Polystyrene Ionomer Aqueous Dispersion. II. Affecting Factors for the Stability and Particle Size of Emulsion

BING LIAO, YUHUI HUANG, GUANGMIN CONG, SHULU ZHAO

Guangzhou Institute of Chemistry, Academia Sinica, P.O. Box 1122, Guangzhou 510650, People's Republic of China

Received 30 June 1997; accepted 23 March 1998

ABSTRACT: Aqueous dispersions of lightly sulfonated polystyrene were prepared. The effects of initial polymer concentration, neutralizer, ionic content, solvent property, and store time on the stability, the particle size, and the distribution of the dispersed phase for the resultant oil-in-water emulsions were studied. It was found that the particle size varied with the variation of polymer concentration and increased with increase in the store time. The effects of the neutralizer and the mixed solvents on the particle size were also significant. The particle size increased with increase in volume of the counterion. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2075–2079, 1998

Key words: lightly sulfonated polystyrene; aqueous dispersion; oil-in-water emulsion

INTRODUCTION

An aqueous polymer dispersion is a binary colloidal system in which particles of polymer are dispersed in a continuous aqueous phase. It can be used as a type of waterborne coating. Aqueous dispersion of polymer also has potential applications in the field, making ultrafine polymer powder alloys with properties different from those commonly resulting from melt blending.

Hydrocarbon polymers are incompatible with water. Therefore a special treatment and/or structural modification is necessary for the polymer to be dispersible in water. This is normally done by incorporating a small amount of ionic groups into the polymer backbone¹ and this special type of polymer is called an ionomer. The ionomers are more hydrophilic in nature² and, hence, dispersible in aqueous medium.

Recently, polyurethane ionomer aqueous dispersions have been widely studied.^{3–7} In this article, polystyrene ionomer with sulfonic groups was emulsified to an aqueous dispersion. The effects of initial polymer concentration, neutralizer, solvents, and store time on the stability and particle size of emulsion were studied. The factors that affected the particle size distribution of emulsion were also studied.

EXPERIMENTAL

Materials

Polystyrene, supplied by Yanshan Chemical Ltd., Beijing, China, $M_w = 110,000$, $M_w/M_n \le 1.15$, was purified by tetrahydrofuran/H₂O and dried under vacuum at 70°C for 48 h prior to use.

Sulfonation Reaction

Sulfonation reactions were carried out in 1,2-dichloroethane at 50°C following the procedure described by Weiss and Sen.⁸ The sulfonation agent was acetyl sulfonate, which was prepared by the

Correspondence to: B. Liao.

Contract grant sponsors: The National Natural Science Foundation of China; Guangdong Provincial Science Foundation; Engineering Plastics State Key Laboratory.

Journal of Applied Polymer Science, Vol. 70, 2075–2079 (1998) © 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/112075-05

Initial SPS	Ionic	
Concentration (wt %)	Contents (mol %)	Particle Size (nm)
10.0	9.7	cannot be emulsified
7.0	9.7	458.5
4.0	9.7	207.8
2.4	9.7	378.4
1.2	9.7	552.1

Table IEffect of Initial SPS Concentration onthe Particle Size of Emulsion forToluene/Methanol Mixed Solvent SystemNeutralized by Ammonia Liquor

reaction of concentrated sulfuric acid with acetic anhydride.

Emulsification Procedure

Sulfonated polystyrene (SPS) was dissolved in a series of mixed solvent systems, such as toluene/ methanol (or ethanol), 1,2-dichloroethane/ethanol, and cyclohexanone/acetone. The solution was then neutralized by stoichiometric sodium hydroxide and ammonia liquor.

Emulsification was carried out by dropping deionized water into a solution of SPS ionomer with constant agitation at room temperature. During the addition, the conductivity was monitored. When the conductivity of the solution reached a constant level, phase inversion was considered to be complete and addition of water was stopped. After phase inversion, an oil-in-water (O/W) emulsion was formed.

Measurements and Apparatus

Electric conductivity during the emulsification process was monitored using a model DDS-11A conductometer, manufactured by the Electric Factory of Shanghai, China. Test temperature was 25°C.

The sulfonic group content in SPS ionomer was measured by titration using a standard sodium hydroxide solution, nominally 0.1*N*, prepared by dissolving 1 g NaOH in 250 mL absolute methanol. Phenolphthalein was used as an indicator.

Particle size and distribution of the resultant O/W emulsions were characterized using a laser light scattering-type particle size analyzer, MALVERN Multi-8 Autosizer (UK), at ambient temperature.

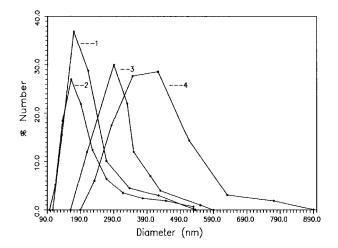


Figure 1 Particle size distribution pattern of SPS emulsion. (Toluene/methanol mixed solvent system, 3/7 vol/vol, neutralized by ammonia liquor. SPS ionomer concentration: curve 1, 2.4 wt %; curve 2, 4.0 wt %; curve 3, 7.0 wt %; curve 4, 1.2 wt %.)

RESULTS AND DISCUSSION

Effects of Initial Polymer Concentration

Effects of initial polymer concentration on the particle size and distribution of emulsion for toluene/methanol (3/7, vol/vol) mixed solvent system (neutralized by ammonia liquor) are shown in Table I and Figure 1.

From Table I, it is clear that the particle size of emulsion is large at lower or higher initial polymer concentration. Only at an optimum polymer concentration is the particle size smallest. For the toluene/methanol mixed solvent system neutral-

Table IIEffects of Initial SPS Concentrationon the Particle of Emulsion

Mixed Solvent System	Initial SPS Concentration (wt %)	Ionic Contents (mol %)	Particle Size (nm)
Toluene/ethanol	5.9	9.7	280.3
	2.9	9.7	189.4
	1.8	9.7	374.8
Cyclohexanone/			
acetone	17.8	9.7	98.9
	11.9	9.7	69.8
	6.0	9.7	116.9
	3.6	9.7	118.1

Mixed Solvent System	Neutralizer	Initial SPS Concentration (wt %)	Particle Size (nm)
Toluene/methanol	unneutralized	4.0	178.3
(3:7, vol/vol)	NaOH	4.0	189.8
	ammonia liquor	4.0	207.8
Toluene/ethanol	unneutralized	1.8	374.8
(1:5, vol/vol)	NaOH	1.8	426.8
	ammonia liquor	1.8	621.8
1,2-dichloroethane/ethanol	unneutralized	6.0	98.8
(1:1, vol/vol)	NaOH	6.0	148.2
	ammonia liquor	6.0	312.3

Table III Effect of Neutralizer on the Particle Size of Emulsions

Ionic content of SPS: 9.7 mol %.

ized by ammonia liquor, optimum polymer concentration is near 4.0 wt %).

The same trend can be found in toluene/ethanol (1 : 5, vol/vol) and cyclohexanone/acetone (1 : 1, vol/vol) mixed systems for unneutralized SPS, as listed in Table II.

In general, the apparent viscosity of ionomer solution in low polar organic solvent increases rapidly with the increase of polymer concentration. This is usually attributed to the occurrence of the association of ionic groups in the ion-containing polymer. In the present mixed solvent systems of toluene/methanol (3:7, vol/vol) and toluene/ethanol (1: 5, vol/vol), the polarities are high enough to disturb the associations of ionic groups; even if there were some ionic aggregation regions, it may be a relatively relaxed structure, especially in dilute solution. In high polymer concentration, an entanglement network morphology may exist and the aggregation of hydrophobic main chains resulted in larger particle size during addition of water under constant agitation. In dilute solution, the droplet of water entering the ionomer solution pushed the hydrophobic polymer main chains together to form a concentrated polymer area and provide a possibility of the aggregation of hydrophobic main chain, so that resulted in the formation of large particles. However, in an optimum polymer concentration, the water droplet may cause both the hydrophobic chain aggregation and the solvation of hydrophilic groups which were unfavorable for the hydrophobic chain aggregation. These competitive effects may cause the relatively small particles in the emulsification process.

Similarly, the particle size distribution was also affected by the polymer concentration (Fig.

1). At the optimum polymer concentration (4.0 wt % SPS), the half-width of the distribution peak was narrower than that in the other polymer concentration.

Effects of Neutralizer

Table III shows that the particle size of emulsions increased in a sequence of H^+ , Na^+ , and NH_4^+ . This trend did not vary with the variation of the mixed solvent system.

These results may be attributed to the differences in volume and ionic strength of the counterions; the smaller the volume of cation, the higher ionic strength. These caused a significant inhibition of the aggregation of hydrophobic main chains of SPS. For the same reason, the higher ionic contents in SPS caused smaller particles in emulsion discussed in the following section. However, further studies are needed to find a clear explanation of this complicated phenomenon in waterborne ionomer emulsion.

Table IV	Effect of Ionic Content on the
Particle S	ize of Emulsion for Toluene/Methanol
(3:7, vol/	vol) Mixed Solvent System

Ionic	Initial SPS	Particle
Content	Concentration	Size
(mol %)	(wt %)	(nm)
9.7 5.8 3.8	4.0 4.0 4.0	$207.8 \\ 490.0 \\ 520.0$

Sulfonic groups were neutralized by ammonia liquor.

Mixed Solvent	Initial SPS Concentration (wt %)	Store Time (months)	Particle Size (nm)
Cyclohexanone/acetone			
(1:1, vol/vol, unneutralized)	6.0	1	116.9
	6.0	3	145.9
1,2-dichloroethane/ethanol			
(1:1, vol/vol, unneutralized)	2.9	1	220.3
	2.9	3	569.9

 Table V
 Effect of the Store Time on the Particle Size of Emulsion

Ionic content of SPS: 9.7 mol %.

Effect of Ionic Content

Effects of ionic content on the particle size of emulsion for the toluene/methanol mixed solvent system are listed in Table IV.

Table IV shows that the particle size of emulsion increased with the decrease in ionic content, which may imply that the stability of emulsion increased with the increase in ionic content. (Usually the smaller particle corresponded with greater stability.)

Effect of Store Time of Emulsions

Effect of the store time of emulsion on the particle size and distribution are shown in Table V and Figures 2 and 3, respectively.

The particle size increased with the increase in the store time for both of the mixed solvent sys-

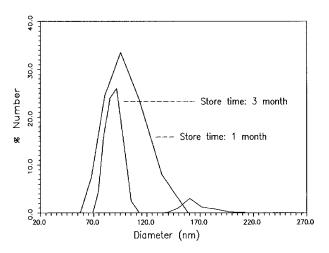


Figure 2 Particle size distribution pattern of SPS emulsion. (Mixed solvents: cyclohexanone/acetone, 1 : 1, vol/vol; unneutralized.)

tems (Table V). This indicates that partial particles were aggregated to form large particles. The particle size distribution curves (in Figs. 2 and 3) clearly show that only a small proportion of unstable particles aggregate to form large particles during the storing time (up to 3 months), which was shown as a small distribution peak located in the large particle size range.

CONCLUSION

The particle size and stability of SPS ionomer waterborne emulsions were greatly affected by polymer concentration, neutralizer, ionic content, store time, and solvent properties. For a definite mixed solvent system, there was a optimum polymer concentration in which the particle size was smaller

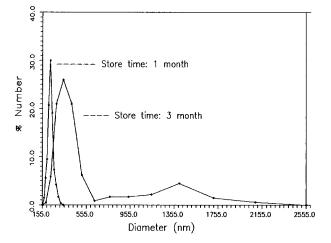


Figure 3 Particle size distribution pattern of SPS emulsion. (Mixed solvent: 1,2-dichloroethane/ethanol, 1:1, vol/vol; unneutralized.)

and the emulsion was much more stable. The particle size and stability of emulsions varied with the variation of neutralizer and decreased in H^+ , Na^+ , and NH_4^+ sequence. The particle size increased with decrease in ionic content. The particle size and its distribution were greatly affected by polymer concentration and the store time of the emulsion.

REFERENCES

 D. Dieterich, W. Keberle, and H. Wiet, Angew. Chem. Int. Eng. Ed., 9, 40 (1970).

- W. C. Chan and S. A. Chen, *Polymer*, 29, 1995 (1988).
- O. Lorenz, H. J. August, H. Hick, and F. Triebs, Angew. Makromol. Chem., 63, 11 (1977).
- B. K. Kim and T. K. Kim, J. Appl. Polym. Sci., 43, 393 (1991).
- J. S. Lee and B. K. Kim, Prog. Org. Coatings, 25, 311 (1995).
- B. K. Kim and C. K. Kim, J. Mater. Sci., Pure Appl. Chem., A32, 1903 (1995).
- B. K. Kim and T. K. Kim, Colloid Polym. Sci., 269, 889 (1991).
- R. A. Weiss and A. Sen, *Polymer*, **32**, 1867 (1991).