Size Control of Polymeric Particle in Soap-Free Emulsion Polymerization†

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Abstract
The process of synthesis of polymeric particle in soap-free system was observed in-situ on the molecular scale by using an atomic force microscope (AFM). Using cationic water-soluble initiators enabled all of the polymeric materials to be adsorbed on the mica surface electrostatically. This adsorption technique of polymeric materials in the bulk obtained the AFM images of them throughout the reaction and to discuss the real growth mechanism of polymeric particles. The followings are found; the polymeric materials are continuously generated in the bulk throughout the reaction; and they make a contribution to the particle growth. Furthermore, soap-free emulsion polymerization (SFEP) of aromatic vinyl monomer using oil-soluble initiators was studied to synthesize micron-sized particles. Oil-soluble initiator, such as AIBN, worked like a water-soluble initiator in SFEP to prepare monodispersed particles with negative charges, probably because of the pi electron cloud of phenyl ring in a monomer. The addition of an electrolyte enabled secondary particles in the bulk to enhance hetero-coagulation rate for particle growth. Changing the concentration and valence of electrolyte enabled us to control the size in SFEP using AIBN. These methods enabled reaction time to be reduced for the synthesis of micron-sized polymeric particles in soap-free system.

Keywords: soap-free emulsion polymerization (SFEP), AFM, initiator, electrolyte, size control, coagulation

1. Introduction
Polymeric particles are widely used as materials for the making the functional products in many industries, such as toner particles, medicines, cosmetics, and so on (Svec F. and Frechet J.M.J., 1996). Emulsion polymerization is one of the most popular and typical methods in the polymerization for synthesis of the polymeric particles. However, the polydisperse particles were prepared. Because the performance of the products depends on the uniformity of the raw materials, the development of the classification technique for particle size was indispensable for enhancement of the quality of the products (Yamamoto T. et al., 2009; Yamamoto T. et al., 2011; Yoshida H. et al., 2010). The low density of the polymeric particles prevented the precise classification from being successful. Although the soap-free emulsion polymerization (SFEP), where the surfactants were not utilized, was synthesis method for sub-micron polymeric particles with small standard deviation of the size (Arai M. et al., 1979; Goodall A.R. et al., 1977), it was difficult to make the micron-sized particles by this method. The micron-sized particles have generally been synthesized by dispersion polymerization using organic solvents and stabilizers (Kawaguchi H., 2000; Lok K.P. and Ober C.K., 1985; Song J.S. et al., 2006; Tseng C.M. et al., 1986; Ugelstad J. et al., 1992). Recently, using 2,2’-azobis(N-(2-carboxyethyl)-2-2-methylpropionami dine) hydrate as a water-soluble initiator in SFEP enabled to synthesize micron-sized polymeric particles (Gu S. et al., 2004; Gu S.C. et al., 2002; Yamada Y. et al., 2005). Thus, the size of polymeric particle was controlled by the various polymerization methods.

Because it was too difficult to observe the synthesis process of particle directly with molecular scale (Hergeth W.-D. et al., 1992; Shouldice G.T.D. et al., 1995), the growth mechanism in the polymerizations was discussed by many studies using the macroscopic data, such as the change of particle number concentration with reaction time, the mass balance, the measurement of particle size using an electron microscopy (Feeney P.J. et al., 1984; Fitch R.M., 1997; Harkins W.D., 1947; Smith W.V., 1948; Song Z.Q. and Poehlein G.W., 1989). These macroscopic data give us some fundamentals to estimate the macro-
scopic mechanism, but were not enough to make the real growth mechanism clarified with molecular scale. Hence, we still did not know the role of polymeric materials remained in the bulk solution, such as oligomers. However, in 2003, a single polymer were able to be observed in-situ by atomic force microscope (AFM) (Arita T. et al., 2003; Arita T. et al., 2004). That was to say that the direct observation of the growth process of polymer particle would be possible. In this paper, a SFEP of styrene in water was studied on the molecular scale by using an AFM to clarify the growth mechanism. A water-soluble cationic initiator was used for all the polymeric products to adsorbed on the negatively-charged mica surface electrostatically and for all the adsorbates to be observable directly by in-situ AFM method.

Furthermore, on the basis of the growth mechanism with molecular scale, the size of the polymeric particles in SFEP could be changed from sub-microns to microns. Hence, to investigate the effect of the solubility of initiator in water on particle size, 2,2'-azobis(2-methylpropionamidine) dihydrochloride (V-50) was used as a water-soluble initiator, 2,2'-azobis(2-methylpropionitrile) (AIABN), dimethyl 2,2'-azobis(2-methylpropionate) (V-601) and 2,2'-Azobis(2-methylbutyronitrile) (V-59) as an oil-soluble initiator in SFEP. AIBN, V-601, and V-59 (Yoshida E., 2010a, b) were dissolved slightly in water to change the number of radicals decomposed from the initiator in water and the generation rate of the particles in bulk. When using oil-soluble initiator for SFEP, the influence of the addition of the electrolytes, other monomer, and water-soluble initiator to the system on particle properties were also investigated.

Thus, this paper describes further two experimental results: 1) investigation of the preparation of polymeric particles through SFEP using an oil-soluble initiator, and 2) development of a synthesis technique for size control of polymeric particles through SFEP with an oil-soluble initiator.

2. Experimental

2.1 Materials

The water was purified using the Milli-Q purification system (Millipore), and, nitrogen gas was then bubbled into the water to remove the dissolved oxygen gas. A styrene monomer (Tokyo Chemical Industry) was washed with a 10% sodium hydroxide (Wako Pure Chemical) solution to remove the polymerization inhibitors, and was then purified by distillation under reduced pressure using a rotary evaporator (EYELA). 4-Fluorostyrene, 4-bromostyrene, 4-chlorostyrene, 2,3,4,5,6-pentafluorovinylbenzene, vinylcyclohexane, methyl methacrylate (MMA), and benzyl methacrylate (BMA) (Tokyo Chemical Industry), were also used, as received, as a monomer in SFEP by oil-soluble initiator.

A water-soluble initiator, V-50 (Wako Pure Chemical), 4,4'-azobis(4-cyanovaleric acid) (V-501, Wako Pure Chemical), and a oil-soluble initiator, AIBN (Sigma Aldrich), V-601 (Wako Pure Chemical), V-59 (Wako Pure Chemical), were also used as radical initiators without further purification. They were monomers and azo compounds with chemical structures as shown in Fig. 1. AIBN, V-601, and V-59 do not dissolve in water as thoroughly as V-50, which was used as an initiator in emulsion polymerization (Qiu J. et al., 1999), as shown in Table 1. Therefore, they are not generally used as initiators for SFEP. In this study, the solubility of the initiator in water is an important factor to control the generation rate of secondary particles in bulk for size control of polymeric particle, hence these three initiators were used as radical initiators for the SFEP of styrene.

Potassium chloride, anhydrous calcium chloride (Katayama Chemical), and anhydrous aluminum chloride (Kishida Chemical) were used as electrolytes without further purification to promote the coagulation for the particle growth.

![Fig. 1 Chemical structure of the following monomers and initiators: (a) MMA; (b) BMA; (c) V-50; (d) AIBN; (e) V-601; (f) V-59; (g) V-501.](image-url)


2.2 Polymerization reaction

For the observations of the growth processes by AFM, the SFEP of styrene was carried out in a reactor of 500 mL with four necks for stirring mechanically with a Teflon turbine blade, purging the nitrogen gas, condensing the reflux with cold water, and sampling an aliquot of the solution with a pipette. The temperature of the reactor was controlled with a water bath. The experimental conditions of SFEP of styrene employed are listed in Table 1. The polymerization reactions were performed as follows. First, a given amount of pure water was poured into the reactor under nitrogen atmosphere, and heated up to a given temperature, agitating with the impeller speed of 180 rpm. Secondary, styrene monomer was added in the reactor after the temperature and agitation were settled. At last, a solution with water and V-50 was added for starting the reaction.

For size control of polymeric particle, the SFEP of various monomers using mainly oil-soluble initiator was carried out in a 30 mL reactor. The rotation speed of the impeller in the reactor and temperature of the reactor were controlled by a heater equipped with a magnetic stirrer (EYELA, RCH-20L). The experimental conditions for the polymerization employed are listed in Table 2. Similarly, as the above paragraph, the polymerization reactions were examined as follows. Given amounts of pure water, initiators, and electrolytes, whose concentration was defined as $C_i$, were poured into the reactor, and monomer was then added. The reactor was agitated with a 130 rpm impeller by a magnetic stirrer, where the surface between the water and monomer phases was not disturbed to prevent the formation and solidification of any monomer droplets with the dissolved oil-soluble initiators. And then, the reactor was heated up to 70 °C by an electric heater. About setting the monomer concentration in the polymerization, when the concentrations of styrene and aluminum chloride were 640 mmol/L and 0.07 mmol/L, respectively, 89.5 wt% of the monomers were not consumed to form the particles and were solidified by AIBN to obtain the polymeric plate. Thus, the monomer concentration was determined to be 64 mmol/L. Because the synthesized particles did not exhibit good dispersion stability at a reaction time, $t_r > 420$ min after starting polymerization with electrolytes, the longest reaction time was 360 min.

2.3 In-situ observation by atomic force microscopy

Observation of the in-situ molecular-scale images of all the material transferred on the mica surface was examined by the atomic force microscope (AFM), a Nanoscope III (Digital Instruments). Samples were prepared as follows. A drop of the solution was taken from the reactor at $t_r$ and then cast on the mica surface in water, such that cationic polymers synthesized by V-50 initiator were adsorbed on the mica surface with negative charges electrostatically (Hahn J. and Webber S.E., 2004). After setting the mica plate to the AFM liquid cell, the excessive polymeric materials were removed by injection of pure water into the cell to terminate the reaction.

Three dimensional and height images of polymeric products adsorbed on the mica surface were obtained by the tapping-mode procedure. The in-situ interaction forces between the AFM probe tip and surface of polystyrene particle fixed on the mica surface were measured following the contact-mode procedure, where the cantilever with a spring constant of 0.58 N/m was used. All the experiments using AFM were examined at the room temperature of 25 ± 2 °C.

### Table 1

<table>
<thead>
<tr>
<th>Solubility in water [wt%]</th>
<th>V-50</th>
<th>AIBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.2</td>
<td>0.04 x 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>120°C</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>Constant rate of decomposing [s^{-1}]</td>
<td>4.0 x 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>(toluene at 70°C)</td>
<td>(toluene at 70°C)</td>
<td></td>
</tr>
<tr>
<td>1.2 x 10^{-4}</td>
<td>6.0 x 10^{-5}</td>
<td></td>
</tr>
<tr>
<td>(toluene at 70°C)</td>
<td>(toluene at 70°C)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Initiator</th>
<th>Electrolyte</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-50</td>
<td>mmol/L</td>
<td>mmol/L</td>
<td>mmol/L</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>70</td>
</tr>
<tr>
<td>water-insoluble</td>
<td>soluble in hot water</td>
<td></td>
<td></td>
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</tbody>
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### Table 2

<table>
<thead>
<tr>
<th>Water [g]</th>
<th>Styrene [g]</th>
<th>V-50 [g/10g-water]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>5.88</td>
<td>0.186</td>
<td>70</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Water [g]</th>
<th>Monomer [mmol/L]</th>
<th>Initiator [mmol/L]</th>
<th>Electrolyte [mmol/L]</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>64</td>
<td>2.03</td>
<td>0~7</td>
<td>70</td>
</tr>
</tbody>
</table>
2.4 Measurement of size and zeta potential of particle

The field emission scanning electron microscope (FE-SEM) (JSM-6340FS, JEOL, S-5200, Hitachi High-Technologies) was operated to determine the particle size. The samples were prepared as follows; a small amount of solution was taken from the reactor at \( t_r \) and then a drop of the solution cast on the freshly cleaved mica plate. The specimen was dried, and then covered with a thin platinum or osmium film using the chemical vapor deposition method (E-1030, Hitachi High-Technologies, Osmium Plasma Coater OPC60A, Filgen). The number-averaged particle size, \( D_p \), was calculated using averaging the data from 200 to 1000 particles in SEM photographs. The coefficient of variation of the particle size distribution, \( C_v \), was then calculated using \( D_p \) and standard deviation (Gu S. et al., 2004).

The ZETASIZER (ZETASIZER 2000, MALVERN Co., Ltd.) was used to evaluate the surface potential of the synthesized particles. The sample of polymer colloid was diluted with the deionized water at a pH of ca. 7.5.

3. Results and discussion

3.1 Growth curve at reaction temperature 70 °C and observation of particle growth by AFM

The growth curve of PSL particles prepared by SFEP using V-50 is shown in Fig. 2. Because it was found that particle continued to grow at least up to \( t_r = 300 \) min, the polymeric products at \( t_r < 300 \) min was observed by AFM to clarify the growth mechanism.

Fig. 3a shows the three-dimensional AFM image of particle at \( t_r = 100 \) min. Fig. 3b shows the interactions between the AFM probe tip and the top of particle surface. It was found that the AFM images of particle tops were very smooth at \( t_r = 100 \) min as shown in Fig. 3a. The features obtained from these data showed that (A) particles were formed by the hard core covered with the soft shell composed of polymeric materials, such as monomers for swelling, oligomers, embryos, and nuclei, and (B) the thickness of the soft shell was measured to be ca. 4 nm at \( t_r = 100 \) min as the yellow area drawn in Fig. 3b indicated.

To study what kind of molecular-scale polymeric products existing in the bulk, the polymeric materials at \( t_r = 100 \) min adsorbed on the mica surface were observed by in-situ AFM. Fig. 4 showed that a lot of non-spherical nanoparticulates were observed, and the average height of the nanoparticulates at \( t_r = 150 \) min coincided approximately with the surface roughness of the particle as shown in Fig. 5. From these observations, it was found that polymeric particulates generated continuously in the bulk solution during the polymerization reaction. As far as the monomers and initiator radicals existed in the bulk, the nucleation of particles always occurred throughout this process. The above results indicated that the deposition of the polymeric materials formed in the bulk on the particle surface as well as the growth by swelling mono-
mers resulted in the rapid growth of particles around $t_r = 150$ min. This was confirmed by the fact that the particle surface had some roughness as indicated by Fig. 5. As far as the most of monomers were remained in the bulk at the beginning of the reaction, the deposition of nano polymeric materials and swelling by monomers would be occurred simultaneously. That was why particles grew with a smooth and soft shell surface as shown in Fig. 3. However, when the most of monomers was consumed, the thickness of the soft shell became thin and the deposited polymeric materials kept their shape as they were, because the amount of monomers in the bulk was too small to make deposited polymers dissolved, as shown in Fig. 5 (Yamamoto T. et al., 2005; Yamamoto T. et al., 2004).

### 3.2 Growth mechanism of polystyrene particles and control of particle size with water-soluble initiator concentration

We summarized the experimental results obtained so far and proposed the molecular-scale growth mechanism for particles in SFEP of styrene by V-50, as shown in Fig. 6 (Yamamoto T. and Higashitani K., 2007; Yamamoto T. et al., 2006a; Yamamoto T. et al., 2006b). When the growth of particles was not observed in terms of the growth plot, the particle surface did not become smooth. Although the polymeric materials still remained in the bulk, they could not make a contribution to the particle growth probably because hydrophobic interaction between the surfaces of particles swollen by monomers in the bulk did not work.

Herein, about the size control of polystyrene particle, the effect of the initiator concentration on the particle size was discussed. Assuming that the final particle size be-

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**Fig. 4** AFM image of polymeric materials at $t_r = 150$ min.

**Fig. 5** AFM image of particle top at $t_r = 150$ min.

**Fig. 6** Schematic representation of particle growth mechanism in SFEP by water-soluble initiator.
came smaller with initiator concentration increasing has been accepted widely in many processes of particle formation. LaMer diagram (Lamer V.K. and Dinegar R.H., 1950) indicated that the nucleation had to be terminated within the period of particle formation to prepare particles with uniform size. On the other hand, it was well known that the final size of particles became larger as initiator concentration increased in the case of SFEP of styrene. This tendency was reverse to the above description and was also obtained in our experiments, as shown in Fig. 7.

The experimental data in this study explained the reason for this reverse tendency. As discussed so far, the nucleation occurred in the bulk throughout the polymerization reaction. However, the total number of particles was determined at least the end of the nucleation period, where the particle growth was so rapid because of the absorption of monomers from the bulk and the simultaneous coagulation among polymeric products. The size of growing particles became different from that of nuclei at this period. Therefore, the polymeric materials nucleated secondary adsorbed on the surface of larger particles, rather than coagulated with each other, probably because the system would be stabilized by their adsorption according to the Ostwald-Ripening law (Wagner C., 1961). If this mechanism is true, almost all the polymeric materials synthesized after nucleation will make a contribution to the growth of particles. The number of the polymeric materials was enlarged with concentration of initiator increased. That was why the final particle size became larger as initiator concentration increased.

### 3.3 SFEP of aromatic vinyl monomer using AIBN

From here, the oil-soluble initiator was used in SFEP replacing water-soluble initiator. Firstly, the polystyrene particle was prepared by SFEP using oil-soluble initiator, AIBN. The polymerizations were performed under the conditions listed in Table 3, without electrolytes. The monodispersed particles with a diameter of 340 nm and a zeta potential of −44.8 mV were prepared as shown in Fig. 8a and Table 4 (Yamamoto T., 2012). The surface potential was so negative that the polystyrene particles showed good dispersion stability after the polymerization. It was believed that, generally, the origin of charge of the particles synthesized by SFEP was the functional group decomposed from the initiator, such as sulfate group, to show good dispersed stability. Although the nitrile group, which was decomposed from AIBN, was electron-attractive functional group, it did not have such negative charges compared with the ionic functional group originated from a water-soluble initiator, such as potassium persulfate (Arai M. et al., 1979; Munro D. et al., 1979). Hence, to investigate why the synthesized polystyrene particles by AIBN were charged negatively in water, the influence of the pi electron cloud of the aromatic vinyl monomer on surface properties of the particle synthesized through SFEP was studied changing kind of monomer for

![Fig. 7](image1)

**Fig. 7** Influence of V-50 concentration on particle size.

![Table 4](image2)

**Table 4** Zeta potential of the particles and particle size measured by FE-SEM in SFEP using aromatic vinyl monomer and AIBN at $C_e = 0$.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Zeta potential [mV]</th>
<th>Particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>−44.8</td>
<td>340</td>
</tr>
<tr>
<td>MMA</td>
<td>0.00</td>
<td>1000</td>
</tr>
<tr>
<td>BMA</td>
<td>−38.8</td>
<td>900</td>
</tr>
</tbody>
</table>

![Fig. 8](image3)

**Fig. 8** FE-SEM photographs of polymeric particles prepared by AIBN with the following monomers at $t_r = 360$ min: (a) styrene; (b) MMA; (c) BMA. When vinylicyclohexane was used as a monomer, the particle was not synthesized.
the SFEP using AIBN.

Secondary, the SFEP of MMA using AIBN was examined according to the experimental recipes listed in Table 3. As the SEM image (Fig. 8b) showed, the synthesized particles were spherical and the average size was about 1.0 μm. However, the dispersion stability was unstable because of the low surface potential, therefore, the particles were coagulated with each other and sedimented soon after finishing the polymerization. Another methacrylic monomers, BMA, which included phenyl ring (Fig. 1b), were polymerized in SFEP replacing MMAs to improve the dispersion stability. SFEP of BMA with AIBN was examined according to the conditions listed in Table 3. As indicated in Fig. 8c and Table 4, the particles with a size of 0.90 μm and a zeta potential of −38.8 mV were synthesized under the same conditions. This zeta potential would be originated from pi electron cloud in BMA monomer (Yamamoto T., 2013).

Finally, 4-fluorostyrene, whose pi electron density in the phenyl ring was smaller compared with styrene monomer because the electron could be attracted by functional group of fluorine atom from the pi electron cloud on the phenyl ring, was applied to the system of SFEP by AIBN as a monomer. 4-Bromostyrene, or 4-chlorostyrene was also selected as a monomer in the polymerization for the same reason. In addition, 2,3,4,5,6-pentafluorovinylbenzene, whose pi electron density on the phenyl ring was much smaller because the five fluorine atoms on the phenyl ring attracted pi electron, and vinylcyclohexane, which did not have pi electron cloud, were chosen as a monomer for the SFEP. SFEP of these monomers were conducted by AIBN under the conditions listed in Table 3 at $C_e = 0$. When vinylcyclohexane was used as a monomer, the particles were not detected by FE-SEM. As summarized in Fig. 9, as the number of fluorine atoms on a phenyl ring increased or the electron negativity of the functional group was strengthened, the surface potential of the particle was reduced with its size larger because the electron density did not concentrate on phenyl ring but was delocalized more attracting from the fluorine atoms and the electron density in the phenyl ring became lower. Clearly, the electron density in phenyl ring in the monomer was related strongly with the zeta potential of the synthesized particle through SFEP by AIBN.

From these results, it was possible to think that the particles with good dispersion stability were not able to be synthesized in the SFEP using AIBN and monomer without the phenyl ring. That was to say the pi electron cloud of the phenyl ring in the monomer was one of the origins of the negative charge of the polystyrene particles. The present study made it clear that the electron density of the pi electron cloud in the aromatic monomer used in SFEP influenced the surface charge of the particles prepared with AIBN (Yamamoto T., 2015). Thus, change of the pi electron density on the phenyl ring in the monomer for SFEP by AIBN enabled the size of the particle to be controllable.

In this way, the polymeric particles were able to be synthesized even using oil-soluble initiator in SFEP. The advantage of using oil-soluble initiator in SFEP was that the ions were not generated in the bulk. In the case of ionic initiator with high water solubility, although the particles were charged by the initiator, the counter ions were in the bulk. Hence, the influence of the ions in the bulk on the experimental results did not need to be considered. The polymer colloid prepared through this method using oil-soluble initiator was appropriate for the fundamental research.

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**Fig. 9** Schematic representation for influence of the strength of the pi electron cloud of the aromatic vinyl monomer on negative charged particle for the SFEP using AIBN.
3.4 Size control by copolymerization in SFEP

In this section, the technique for controlling of particle size in SFEP was developed by changing the mole fraction of MMA in copolymerization of styrene and MMA without surfactant. At first, Fig. 10 shows the particle size or zeta potential as a function of the monomer mole fraction of MMA in the copolymerization of styrene and MMA using a typical initiator, V-50, under the conditions listed in Table 3 at \( C_e = 0 \). Particle size showed nearly constant with the mole fraction of MMA increased. The dispersion stability of the synthesized particles showed so stable, and the zeta potential exhibited no dependency on the mole fraction of MMA. Positive value of zeta potential of the particles was originated from the functional groups of the V-50 water-soluble initiator and so high that the coagulation for the enlargement of particle size were not occurred. Hence, the size of particle became constant as the mole fraction of MMA increased.

In contrast, in the case of this copolymerization by AIBN, the dispersion stability of the synthesized particle depended on the monomer used in the copolymerization. Fig. 11 shows the effect on surface properties of the MMA monomer ratio to the total monomers for the copolymerization of MMA and styrene; the particle size increased with increasing mole fraction of MMA. The surface potential of the synthesized particles became smaller with the mole fraction of MMA increasing because the proportion of phenyl rings in the particle, which was attribute to the styrene monomers and would be the origin of the negative charge, decreased. Hence, coagulation between particles during the copolymerization was promoted for size enlargement as the ratio of MMA increased (Yamamoto T. and Kawaguchi K., 2016).

![Fig. 10 Particle size or zeta potential as a function of the monomer mole fraction of MMA for the soap-free emulsion copolymerization of MMA and styrene by V-50.](image)

![Fig. 11 Particle size or zeta potential as a function of the monomer mole fraction of MMA for the soap-free emulsion copolymerization of MMA and styrene by AIBN.](image)

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Zeta potential [mV]</th>
<th>Particle size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-50</td>
<td>53.4</td>
<td>160</td>
</tr>
<tr>
<td>AIBN</td>
<td>-44.8</td>
<td>340</td>
</tr>
<tr>
<td>V-601</td>
<td>-47.9</td>
<td>310</td>
</tr>
<tr>
<td>V-59</td>
<td>-41.5</td>
<td>460</td>
</tr>
</tbody>
</table>

3.5 SFEP of styrene with various oil-soluble initiators

To study the influence of oil-soluble initiator on particle properties; zeta potential and particle size, in the SFEP of styrene, V-601 or V-59 was used as an initiator according to the recipe as listed in Table 3 at \( C_e = 0 \). The experimental data are summarized in Table 5. Each polymeric particle showed the dispersion stable at \( t_i > 360 \text{ min} \) because of high surface potential.

The atoms of nitrogen and oxygen in negatively polarized were included in V-59 and V-601, respectively. Thus, they also could function like AIBN initiator. We thought that the AIBN was more hydrophilic than V-59 because V-59 obtained two more hydrophobic groups, CH₂, than AIBN to prepare more hydrophobic particle and its size became larger for the coagulation. In the case of the SFEP using V-601, the electron more can be attracted by the functional group of the decomposed initiator, carbonyl group, from the pi electron cloud on the phenyl ring in styrene monomer because the electronegativity of oxygen atom was higher than those of atoms composed of the initiators. Hence, the surface potential of the particles by...
The highest in Table 5 to synthesize the smallest particle among oil-soluble initiators in the present research. These experimental data suggested that the surface properties of the particle prepared through SFEP with oil-soluble initiator were controlled by electronegativity of the component atoms of the initiator.

These experimental data showed one of the reasons why the particles with negative charge was synthesized in SFEP even using AIBN, although it was not clarified completely yet. In addition, the functional group decomposed from the oil-soluble initiator or changing the electron density of the phenyl ring by substituent group of the monomer was related qualitatively. Hence, it was found that the pi electron cloud on the phenyl ring in the monomer was related strongly with negative value of zeta potential of the polystyrene particle prepared through SFEP with AIBN.

3.6 Size control by electrolyte in SFEP

On the basis of the above experimental data, discussion, and proposed growth mechanism, oil-soluble initiator enabled the surface potential of the synthesized particles to be smaller and the coagulation to be occurred easily during growth process to make the size enlarged. To study the influence of cationic ion on particle size, SFEP of styrene with potassium chloride, calcium chloride, or aluminum chloride at $C_e = 0.7 \text{ mmol/L}$ was performed for 360 min using AIBN by the experimental recipes listed in Table 3. Fig. 12 shows the FE-SEM photographs of the synthesized polystyrene particles. It was found that the sizes became larger with the help of electrolyte compared with Fig. 8a. The addition of an electrolyte helped to reduce the surface potential and the electrical double layer by counter ions against the charge of the particles, as DLVO theory indicated (Verwey E.J.W. and Overbeek J.T.G., 1948), hence, the surface potentials were reduced. Repulsive interactions between the particles formed in the bulk were weakened, and coagulations between the particles occurred easily, so the size of the particle became larger according to our proposed growth model (Yamamoto T. and Kawaguchi K., 2015; Yamamoto T. et al., 2006b; Yamamoto T. and Yokoyama T., 2015). As Schulze-Hardy rule indicated (Overbeek J.T.G., 1980), the coagulating effect was larger at the same concentration of electrolyte with increasing the valence of the ion (Verwey E.J.W. and Overbeek J.T.G., 1948). Here, as divalent or trivalent electrolytes, calcium chloride or aluminum chloride was applied to the SFEP to research the coagulation effect on particle growth. FE-SEM images in Figs. 12b and c show the particles synthesized at $t_r = 360 \text{ min}$ by SFEP with calcium chloride and aluminum chloride, respectively, under the condition of $C_e = 0.7 \text{ mmol/L}$. The size of the particles prepared with calcium and aluminum chlorides became enlarged compared with those prepared with potassium chloride, compared with Fig. 12a. Particles with a number-averaged size of 2.17 μm and a $C_v$ of 11.1% were able to be synthesized even at $t_r = 360 \text{ min}$, by the addition of aluminum chloride as shown in Fig. 12c. These data showed that the size of particle was larger with the valence of electrolyte increasing, which agreed with the DLVO theory from the point of the coagulation.

Similarly, the previous research showed that an electrolyte, such as sodium chloride, helped the silica particle size to be enlarged (Nakabayashi H. et al., 2010). The coagulation process controlled by the solubility of the initiator and the electrolyte concentration in the aqueous phase played an important role to make micron-sized particles in SFEP.

Fig. 13 shows the influence of the concentration of potassium chloride on size of the particle synthesized by SFEP with AIBN for 360 min changing the concentration of potassium chloride from 0.007 mmol/L to 7 mmol/L, under the experimental conditions in Table 3. It was found that the particle size became larger with the concentration increasing. When the concentration of potassium chloride was at $C_e = 7 \text{ mmol/L}$, a number-averaged size and $C_v$ of the synthesized particles were 2.04 μm and 5.4%, respectively. This experimental data showed that the reaction time for making micron-sized monodispersed particles in a one-batch system was reduced. Thus, in the system of SFEP of styrene using AIBN, controlling the size of the polystyrene particles size was achieved changing the valance of electrolyte and its concentration.

![Fig. 12](Image) Effect of the following electrolyte at the concentration of 0.7 mmol/L on particle size through SFEP of styrene using AIBN. (a) KCl ($D_p = 0.97 \mu m$); (b) CaCl$_2$ ($D_p = 1.04 \mu m$); (c) AlCl$_3$ ($D_p = 2.17 \mu m$).
The amount of polymeric radicals at the beginning of the polymerization using AIBN was much smaller than that of V-50 because both the decomposition rate and water solubility of AIBN were much smaller than those of V-50, as listed in Table 1. Hence, the number of particles at the beginning of the polymerization of AIBN was much smaller than that at the beginning of the polymerization of V-50, and the consumption rate of the monomer was smaller in the case of AIBN. This makes it possible to think that the size was smaller, \( D_p = 0.23 \mu m \), even when the electrolytes were added to the system by V-50 because the number concentration of final particles in the polymer colloid using V-50 was larger, and the period for particle growth was reduced. Secondary particles were formed continuously in the bulk and deposited on the large particle surface to make a contribution to particle growth in both cases. However, the rate of generation of polymeric radicals in the case of SFEP by AIBN was so slower that particles continued to grow for a longer time and became larger. Also, the electrolyte in the system worked like a catalyst for promotion of the particle growth because secondary particles hetero-coagulations were occurred for the growth efficiently by reduction of the thickness of the electrical double layer, and prevented their self-growth.

This technique using an oil-soluble initiator and electrolyte for the preparation of micron-sized particles in water would be effective in the field of industry, because organic solvents and surfactants were not included in the system.

From these experimental results, it was possible to say that the cationic ion in electrolyte played an important role to control particle size in SFEP using oil-soluble initiator (Yamamoto T. and Kawaguchi K., 2015). Furthermore, nano particles with the size under 100 nm were successfully synthesized taking ionic radius of the counter ion in a water-soluble initiator into consideration (Yamamoto T. and Yokoyama T., 2015).

### 3.7 Size control using oil- and water-soluble initiators in SFEP

From the results obtained so far, oil-soluble initiators played the same role as typical initiator in the conventional SFEP. In this section, SFEP of styrene using both oil- and water-soluble initiators was examined. To study the effect of the concentration of V-501, \( C_i \), on particle properties, SFEPs of styrene were carried out changing \( C_i \) at the constant concentrations of styrene monomer and AIBN. The reason why V-501 was selected was that the particles were synthesized in the SFEP using water-soluble initiator with carboxyl groups at high pH because of ionized initiator radicals derived from the initiators (Gu S. et al., 2004; Moribe H. et al., 2011; Yamada Y. et al., 2005). It was confirmed that the particles were not able to be formed independently by V-501 in normal water. Hence, the polystyrene particles were synthesized by AIBN in this system. As shown in Fig. 14, the particle size became enlarged as \( C_i \) was increased because of the

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**Fig. 13** Influence of concentration of potassium chloride on particle size through SFEP of styrene using AIBN. (a) \( C_e = 0.007 \text{ mmol/L} \) (\( D_p = 0.78 \mu m \)); (b) \( C_e = 7 \text{ mmol/L} \) (\( D_p = 2.04 \mu m \)).

**Fig. 14** SEM images of polystyrene particles through SFEP using AIBN with V-501 at the following concentration: (a) \( C_i = 0.7 \text{ mmol/L} \) (\( D_p = 0.80 \mu m \)); (b) \( C_i = 1.4 \text{ mmol/L} \) (\( D_p = 0.86 \mu m \)); (c) \( C_i = 2.0 \text{ mmol/L} \) (\( D_p = 0.95 \mu m \)).
The molecular-scale investigation on the growth process of polystyrene particles in SFEP with a cationic and water-soluble initiator by in-situ AFM method gave us some followings at least qualitatively.

- Tiny polymeric particulates were generated in the bulk throughout the polymerization, and their deposition on the larger particle surface resulted in the particle growth.
- The particle size was increased with the water-soluble initiator increased according to our proposed growth mechanism through hetero coagulation.
- Even though the tiny polymeric particulates were in the bulk, the particle growth was not observed when the monomers were consumed. The roughness of the surface depended on the balance of the polymeric nano particulates and the amount of monomers dosed.

SFEPs of aromatic vinyl monomer using oil-soluble initiators were carried out to develop the technique for controlling particle size. Preparation of micron-sized polystyrene particles through SFEP using oil-soluble initiators with electrolytes or water-soluble initiator was achieved. The conclusions were as followings.

- When an oil soluble initiator, such as AIBN, V-59, and V-601, was used in SFEP of styrene, the initiator was dissolved a little in water and the monodispersed polymeric particles were prepared as the conventional SFEP. The monodispersed particles showed negative charges, which would be originated from the pi electron density of phenyl ring in styrene and the polarization of the functional groups decomposed from the oil-soluble initiators. Thus, even oil-soluble initiator was useful for SFEP assuming that the negative charges were given to the synthesized particles by aromatic vinyl monomer used in the polymerization and made a contribution to keeping their dispersion stability good.
- Surface charge and particle size were able to be controlled changing the pi electron density of aromatic vinyl monomer with functional groups.
- Addition of an electrolyte was an effective method for enlargement of particle size because the secondary particles formed in the bulk made an contribution to particle growth through hetero-coagulation by reduction of surface potential, and prevented their self-growth. The larger effect by this method was obtained in the case of the polymerization by an initiator with lower water solubility.
- The particle size became larger with the concentration of electrolyte increasing in SFEP with an oil-soluble initiator.
- At the same concentration of electrolyte for enlargement of particle size in SFEP, the coagulation for particle growth effect became larger with the valence of the electrolyte increasing.
- Particle size in SFEP of styrene using AIBN was controllable changing the valence of electrolyte and its concentration.
- When the copolymerization of styrene and MMA using AIBN in the soap-free system, the surface charge and particle size could be controlled changing the monomer fraction of MMA.
- In addition of a water-soluble initiator, V-501, to the system using AIBN, the particle size became larger due to the grow promotion through coagulation between particles because of the reduction of surface potential by weak acid of V-501 as the concentration of V-501 was increased and the polymerization was proceeded.

From the above conclusions, it was possible to say that the technique for control of size of the particle was developed through the polymerization in SFEP using electrolyte or initiators or combination of monomers with and without phenyl ring or water- and oil-soluble initiators.

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### Nomenclature

- $C_e$: concentration of electrolyte (mmol/L)
- $C_i$: concentration of V-501 (mmol/L)
- $D_p$: number-averaged particle size ($\mu$m)
- $h$: distance between surfaces (nm)
- $F$: force (nN)
- $t_r$: reaction time (min)
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Author's short biography

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Tetsuya Yamamoto is an Associate Professor of the Department of Materials Innovation Design Engineering, Nagoya University. After he received his Ph.D. from Department of Chemical Engineering, Kyoto University in 2005, he worked as an Assistant Professor, Hiroshima University from 2005 to 2014. He was also a guest researcher in Max Planck Institute for Polymer Research in 2012.

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Ko Higashitani graduated from Department of Chemical Engineering, Kyoto University, Japan in 1968. He worked on Viscoelastic Fluids as a Ph.D. student under the supervision of Prof. A.S. Lodge in Department of Chemical Engineering, University of Wisconsin-Madison, USA. After he received a Ph.D. degree in 1973, he joined Department of Applied Chemistry, Kyushu Institute of Technology, Japan, as a lecturer, and then became a professor in 1983. He moved to Department of Chemical Engineering, Kyoto University in 1992. He is now an Emeritus Professor, Kyoto University.

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