

# 폴리스타일렌 나노입자의 입도 조절에 관한 연구

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## A Study on the Size Control of Nanosized Polystyrene

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계면활성제(polyvinylpyrrolidone, PVP)와 개시제(benzoyl peroxide, BPO)를 95% 알코올을 용매 속에 첨가하여 styrene monomer로부터 나노 크기의 균일한 분포 영역을 갖는 polystyrene (PS)을 제조하였다. Emulsion polymerization방법을 사용하였으므로 중합과정에서 PS입도 크기에 많은 변수가 영향을 미칠 수 있다. 본 연구에서는 단량체, 계면활성제 및 개시제 등의 농도 영향은 배제하고 가장 큰 변수들로 고려되는 교반 속도와 초음파 조사시간의 영향을 주로 연구하였다. 초음파 조사시간을 조절한 결과 400 nm의 나노 크기를 갖는 PS 입자를 제조할 수 있었다.

Nanosized polystyrene (PS) particles with the narrow size distribution were synthesized from styrene monomer at the presence of the surfactant (polyvinylpyrrolidone, PVP), the solvent of 95 % alcohol, and the initiator of benzoyl peroxide (BPO). Since the emulsion polymerization method was applied, many factors could have effects on the size of PS particles during polymeric process. Aside from the concentration of monomer, surfactant and initiator, the factors such as the stirring speed and the ultrasonic radiation were mainly studied. By adjusting the radiating time, PS particles with their size of about 400 nm were synthesized.

**Keywords:** ultrasonic radiation, nanoparticle, polystyrene, surfactant, spots

### 1. Introduction

Synthesis of nanoparticles is becoming an increasingly important aspects of polymeric science. Because the particle size, the morphology of nanoparticles and their assembly into structures perform specific functions and deliver specific effects[1], it can display novel optical, electronic, chemical and structural properties that may find many important technological applications in the near future.

There are two main ways for the production of nanoparticles : solid-state processes and colloidal processes. To synthesize nanoparticles with adjustable size, morphology, and possibly a specific function, colloidal processes are proving themselves quite advantageous. Emulsion polymerization is one of the those most common methods because it has several advantages[2,3]. First of all, the physical state of the colloidal system makes it easy to control the polymeric process. Moreover, the latex product is often directly valuable and the small particle size could bring about low residual monomer levels[4]. In emulsion polymerizations, surfactants are usually necessary in order to achieve stabi-

lization of the latex particles produced during polymerization[5].

Concentration of surfactant is one of many factors that effect the size of the particles, however, the presence of two much surfactant is a disadvantage for certain applications of emulsion polymers like coatings, paints, and polishes[6]. To improve some properties of polymer latex, one may have to search other methods to control the size of the polymeric particles. For free radical polymerization, either increase the concentration of initiator or decreasing the concentration of monomer can lead to decrease of particle size and molecular weight[7]. Others such as control of stirring speed, the usage of inhibitor are common methods applied. In other published researches,  $\gamma$  ray irradiation is reported in Lal Said Jan's[8] research when nanoparticles of polystyrene and polyaniline were prepared, and UV light radiation [9], electron beam (EB) irradiation[10] were also exploited by researchers. In this present study, ultrasonic radiation would be investigated in how it affects the feature and the size of polystyrene nanoparticles. In former studies, PS microparticles with their diameters range from 2.0 to 3.5  $\mu\text{m}$  has been published[11], however, PS nanoparticles with their size distributed from 300 nm to 500 nm have been successfully synthesized by applying ultrasonic radiation in this paper.

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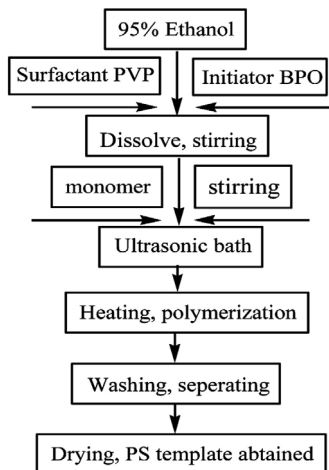


Figure 1. Schematic process for synthesis of nanosized PS particles.

## 2. Experimental

### 2.1. Materials/Reagents

Styrene monomer of 99.9%, was provided by Kanto Chemical CO. Inc. Initiator benzoyl peroxide (BPO) is produced by Alfa Aesar A Johnson Matthey Company. Surfactant polyvinylpyrrolidone (PVP) was bought from Sigma-Aldrich Chemical.

### 2.2. Preparation of Polystyrene Templates

Numerous methods have been developed by researchers to get access to synthesize different size of polystyrene latex or particles. In order to synthesize polystyrene spheres, surfactant PVP was first mixed with 95% ethanol, then initiator BPO was added into the mixture, rendered it under ultrasonic bath for about one minute until both the PVP and BPO were completely dissolved. Then styrene monomer was added to the former mixture after it's diluted by ethanol, keep the ultrasonic bath for 8 min while the solution was under a 400 rpm stirring condition. After ultrasonic treated it was transferred into a three necks flask and the polymerization process started at the presence of 70 °C water bathe heating.

After reacting for 24 h, the emulsion was washed three times through 95% ethanol through centrifuge, finally the PS was dried and ready for use. Turn to Figure 1 to see the schematic process for synthesis of nanosized PS particles.

## 3. Result and Discussion

### 3.1. Factor of Ultrasonic Radiating Time

It must be noted that there were several factors may have effects on the size of PS particles. Here the main two factors of ultrasonic treating time and stirring speed were taken into account. First of all, from SEM images it could be concluded that when other factors such as concentration of initiator, monomer and surfactant, the stirring speed (fixed at 450 rpm) remain unchanged, if the emulsion was radiated for about 5 minutes, the diameter of the particles decreased sharply from 2500 nm to about 500 nm. After this, the size of PS particles slightly

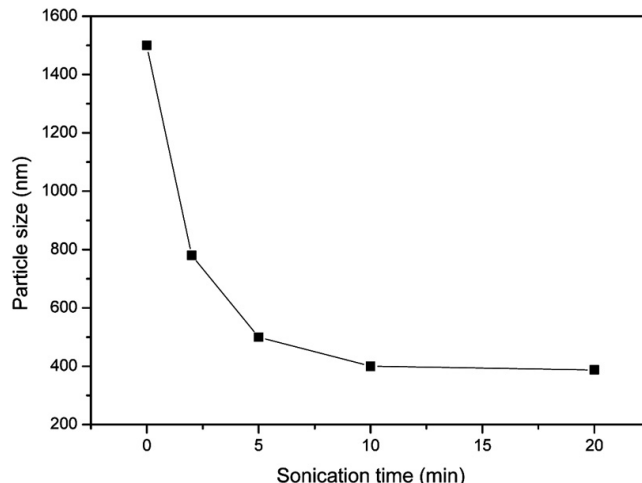


Figure 2. Effect of ultrasonic radiating time on the diameter of PS particles.

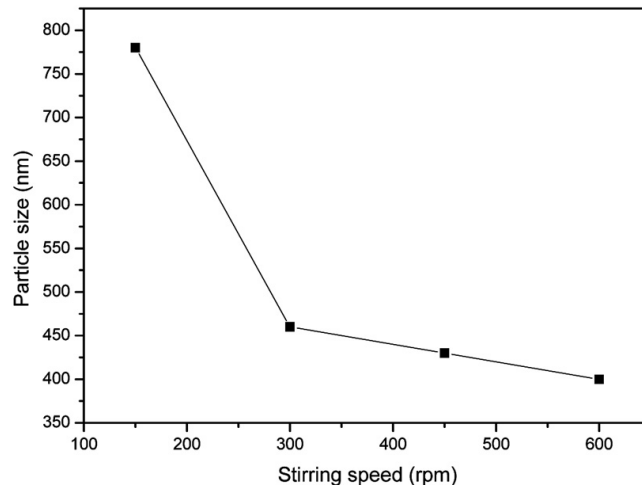


Figure 3. Effect of stirring speed on the diameter of PS particles.

decreased from 500 nm to 400 nm as the radiating time lasted for another 5 minutes. Moreover, in the following 10 minutes, the average decrease was around 1~2 nm per minute (See Figure 2). This probably could be interpreted as that as the work of ultrasonic washer was constant, which emitted constant energy in per area unit. Thus, when the size of the particle decreased to a certain extent, the particles were not be able to absorb enough energy to break themselves into smaller particles because of its limited surface area. SEM images in Figure 3 (a, b, c) identified ultrasonic radiating time of 0, 5, 10, and 20 min, respectively.

One must pay attention to SEM images of d) in Figure 3. It is obvious that on the surface of the particles, kinds of small spots could be observed. This phenomenon could be probably attributed to the long period of radiating time. It is proposed that at the first several minutes, styrene monomer has been dispersed as small as possible into droplets in solvent. With the radiation kept going on, the liquid system would be able to absorb enough energy to lift up the temperature of the mixture, this means the droplets have the probability of starting polymer-

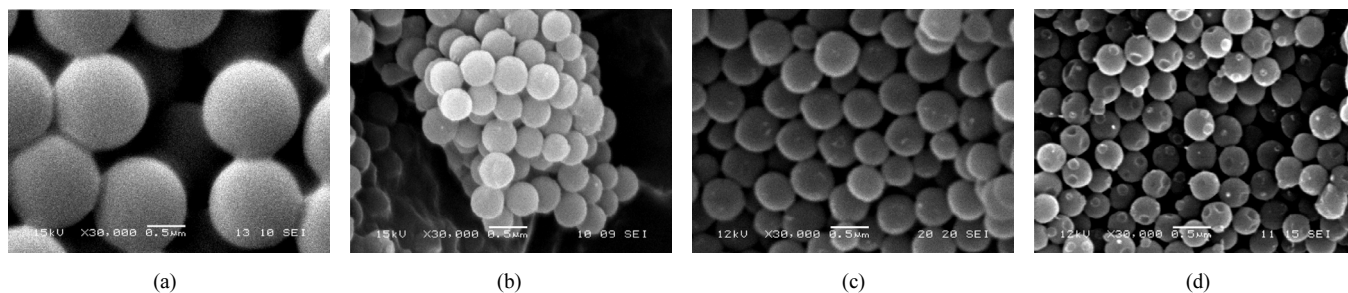


Figure 4. SEM images of PS particles synthesized from the emulsion that with ultrasonic radiation of : (a) 0 min, (b) 5 min, (c) 10 min, and (d) 20 min.

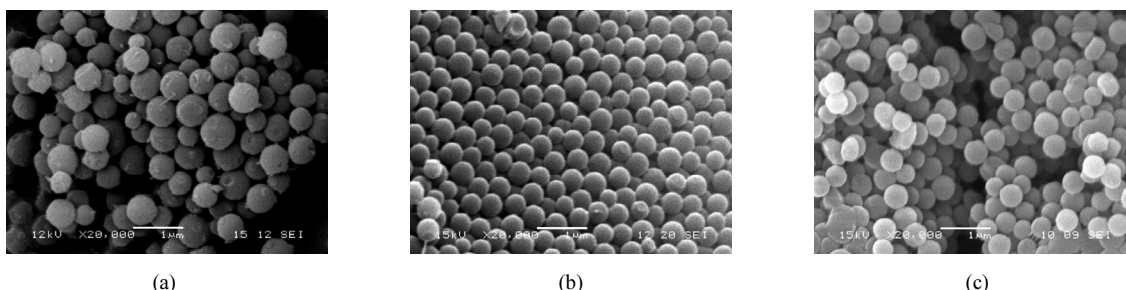


Figure 5. SEM images of PS particles synthesized from the emulsion that applied a stirring speed of : (a) 150 rpm, (b) 400 rpm, and (c) 600 rpm.

ization before they are treating with water bath at higher temperature. Therefore, in the following ultrasonic radiation, as the polymerization continue, the seed of PS would grow gradually, until it is bigger enough to escape from the restriction of the droplet. Finally, nanosized PS particles with small spots on their surface are obtained after complete polymerization.

### 3.2. Factor of Stirring Speed

With ultrasonic bath time fixed as 8 minutes and other factors be constant, when the stirring speed was set to 150 rpm, the size distributed between 700 and 900 nm, which decreased substantially to 450 nm when the speed changed from 150 rpm to 450 rpm via 300 rpm, and the SEM images show that, the PS particle size changed from about 430 nm to 380 nm when the speed was adjusted to 600 rpm (See Figure 4). And SEM images in Figure 5 (a, b and c) describe the effect of stirring speed of 150 rpm, 450 rpm and 600 rpm on the diameter of PS spheres, respectively.

## 4. Conclusions

The diameter of PS particles could be controlled in a narrow distribution and it is about 400 nm when the monomer is 4% by volume, the stirring speed is set to 450 rpm and the ultrasonic radiation is applied for 8 min.

The size of PS templates decreased when the stirring speed increased and the ultrasonic radiating time prolonged.

Nanosized PS particles with small spots on its surface could be synthesized by ultrasonic radiation control during polymeric procedure.

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## Reference

1. G. Bognolo, *Adv. Colloid Interface Sci.*, **106**, 169 (2003).
2. J. Zhang, Z. Chen, Z. Wang, W. Zhang, and N. Ming, *Materials Letters*, **57**, 4466 (2003).
3. S. Wang, X. Wang, and Z. Zhang, *European Polymer Journal*, **43**, 178 (2007).
4. S. Rosen, *Fundamental Principles of Polymeric Material*, 1, 6, Wiley Interscience, USA (1993).
5. D. Zha, L. Qi, H. Chin, and J. Ma, *J. Colloid Interface Sci.*, **246**, 413 (2002).
6. G. Odian, *Principles of Polymerization*, 4, 110, Wiley Interscience, USA (1991).
7. M. P. Stevens. *Polymer Chemistry*, 6, 352, Oxford University Press, New York (1999).
8. L. S. Jan, S. Radiman, M. A. Siddig, S. V. Muniandy, M. A. Hamid, and H. D. Jamali, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **251**, 43 (2004).
9. C. Decker, T. Nguyen, and T. Viet, *Macromol. Chem. Phys.*, **200**, 358 (1999).
10. B. Qu and B. Ranby, *Polym. Eng. Sci.*, **35**, 1161 (1995).
11. H. K. Shin, Y. S. Park, and J. W. Woo, *Korea Ind. Eng. Chem.*, **13**, 482 (2002).