracted with water in a Soxhlet extractor, and the extraction process was monitored by Fourier transform infrared spectroscopy (FTIR) and by the weight loss measurement. The weight loss of the sample is described as the following equation:

$$\text{Weight loss} = \frac{W_a - W_b}{W_a} \times 100\%$$

where W_a and W_b denote the dry weight of sample before and after extraction, respectively.

Characterization

The monomer conversion (Conv.) of the polymerization was determined gravimetrically. About 2 mL latex was sampled and inhibitor (3 droplets of 2 wt% *p*-dihydroxybenzene aqueous solution) was then added, and the sample was dried at 90°C till the weight was constant. Then the monomer conversion was calculated as follows:

$$\text{Conv.} = \frac{W_1 / W_0}{S} \times 100\%$$

where W_0 and W_1 denote the weight of the original latex sample and the dried sample, respectively. S represents the theoretical solid content assuming all of the monomers were polymerized.

The hydrodynamic diameter of the latex particles (D_p^{DSL}) and particle size distribution (polydispersity index, PI) were determined by dynamic light scattering (DLS) on ZetaSizer 3000HS (Malvern, UK) at 25°C.

FTIR spectra of the purified polymer by water extraction were recorded on a Nicolet 560 Fourier transform infrared analyzer (Nicolet, USA) within the scope of 400–4000 cm⁻¹. NaSS unit content of the purified polymer was calculated according to sulfur content, which was determined on a VISTA-MPX ACPOES Elementary Analyzer (Elemental, Germany).

RESULTS AND DISCUSSION

Removal of Water-soluble Substances

Some techniques including methanol coagulation, centrifugation-redispersion, ion-exchange and dialysis have been utilized to purify the P(St-NaSS) latex and clean the surface of the latex particles^[14, 17, 21, 22]. In order to investigate how many NaSS units could be stabilized in the particles especially when they are used in aqueous

system at relatively high temperature, Soxhlet extraction technique was used and appropriate conditions were obtained by comparison.

Results showed that when methanol was used as eluent, small molecules including NaSS, NaHCO_3 and SDS could be entirely removed within 6 h, but PSt and PNaSS could not be extracted even the extraction time extended to 24 h, implying that methanol was not a suitable solvent in the extraction purification of P(St-NaSS) latex polymer to remove homopolymer of NaSS^[20].

As the control experiment, a mixture of PNaSS and PSt with equal mole of NaSS and St units was extracted with water. It can be seen from FTIR spectra (Fig. 1) that the characteristic peaks of PNaSS in the range from 1010 cm^{-1} to 1185 cm^{-1} ^[20, 23] disappeared after 28 h extraction, suggesting that nearly all of PNaSS had been extracted from the original mixture sample, and the residue was only PSt as indicated in IR spectrum. This result was also in accord with the result of water extraction: the weight loss of the PSt/PNaSS mixture after 28 h extraction was 66.8%, which was close to the PNaSS content in the mixture. So, the P(St-NaSS) latex particles were purified with water extraction for 28 h to remove water-soluble materials in the following work.

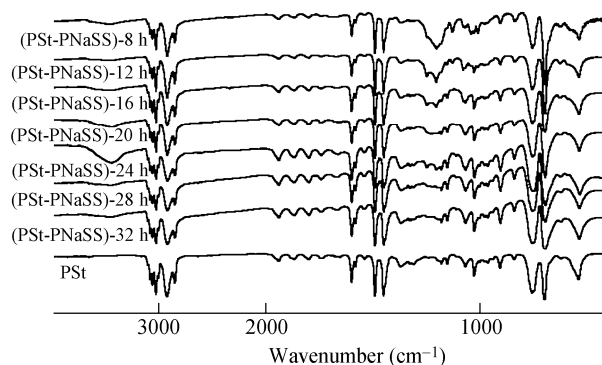


Fig. 1 FTIR spectra of the PSt/PNaSS mixture versus water extraction time

Effect of Feeding Time

Strategy of monomer feeding is very important for polymerization process and polymer composition in emulsion copolymerization. In our previous work, batch emulsion polymerization has been used to synthesize P(St-NaSS) latex, and found that the NaSS unit ratio in copolymer was no more than 4.53 mol% no matter how much NaSS/St was used in the recipe^[20]. In general, extending monomer feeding time can improve the copolymerization probability of the monomers with different polarity, and “starved feeding process” is often used to control the composition of latex copolymer. Here, semi-continuous emulsion polymerization was used to increase NaSS units of P(St-NaSS), and the influence of monomer feeding time on the weight loss of the latex product in water extraction and the composition of the purified P(St-NaSS) was investigated at a given mole ratio of 15/85 for NaSS/St in the recipe under the same condition, and results are summarized in Table 2.

Table 2. Influence of the feeding time on the composition of the emulsion product at a given mole ratio of 15/85 for NaSS/St in the polymerization recipe

Feeding time (h)	Conv. (wt%)	Weight loss (wt%)	Sulfur content (wt%)	NaSS unit content (mol%)
0.5	96.2	22.3	1.39	4.73
1.0	96.8	20.9	1.54	5.26
1.5	97.3	19.6	1.60	5.48
3.0	98.9	19.0	1.61	5.52
4.5	98.8	18.9	1.59	5.44
6.0	99.1	18.2	1.59	5.44
7.5	99.0	18.5	1.61	5.52

It can be seen that with the increase of monomer feeding time, the weight loss of the product in the water extraction tended to decrease, and the NaSS unit content of the purified product tended to increase. These

variations were obvious when feeding time was less than 1.5 h and became much weakened after this time. For example, when the feeding time extended from 0.5 h to 1.5 h, the weight loss decreased from 22.3% to 19.6%, and NaSS unit content increased from 4.73 mol% to 5.48 mol%, while the feeding time extended from 1.5 h to 7.5 h, the decrease of weight loss was only 1.1% (from 19.6% to 18.5%), and the increase of NaSS unit content was only 0.04 mol%, suggesting that the P(St-NaSS) composition was nearly constant when the feeding time was longer than 1.5 h. This might be attributed to the great solubility difference between St and NaSS and the negative charge of NaSS, which was difficult to penetrate the barrier of anionic surface of the growing particles because of electrostatic repulsion and tended to exist in the aqueous phase. So, to ensure the maximum NaSS unit content of the copolymer, 3 h of the monomer feeding time was utilized in the following emulsion copolymerization.

Effect of NaSS/St Mole Ratio

Previous study on the conversion soap-free emulsion copolymerization of St and NaSS showed that polyelectrolyte, which will result in the secondary nucleation and instability, would be formed when NaSS charge was over 2 wt%^[17]. In this work, when the semi-continuous emulsion copolymerization was used in the presence of surfactant, all of the polymerizations with different NaSS/St ratio could be carried out smoothly without any coagulum. The data in Table 3 indicated that the introduction of NaSS could increase the monomer conversion and the hydrodynamic particle size (D_p^{DLS}). Moreover, the particle size distribution (Poly index) became broader with the increase of NaSS/St, which probably resulted from the increased number of secondary particles generated by homogeneous nucleation and the aggregation of particles promoted by polyelectrolyte PNaSS at a higher level of NaSS amount.

Table 3. Influence of NaSS/St mole ratio on copolymerization and latex particles

NaSS/St (mole ratio)	0	5/95	10/90	15/85	20/80	25/75
Conv. (wt%)	95.2	97.0	97.9	98.9	98.3	98.7
D_p^{DLS} (nm)	82	143	153.0	163.4	160.2	167.8
Poly index	0.046	0.048	0.051	0.214	0.283	0.324

As can be seen from Table 4, with increasing NaSS/St mole ratio from 5/95 to 25/75, the weight loss of the latex product in water extraction increased significantly from 1.8% to 38.3%, but the NaSS unit content of the purified P(St-NaSS) was only increased from 4.92 mol% to 6.65 mol%. The reason is that at a higher NaSS concentration, much more NaSS molecules were consumed in aqueous phase than in the growing particles to form water soluble polymers including PNaSS and NaSS-enriched P(St-NaSS), which could be removed by water extraction.

Table 4. Influence of NaSS/St ratio on the composition of the emulsion product

NaSS/St (mole ratio)	5/95	10/90	15/85	20/80	25/75
Weight loss (wt%)	1.8	10.6	19.0	25.6	38.3
Sulfur content (wt%)	1.47	1.49	1.61	1.89	1.92
NaSS unit content (mol%)	4.92	5.09	5.52	6.54	6.65

Effect of Crosslinker

As indicated, increasing the monomer feeding time or increasing the NaSS/St ratio could increase NaSS unit content of the purified copolymer to a certain extent. To further increase NaSS unit content, crosslinker DVB was introduced into the polymerization system, and the influence of DVB amount on the polymerization and the copolymer composition was investigated at a given mole ratio of 25/75 for NaSS/St.

Experiments showed that the emulsion copolymerization could be carried out smoothly when the amount of DVB was less than or equal to 11 mol% of the total amount of NaSS and St, and monomer conversion reached more than 95% as indicated in Table 5. Since the crosslinking structure limited the swelling of the particles, the particle size gradually decreased with the increase of DVB amount. As expected, the weight loss of the product

decreased and the NaSS content of the purified copolymer increased with the increase of DVB amount. When the sample without DVB was compared with the sample with 11 mol% DVB, the weight loss decreased from 38.3% to 26.5%, and the NaSS unit content increased from 6.65 mol% to 7.31 mol%.

Table 5. Influence of DVB on monomer conversion, particle size and the composition of the latex product

NaSS/St/DVB (mol)	Conv. (%)	D_p^{DLS} (nm)	Weight loss (wt%)	NaSS unit (mol%)
25/75/0	98.7	167.8	38.3	6.65
25/75/1	95.3	126.7	38.1	6.72
25/75/5	96.7	89.6	35.6	6.94
25/75/11	95.2	70.5	26.5	7.31

CONCLUSIONS

P(St-NaSS) latex particles were prepared by semi-continuous emulsion copolymerization. The homopolymer of NaSS in the emulsion product could be removed by water extraction for 28 h. Increasing NaSS/St mole ratio and monomer feeding time were beneficial to increase NaSS unit content of the purified copolymer to a certain extent. Introduction of crosslinker could decrease the weight loss and increase the NaSS unit content, but when the amount of DVB exceeded 11 mol% of total monomers, the copolymerization process became unstable. The NaSS unit content of the purified copolymer reached 7.31 mol% for the copolymerization system with the 25/75 mole ratio of NaSS/St and 11 mol% DVB of total monomers at the optimal monomer feeding time of 3 h.

REFERENCES

- 1 Tsaor, S. and Fitch, R., *J. Colloid Interface Sci.*, 1987, 115: 463
- 2 Chen, S., Krishnan, L., Srinivasan, S. and Benziger, J., *J. Membr. Sci.*, 2004, 243: 327
- 3 Boardman, N., *J. Chromatogr. A*, 1959, 2: 398
- 4 Aoki, S., Otsu, T. and Imoto, M., *Makromol. Chem.*, 1966, 99: 133
- 5 Hanai, T. and Walton, H., *Anal. Chem.*, 1977, 49: 764
- 6 Kim, J., Elaasser, M., Klein, A. and Vanderhoff, J., *J. Appl. Polym. Sci.*, 1988, 35: 2117
- 7 Oh, J. and Kim, J., *Enzyme Microb. Technol.*, 2000, 27: 356
- 8 Herold, B., Bourne, N., Marcellino, D., Kirkpatrick, R., Strauss, D. and Zaneveld, L., *J. Infect. Dis.*, 2000, 181: 770
- 9 Kim, J., Kim, H., Nah, Y. and Eisenberg, A., *Polymer Bull.*, 1998, 41: 609
- 10 Forster, S. and Schmidt, M., *Adv. Polym. Sci.*, 1995, 120: 51
- 11 Hong, L. and Chen, N., *J. Polym. Sci. Part B: Polym. Phys.*, 2000, 38: 1530
- 12 Chen, N. and Hong, L., *Polymer*, 2004, 45: 2403
- 13 Kim, J., Mumi, S., Lee, C., Lee, Y. and Ihn, K., *J. Appl. Polym. Sci.*, 2008, 107: 2150
- 14 Weiss, R., Truner, S. and Lundberg, R., *J. Polym. Sci. Part A: Polym. Chem.*, 1985, 23: 525
- 15 Turner, S., Weiss, R. and Lundberg, R., *J. Polym. Sci. Part A: Polym. Chem.*, 1985, 23: 535
- 16 Kim, J., Chainey, M., Elaasser, M. and Vanderhoff, J., *J. Polym. Sci. Part A: Polym. Chem.*, 1989, 27: 3187
- 17 Kim, J., Chainey, M., Elaasser, M. and Vanderhoff, J., *J. Polym. Sci. Part A: Polym. Chem.*, 1992, 30: 171
- 18 Sunkara, H., Jethmalani, J. and Ford, W., *J. Polym. Sci. Part A: Polym. Chem.*, 1994, 32: 1431
- 19 Peula Garcia, J., Hidalgo Alvarez, R. and delasNieves, F., *Colloids Surf. A*, 1997, 127: 19
- 20 Huang, S.M., Kan, C.Y., Li, Y., Liu, D.S. and Shinji, T., *Petrochemical Technology(in Chinese)*, 2005, 34: 632
- 21 Delasnives, F., Daniels, E. and Elaasser, M., *Colloids Surf. A*, 1991, 60: 107
- 22 Bastos, D. and Nieves, F., *Colloid Polym. Sci.*, 1993, 271: 860
- 23 Yang, J., Jablonsky, M. and Mays, J., *Polymer*, 2002, 43: 5125