

# Anomalous Particle through Soap-Free Emulsion Polymerization of Styrene using Oil-Soluble Initiator

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## **Abstract**

One of oil-soluble initiators, VF-096, might work as cross-linker. This initiator would enable to synthesize the particle with cross-linking, which was involved with the particle morphology. Soap-free emulsion polymerization of styrene using this initiator was carried out to develop the method to control the particle morphology in one batch system. As a result, it was found that anomalous particle was generated without stirring and the particle morphology changed to be spherical by increasing shear stress through the stirring. One of the origins of the anomalous particle was the phase separation of the water in the particle and release of it from inside of the particle to the bulk.

**Keywords:** Soap-free emulsion polymerization, Anomalous particle, Oil-soluble initiator

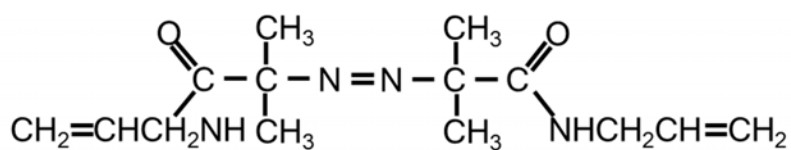
## Introduction

Water-soluble initiator, such as potassium persulfate, was often used in the conventional soap-free emulsion polymerization because the ionic radicals derived from the initiator made a contribution to keep the synthesized polymeric particles stabilized in water [1-3]. In this system, the anomalous particles were observed at the initial stage of the polymerization [4]. Ionic radicals decided which the surface potential of the particle was negative or positive. However, our recent studies showed the monodispersed particles with good dispersion stability were able to be synthesized in this kind of polymerization even using an oil-soluble initiator, such as 2,2'-azobis(2-methylpropionitrile) (AIBN) [5,6]. Because negatively charged particle would be formed using the aromatic vinyl monomer in the polymerization by AIBN, the negative charge was deeply involved in phenyl ring in the monomer [6,7]. It was clear that polymeric particles were able to be synthesized by soap-free emulsion of aromatic vinyl monomer using oil-soluble initiator. These synthesized particles at the end of the polymerization were spherical. However, the anomalous particles are required in the field of print and photology. Most of the methods for the synthesis of anomalous particle were complicated using organic solvent and cross-linker and surfactants [8,9]. And, some methods were consisted of more than two steps [10]. Both vinyl monomer and cross-linker such as divinylbenzene were often utilized to synthesize anomalous particles by the polymerization [11,12]. One of the initiators might work as cross-linker, 2,2'-azobis[N-(2-propenyl)-2-methylpropionamide] (VF-096, Wako Pure Chemical Industries). This was an oil-soluble initiator and able to be applied to our recent polymerization [5]. Hence, the present study focused on the soap-free emulsion polymerization of styrene using VF-096 to develop the synthesis method for anomalous particle by one batch system without surfactant.

## Experimental

### Materials

To synthesize the polymeric particles, the chemical materials used for the soap-free emulsion polymerization in this study were prepared as follows. The water was purified using the purification system (WG250, Yamato Scientific), and nitrogen gas was then bubbled into the water to remove the dissolved oxygen. A styrene monomer (Tokyo Chemical Industry) was washed four times with a 10 % sodium hydroxide solution to remove the polymerization inhibitors, and was then purified by distillation under reduced pressure. VF-096, whose chemical structure was shown in **Fig. 1**, was used as radical and oil-soluble initiator and monomer without further purification.



**Fig. 1** Chemical structure of VF-096.

### Polymerization

The polymerization of styrene monomer and VF-096, whose 10 hours half-life decomposition temperature was 96 °C, was performed in a 30 ml round-bottom reactor. The temperature of the reactor was controlled by a heater equipped with a magnetic stirrer (RCH-20L, EYELA). At first, the stirring was not operated because the particle morphologies were affected by the shear stress. The recipe for the polymerization employed here was shown in **Table 1**. The polymerization experiments were carried out as follows. Given amounts of pure

water and initiator were poured into the reactor, and heated to 96 °C for 30 minutes to make the state of VF-096 liquid using an electric heater, and styrene monomer was then added to start the polymerization.

**Table 1.** Experimental conditions of polymerization

Water [g]	15
Monomer [mmol/l]	640
Initiator [mmol/l]	23.7
Temperature [°C]	96

### Analysis

A small amount of solution was sampled from the reactor at the reaction time,  $t_i$ , and then a drop of solution was placed on the freshly cleaved mica plate. Then, the specimen was dried and coated with a thin osmium film by vapor deposition (Osmium Plasma Coater OPC60A, Filgen) and observed using a field emission scanning electron microcopy (JSM-7500FA, JEOL).

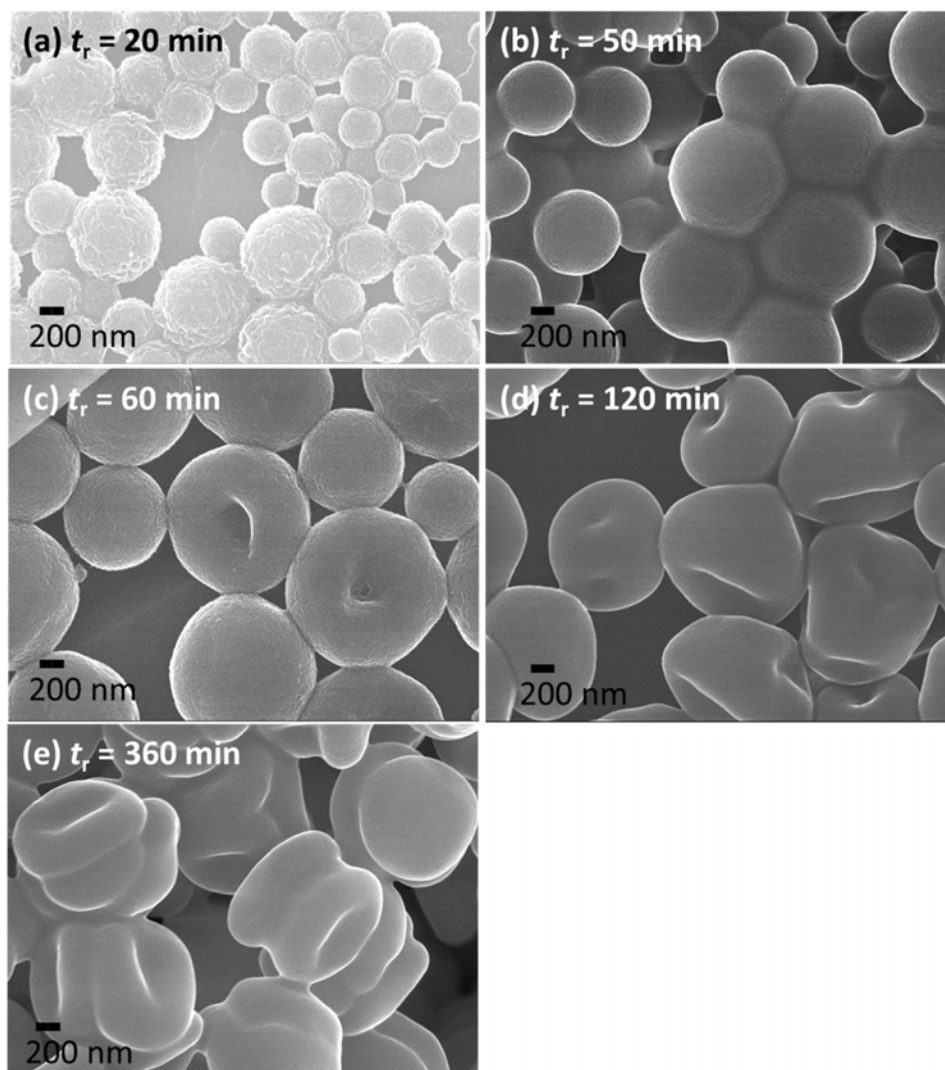
When observing the cross-section of the particles by FE-SEM, the sample powders obtained from the polymer colloid using a centrifugal separator (3700, KUBOTA) were embedded in the epoxy resin (AR-R30, Nichiban) and cut using the argon beam by Cross Section Polisher (IB-09020CP, JEOL), which was operated in the cooling condition by liquid nitrogen at the accelerating voltage of 4 kV for 30 h to prevent the thermal deformation of the sample.

The zeta potential of the particles in this diluted solution was measured using a Zetasizer (Nano-ZS, MALVERN Co., Ltd.) at a pH of ca. 7.0.

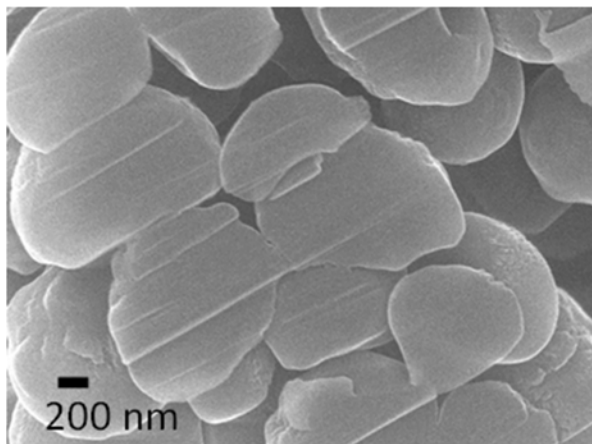
## Results and discussion

To investigate the change of the particle morphologies by the reaction time in the polymerization, the particles synthesized at each reaction time were observed by FE-SEM as show in **Fig. 2**. Spherical particles with some roughness was found at  $t_r = 20$  min. And, the particles grew with smoother surface at  $t_r = 50$  min. As the reaction time proceeded after  $t_r = 60$  min, the depressions were appeared in the particle surfaces and the number of depressions was increased. It was clear that particle morphology changed from sphere to anomalous.

Especially, to investigate inside structure of the particles at  $t_r = 360$  min by FE-SEM, cross-sections of the particles were observed by FE-SEM. The experimental result was shown in **Fig. 3**. The void was not found in the inner structures of the particles, which indicated that the depression was not originated from the absorption of the gas inside of the particles.



**Fig. 2** SEM images of the particles synthesized at each reaction time:  
(a)  $t_r = 20$  min; (b)  $t_r = 50$  min; (c)  $t_r = 60$  min; (d)  $t_r = 120$  min; (e)  $t_r = 360$  min.

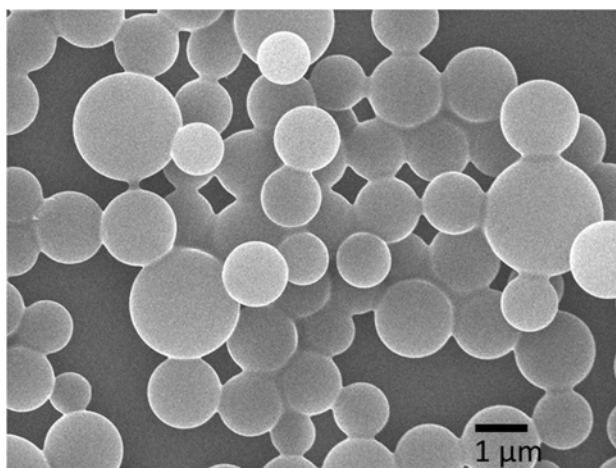


**Fig. 3** SEM image of cross-section of the particles synthesized at  $t_r= 360$  min.

From the previous works, the depression would be attributed to the phase separation of the poor solvent, water in the case of our system, in the particles [13]. To make sure if this mechanism was applied to the present polymerization or not, good solvent for polystyrene, 0.01 mole of toluene (Wako Pure Chemical Industries), was added to the system before the addition of the styrene monomer. **Fig. 4** indicated the particles synthesized with toluene at  $t_r = 360$  min observed by FE-SEM. The spherical particles were obtained and the size was bigger than that of the particle without toluene. Toluene worked as good solvent for polystyrene and some of them stayed in the particle without the phase separation to keep the shape spherical because the part of the synthesized particles including the many solvents with low density was floated in the aqueous phase. From these experimental results, one of the origins of the depression of the particle was the phase separation of the water in the particle and release of it from inside of the particle to the bulk. Hence, there was no void inside of the particle. To keep water inside of the particle, cross-linkers were required to create three-



dimensional networks in the particle like gel particle [14,15]. Hence, VF-096 would work as a cross-linker in the particles.

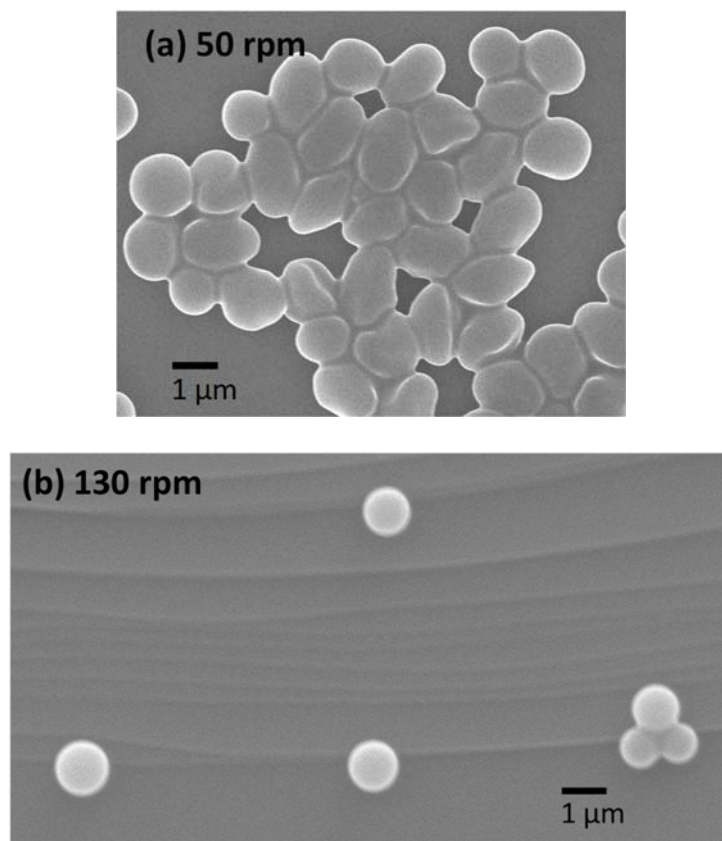


**Fig. 4** SEM image of the particles synthesized with toluene at  $t_r = 360$  min.

Finally, to investigate the influence of the shear stress by the stirring on the particle morphology, the polymerization according to **Table 1** was carried out with stirring by the magnetic stirrer (RCH-20L, EYELA). **Fig. 5** showed the SEM images of the particles at  $t_r = 360$  min changing the rotation of speed of stirrer. It was found that the particle shape was approaching to be spherical as the stirrer speed was increased. The shear stress by stirring would promote the diffusion of monomers from the monomer phase to the bulk and the polymerization reaction in the particle by much more supplied monomers. And, newly born tiny and swollen particles in the bulk adsorbed on the surface of larger particles [3], the shear stress would make the surface of the soft particle deformed to be stabilized in the water. Additionally, when the poor solvents were released from the particle, the shear stress would

also make the particle morphology approaching to be spherical by deforming. Thus, it was interesting that particle morphology was controllable by only stirring speed.

Furthermore, soap-free emulsion polymerization of styrene using VF-096 enabled to control the particle morphology and dispersion stability as shown in **Table 2** with the shear stress by stirring and concertation of VF-096. Stirring promote the diffusion and polymerization of styrene, which would be attributed to the negative charge of the anomalous particle, and the surface potential was enhanced. This was evidence for the copolymerization of styrene and VF-096 because the same tendency was observed in the copolymerization of styrene and methyl methacrylate by AIBN [16].



**Fig. 5** Effect of stirring speed on morphology of the particles at  $t_r=360$  min: (a) 50 rpm; (b) 130 rpm.

**Table 2.** Zeta potential of the synthesized particle at each concentration of VF-096 and stirring speed

VF-096 concentration	17.8 mM	23.7 mM
0 rpm	-8.2 mV	-4.5 mV
50 rpm	-29.8 mV	-26.0 mV

## Conclusions

In our conclusion, although the cross-linking reaction by VF-096 was not able to be confirmed in this study, it was found that the anomalous particles were able to be synthesized by soap-free emulsion polymerization of styrene using oil-soluble initiator, which indicated that this method was so simple using only two kinds of chemical materials in one batch system. Soap-free emulsion polymerization of styrene using VF-096 also enabled to control the particle morphology and dispersion stability with the shear stress by stirring.

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## References

1. Goodall, A. R., Wilkinson, M. C., & Hearn, J. (1977). Mechanism of Emulsion Polymerization of Styrene in Soap-Free Systems. [Article]. *J Polym Sci Pol Chem*, 15(9), 2193-2218, doi:DOI 10.1002/pol.1977.170150912.
2. Arai, M., Arai, K., & Saito, S. (1979). POLYMER PARTICLE FORMATION IN SOAPLESS EMULSION POLYMERIZATION. [Article]. *J Polym Sci Pol Chem*, 17(11), 3655-3665, doi:10.1002/pol.1979.170171121.
3. Yamamoto, T., Nakayama, M., Kanda, Y., & Higashitani, K. (2006). Growth mechanism of soap-free polymerization of styrene investigated by AFM. *J Colloid Interface Sci*, 297(1), 112-121, doi:10.1016/j.jcis.2005.10.025.
4. Cox, R. A., Wilkinson, M. C., Creasey, J. M., Goodall, A. R., & Hearn, J. (1977). Study of the anomalous particles formed during the surfactant-free emulsion polymerization of styrene. *Journal of Polymer Science: Polymer Chemistry Edition*, 15(10), 2311-2319, doi:10.1002/pol.1977.170151003.
5. Yamamoto, T. (2012). Synthesis of micron-sized polymeric particles in soap-free emulsion polymerization using oil-soluble initiators and electrolytes. [Article]. *Colloid Polym Sci*, 290(11), 1023-1031, doi:DOI 10.1007/s00396-012-2618-x.
6. Yamamoto, T. (2012). Soap-free emulsion polymerization of aromatic vinyl monomer using AIBN. [Article]. *Colloid Polym Sci*, 290(17), 1833-1835, doi:DOI 10.1007/s00396-012-2807-7.
7. Yamamoto, T. (2015). Effect of the Amount of  $\pi$  Electrons in Aromatic Monomer on the Surface Potential of Polymeric Particles Obtained through Soap-free Emulsion Polymerization Using AIBN. *Chemistry Letters*, 44(11), 1555-1556, doi:10.1246/cl.150759.
8. Nagao, D., Ohta, T., Ishii, H., Imhof, A., & Konno, M. (2012). Novel mini-reactor of silicone oil droplets for synthesis of morphology-controlled polymer particles. *Langmuir*, 28(51), 17642-17646, doi:10.1021/la304348g.
9. Du, Y.-Z., Tomohiro, T., & Kodaka, M. (2004). Synthesis of Hemispherical Poly(2-hydroxyethyl methacrylate-co-methyl methacrylate)/Poly(styrene-co-glycidyl methacrylate) Composite Particles with Heterobifunctional Groups by Soap-Free Seeded Emulsion Polymerization. *Macromolecules*, 37(3), 803-812, doi:10.1021/ma030424o.
10. Chen, Y. C., Dimonie, V., & El-Aasser, M. S. (1991). Effect of interfacial phenomena on the development of particle morphology in a polymer latex system. *Macromolecules*, 24(13), 3779-3787, doi:10.1021/ma00013a007.
11. Li, W.-H., & Stver, H. D. H. (1998). Porous monodisperse poly(divinylbenzene) microspheres by precipitation polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, 36(10), 1543-1551, doi:10.1002/(SICI)1099-0518(19980730)36:10<1543::AID-POLA7>3.0.CO;2-R.
12. Song, J.-S., & Winnik, M. A. (2005). Cross-Linked, Monodisperse, Micron-Sized Polystyrene Particles by Two-Stage Dispersion Polymerization. *Macromolecules*, 38(20), 8300-8307, doi:10.1021/ma050992z.
13. Sundberg, D. C., Casassa, A. P., Pantazopoulos, J., Muscato, M. R., Kronberg, B., & Berg, J. (1990). Morphology development of polymeric microparticles in aqueous dispersions. I. Thermodynamic considerations. *Journal of Applied Polymer Science*, 41(78), 1425-1442, doi:10.1002/app.1990.070410706.

14. Zhang, X.-Z., & Zhuo, R.-X. (2000). Novel synthesis of temperature-sensitive poly(N-isopropylacrylamide) hydrogel with fast deswelling rate. *Eur Polym J*, 36(3), 643-645, doi:10.1016/S0014-3057(99)00089-0.
15. Zhang, X.-Z., & Zhuo, R.-X. (2001). Dynamic Properties of Temperature-Sensitive Poly(N-isopropylacrylamide) Gel Cross-Linked through Siloxane Linkage. *Langmuir*, 17(1), 12-16, doi:10.1021/la000170p.
16. Yamamoto, T., & Kawaguchi, K. (2015). Effect of electrolyte species on size of particle through soap-free emulsion polymerization of styrene using AIBN and electrolyte. *Colloid Polym Sci*, 293(3), 1003-1006, doi:10.1007/s00396-015-3511-1.