Effects of the Amount and Introducing Time of Emulsifier on the Preparation of Carboxylated Polystyrene Particles

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Abstract.Carboxylated polystyrene particles were synthesized by batch emulsion copolymerization of styrene (St) and methacrylic acid (MAA) at 70 °C for 7 h. The effects of introducing time and amount of emulsifier SDS on the polymerization and properties of polymer particles were investigated. Results showed that introducing SDS after initiating polymerization for 3 h was beneficial to forming latex particles with monodisperse size and smooth sphere, and the properties of the resultant particles, including size and size distribution, zeta potential as well as carboxyl distribution were hardly influenced by the amount of SDS in this situation. Furthermore, the mechanism of polymerization was briefly discussed

Introduction

Monodisperse polymer particles have been intensively studied in the past few decades due to their characteristics of microcosmic size, uniform distribution and high specific surface area [1-2]. These properties make it an exciting material in chromatography, catalyst carrier, biotechnology and electronic industry [3-6]. Since the pioneer synthetic method of monodispersepolymer particles was reported [7], global research and development effort has been done to extend the synthetic techniques and provide many valuable results [8-10]. Comparing with other polymerization techniques such as dispersion polymerization, precipitation polymerization, SPG membrane technique, and living radical polymerization method [11-14], emulsion polymerization belongs to simple technology, friendly environment, and stable quality, and is feasible for production in large scale. According to the concept of "particles design", polymer particles could be endowed with diverse structures and properties, such as core-shell, porous, hair-like, sensitivity and surface modification, which make the polymer particles serve as functional materials in various fields [15-17].

Emulsifier is the most important controlling factors in emulsion polymerization. The previous researches were mostly focused on the effects of the amount of emulsifier on polymerization. With the aim of controlling the morphology of polymer particles and studying the relationship between the emulsifier and the particle morphology, the introducing time and the amount of the emulsifier on the polymerization and the properties of resultant P(St-MAA) particles were investigated in this study. In addition, the forming mechanism of latex particles was proposed based on the experiment results.

Experimental Section

Materials. Styrene (St) and methacrylic acid (MAA) (both A.R.grade, GuangFu Fine Chemical Industry Research Institute, Tianjin, China) were purified by distillation under reduced pressure and stored in an refrigerator. Ammonium persulfate (APS) (A.R.grade, GuangFu Fine Chemical Industry Research Institute, Tianjin, China) was purified by recrystallization twice. Sodium dodecyl sulfate (SDS), NaOH, and H2SO4 (all A.R.grade, ZhiYuan Chemical Regent Co., Ltd., Tianjin, China) were used as received. Deionized water was employed.

Preparation of carboxylated PSt particles. Caboxylated PSt particles were prepared by emulsion polymerization in a 250 ml four-necked round bottom flask equipped with an inlet of nitrogen gas, a reflux condenser, a mechanical stirrer and a thermometer. 20 g of St and MAA (the mole ratio of St/MAA was 94:6) and 100 g of H_2O were charged into the reactor, and polymerized at

70 °C for 7 h. Meantime, 0.336 g APS dissolved in 25 g H_2O was introduced at the beginning, 2 h and 4 h of polymerization with a ratio of 12:8:5. Certain amount of SDS dissolved in 10 g H_2O were introduced into the reactor at different time during the process of polymerization.

Characterization. The monomer conversion of polymerization (Conv. *wt*%) were determined by gravimetric analysis. The **hydrodynamic** diameter (D_p^{DLS}) , polydispersity Index (Poly. Index) and zeta potential (ζ) of the latex particles were measured on Zetasizer 3000HS (Malvern, UK). The number-average diameter (D_p) and morphology of the dried latex particles were characterized using transmission electron microscopy (TEM, JEOL JEM-2100EX, Japan) at 70 KV using 2% aqueous solution of phosphotungstic acid as staining agent. The surface appearance of the latex particles was observed by scanning electron microscope (SEM, JSM 7401F, Japan). The distribution of carboxyl groups in the emulsion system was determined by conductometric titration with DDS-307 conductometer (Leici, Shanghai, China) according to the literature [18]. S_c , F_c and E_c represented the percentage of-COOH bounded on the surface of latex particles, free in the aqueous phase and embedded inside the latex particles respectively.

Results and Discussion

Introducing SDS at different time. In order to investigate the influences of SDS introducing time on the emulsion polymerization and particle properties, 0.467 g SDS which was 1.5 times of its critical micelle concentration (CMC) was added into the reaction system at different time of the polymerization. The results were given in Table 1, and morphology of the obtained products was shown in Fig. 1 and 2.

Introducing time of SDS (h)	Conv.(%)	$D_{\rm p}({\rm nm})$	$D_{\rm p}^{\rm DLS}({\rm nm})$	Poly. Index	$\zeta (mV)$
1	92.9	121	196	0.0220	40.1
2	93.3		347	0.0847	35.8
3	92.6	236	314	0.0521	43.3
4	92.1	246	314	0.0020	46.6

Table 1. Influence of SDS introducing time on the properties of carboxylated PSt particles.



Fig. 1. TEM photographs of caboxylated PSt particles prepared by introducing SDS at different time of polymerization process (a) 1h, (b) 2h, (c) 3h, (d) 4h



Fig.2. SEM photographs of caboxylated PSt particles prepared by introducing SDS at different time of polymerization process (a) 1h, (b) 2h, (c) 3h, (d) 4h

It was found that the stability of polymerization and the monomer conversion were not much different regardless of the introducing time of SDS. When SDS was added into the reaction system at 1 h of polymerization, the latex particles showed small size and wide distribution. Both the size and the polydispersity Index became larger when SDS was added at 2 h of polymerization, and particles with uneven surface and entirely different size were clearly presented under electron microscope observation (Figure 1b and Figure 2b). In comparison, the obtained particles getting uniform with smooth surface and size almost unchanged if SDS introducing time was put off till 3h or 4h of polymerization. Moreover, a similar tendency was also obtained for the hydrodynamic diameter (D_p^{DLS}) of the particles except that the value of D_p^{DLS} was bigger than that of D_p because of hydration.

Influence of the amount of SDS. Altering the amount of emulsifier is the most convenient and effective method to dominate the size of latex particles in conventional emulsion polymerization. Fixing SDS introducing time at 3h of polymerization, the influences of SDS amount on the emulsion polymerization and particle properties were given in Table 2, and morphology of the obtained products was shown in Fig. 3.

Amount of SDS (g)	Conv.(%)	$D_{\rm p}({\rm nm})$	$D_{\rm p}^{\rm DLS}({\rm nm})$	Poly. Index	ζ(mV)
0	97.3	288	425	0.0402	37.6
0.467	92.6	236	314	0.0521	43.3
0.622	95.1	253	319	0.0443	44.3
1.244	94.0	269	362	0.0338	46.0

Table 2. Influence of SDS amount on the properties of carboxylated PSt particles.



Fig.3. TEM photographs of caboxylated PSt particles prepared by introducingdifferent amount of SDS at 3h ofpolymerization process (a) 0g, (b) 0.622g, (c) 1.244g

All of the polymerization could be carried out smoothly with very little coagulation formed and the monomer conversions were more than 90 wt%. It was shown that except the size of latex particles prepared with soap-free emulsion polymerization was bigger than that of other latex particles, the size, size distribution, zeta potential and the distribution of carboxyl groups, as shown in Table 3, of the obtained latex particles were almost not or slightly affected by increasing the introducing amount of SDS during the polymerization process, which were quite different with conventional emulsion polymerization. Furthermore, the trend of-COOH bounded on the particle surface(S_c) was in accordance with that of zeta potential (ζ).

Amount of SDS (g)	$F_{C}(\%)$	$S_{C}(\%)$	$E_{C}(\%)$
0	15.2	36.5	48.3
0.467	11.8	38.5	49.7
0.622	17.1	39.5	43.4
1.244	10.1	39.7	50.2

Table 3. Influence of SDS amount on the distribution of carboxyl groups.

The mechanism of polymerization could be deduced as follows. Initial particles were formed by micellar nucleation because of the hydrophobicity of St, and copolymerization of MAA played a role of surfactant to protect the stability of emulsion. Therefore, even without introducing SDS into the reaction system, the carboxyl groups bounded on the surface of latex particles ensured the successful polymerization. As the polymerization time increased, the surface charge density of latex particles decreased with the growth of initial particles, coalescence between such unstable latex particles was inevitable, which resulted in the increasing of particle size, the broadening of particle size distribution, and widely divergence of morphology between initial particle and aggregated particles. After the coalescence wound up, the particles turned to be smooth spheres with well-distributed size, and introducing SDS at this time was only favorable to enhance the stability of the reaction system, but would not influence the properties of coalescence particles.

Conclusions

In this study, PSt latex particles containing carboxyl groups were synthesized by batch emulsion polymerization at 70 °C for 7 h. The morphology of resultant particles was significantly influenced by the introducing time of emulsifier SDS. When SDS was introduced into the polymerization system prematurely, such as 1h or 2h of polymerization, the resultant latex particles exhibited polydispersity, resulting from the coalescence interruption of initial particles. While introducing SDS at 3h of polymerization, monodisperse latex particles with smooth surface could be obtained and altering the amount of SDS at this time had little impact on the properties of polymer particles.

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