

# Size Control of Particle through Soap-Free Emulsion Polymerization of Styrene by Oil-Soluble Initiator Using Water-Soluble Initiator with Weak Acid

*AUTHOR NAME. Tetsuya Yamamoto\*, Kan Kawaguchi, Yuya Takahashi*

*AUTHOR ADDRESS. Department of Chemical Engineering, Nagoya University,*

*Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan*

AUTHOR EMAIL ADDRESS: ytetsuya@nuce.nagoya-u.ac.jp

**RECEIVED DATE**

TITLE RUNNING HEAD.

CORRESPONDING AUTHOR FOOTNOTE. Phone: +81-52-789-3378, Fax: +81-52-789-3271,

E-mail: ytetsuya@nuce.nagoya-u.ac.jp

## **Abstract**

The soap-free emulsion polymerization of styrene by oil-soluble initiator, 2,2'-azobis(2-methylpropionitrile) (AIBN), with water-soluble initiator, 4,4'-Azobis(4-cyanovaleric acid) (V-501), was carried out in water to control size of the synthesized polymeric particles. Particle size and surface potential were investigated changing the concentration of V-501 in the polymerization. As a result, the particle size was enlarged increasing the concentration of V-501 because V-501 was weak acid and helped the reduction of the surface potential to promote the particle growth through the coagulation. And also, V-501 could work as radical initiator and promote the polymerization reaction efficiently to improve the number concentration of particle.

*Keywords.* Soap-free Emulsion Polymerization, Size Control, Oil-Soluble Initiator, Water-Soluble Initiator

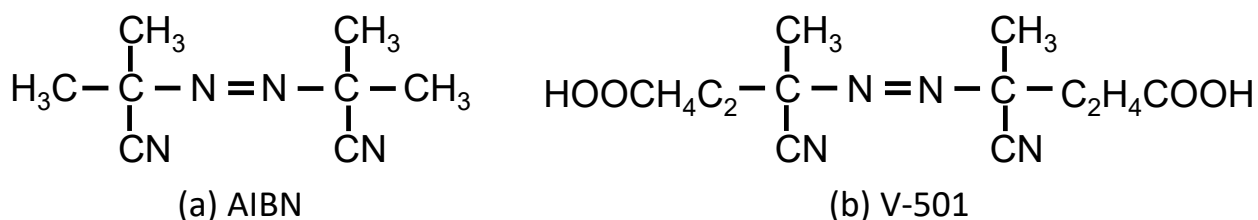
## 1. Introduction

Emulsion polymerization [1, 2] was generally used for preparation of polymeric particles with the minimum size of 33 nm [3, 4]. Particles were also able to be synthesized in water using surface active effect derived from the ionic water-soluble initiator in this method without surfactant [5, 6]. This environmental-friendly polymerization, soap-free emulsion polymerization, was suitable to prepare the particle with clean surface and the size was required up to micron-sized. For example, surfactant-free micron-sized particles, which were utilized as toner particles, would be easy for handling [7]. In our recent research, soap-free emulsion polymerization of aromatic vinyl monomers even using oil-soluble initiator in the aqueous phase was developed to prepare polymeric particles [8, 9]. The negative charges of the synthesized particles to show their good dispersion stabilities in water would be attributed to the phenyl ring in the monomer used in the polymerization [10, 11]. Addition of electrolyte to this system enabled the particle growth through coagulation to be promoted by reducing the thickness of electrical double layer. This method was efficient to make particle enlarged for short reaction time [8, 12]. Thus, surface potential of the particle was a very important factor to control the particle size [12-16]. On the other hand, in fact, only increasing the concentration of initiator enabled the particle size to be enlarged in the conventional soap-free emulsion polymerization of styrene using water-soluble initiator [5, 17]. In the case of using oil-soluble initiator in the soap-free emulsion polymerization, however, it was partially dissolved in the monomer phase to make the monomers solidified. Hence, increase of the concentration of oil-soluble initiator for making particle size larger could lead to waste the monomers by their solidification. Additionally, the electrolytes added to the system for controlling the particle size were remained in the bulk as impurities. In the present study, to prevent the solidification and impurities and increase of the number of initiator radicals in the bulk, the water-soluble initiator with weak acid, which was not dissolved in the monomer phase and contributed to the reduction of surface potential, was added to the system of soap-free emulsion polymerization of styrene by oil-soluble initiator to promote the particle growth.

## 2. Experimental

### 2.1 Materials

The water used in the soap-free emulsion polymerization was purified using a purification system (Auto Still WG250, Yamato), and nitrogen gas was then bubbled into the water to remove any dissolved oxygen. Styrene monomers (Tokyo Chemical Industry) were washed four times with a 10% sodium hydroxide solution to remove the polymerization inhibitors, and then purified by distillation under reduced pressure. 2,2'-azobis(2-methylpropionitrile) (AIBN, Sigma Aldrich Co. LLC.), which was well known as a typical oil-soluble initiator as shown in **Fig. 1a**, and 4,4'-Azobis(4-cyanovaleric acid) (V-501, Wako Pure Chemical Industries, Ltd.), which was water-soluble initiator with carboxyl groups as shown in **Fig. 1b**, were used in the polymerization without further purification. V-501, whose  $pK_a$  was 3.85, was weak acid. Acetic acid (Kanto Chemical Co.,INC.) was used as a weak acid to control the concentration of carboxyl group in the reactor to investigate the function of V-501 which included the carboxyl groups.



**Fig. 1.** Chemical structure of the following initiator: (a) AIBN; (b) V-501.

### 2.2 Polymerization reaction

The polymerization reaction was performed in a 30 mL round-bottom reactor. The temperature of the reactor and the rotation speed of the impeller in the reactor were controlled by a magnetic stirrer equipped with a heater (RCH-20L, EYELA). The recipe employed for the polymerization referred to the previous literature [8] is listed in Table 1. The reaction time was set to 6 hours.

**Table 1.** Experimental conditions of polymerization

Water [g]	15
Styrene [mmol/l]	64
Initiator of AIBN [mmol/l]	2.0
Initiator of V-501 [mmol/l]	<i>C</i>
Temperature [°C]	70
Rotation speed of impeller [rpm]	130

The polymerization experiments were carried out as follows. The given amounts of pure water, AIBN, and V-501 were poured into the reactor, and the monomers were then added. The reactor was sealed with a cap, and heated to 70 °C using an electric heater. The concentration of V-501 in the water was defined as *C*. The reaction mixture was agitated at 130 rpm with an impeller using a magnetic stirrer.

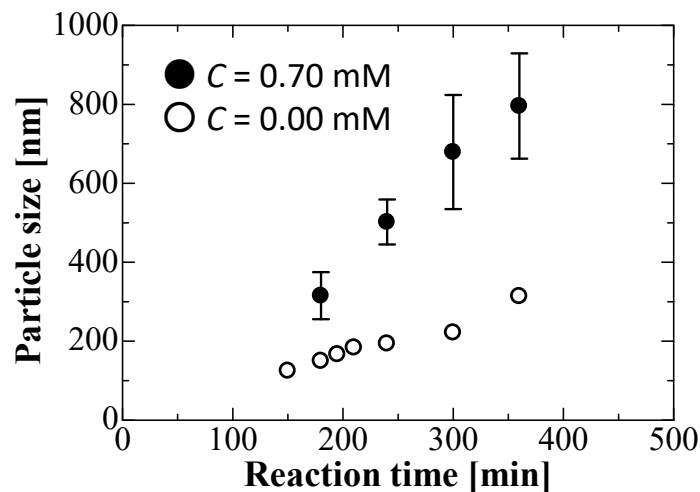
### 2.3 Characterization

The size of the synthesized particles was measured using field emission scanning electron microscopy (FE-SEM) (JSM-7500FA, JEOL). SEM samples were prepared as follows: a small amount of solution was sampled from the reactor, and a drop of the solution was then placed on a freshly cleaved mica plate. The specimen was dried, and then coated with a thin osmium oxide film using the chemical vapor deposition (CVD) method (Osmium Plasma Coater OPC60A, Filgen). The number-averaged particle size was calculated using averaging the data from more than 200 particles in SEM photographs. The zeta potential of the particle in the suspension was measured using a ZETASIZER Nano-ZS (MALVERN Co., Ltd.). The number concentration of particle in the suspension was measured using electric pulsed resistance method by a qNano (Izon Science Ltd.) [18].

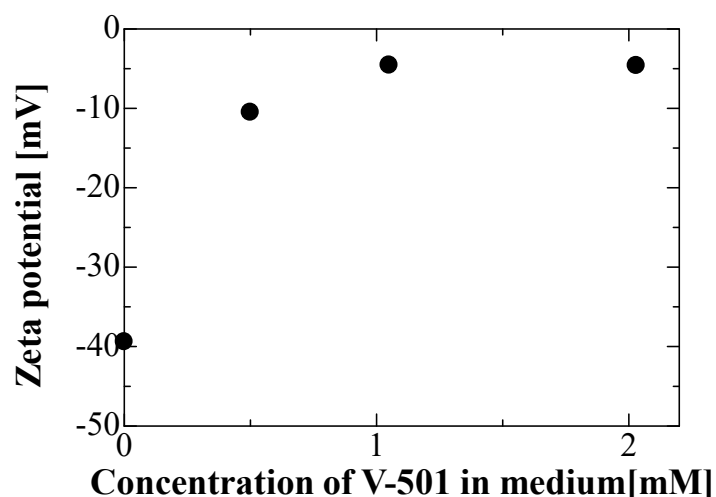
### 3. Results and discussion

#### 3.1 Promotion of particle growth with the help of V-501

Comparison of growth plots between  $C = 0.0$  and  $0.70$  mM was carried out as shown in **Fig. 2**. When using only AIBN, particle size was increased gradually. On the other hand, particle grew rapidly using both AIBN and V-501 as initiators. It was found that using V-501 enabled particle growth to be promoted. To clarify the reason of this increase of particle size by V-501, the zeta potential of the particle synthesized at  $C = 0.70$  mM was measured in the solution with various concentrations of V-501 by ZETASIZER. The influence of the concentration of V-501 in medium on zeta potential was shown in **Fig. 3**. Surface potential was reduced as the concentration of V-501 was increased and the pH showed between 3.56 and 4.05 by the measurement of pH meter (LAQUA F-74, Horiba). Particle coagulations were expected in their growth processes due to the decrease of their surface potentials because of low pH according to DLVO theory [19]. That was why the size became larger rapidly. This phenomenon was very similar with that using the soap-free emulsion polymerization of styrene by AIBN with help of electrolyte. V-501 could make surface potential reduced and played the same role as electrolyte in the polymerization of styrene using AIBN [8, 12].



**Fig. 2.** Growth plots of polystyrene particle using AIBN and V-501.

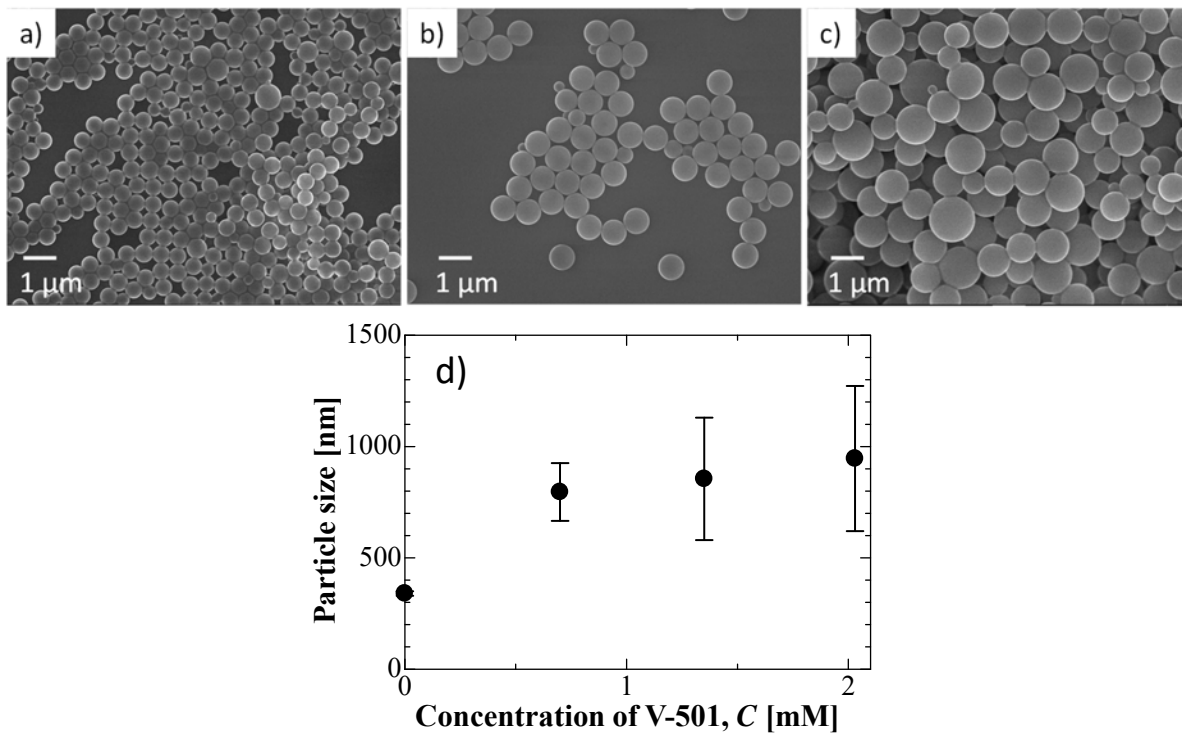


**Fig. 3.** Influence of concentration of V-501 in medium on zeta potential of polystyrene particle synthesized by AIBN at  $C = 0.70$  mM.

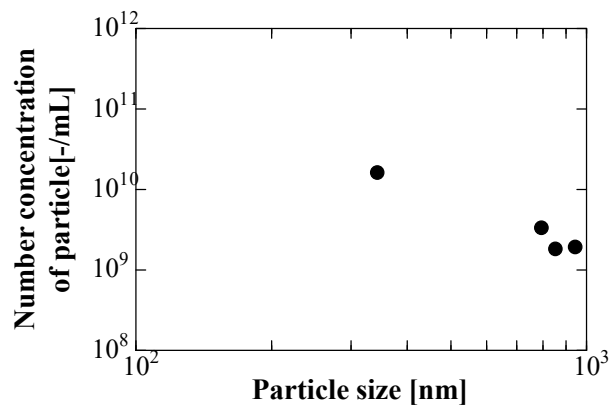
### 3.2 Effect of concentration of V-501 in the polymerization using AIBN on particle properties

To study the effect of the concentration of V-501,  $C$ , on particle properties, soap-free emulsion polymerizations of styrene were carried out changing  $C$  at the constant concentrations of AIBN and styrene monomer. The particle properties were evaluated using FE-SEM, q-Nano and ZETASIZER. As shown in **Fig. 4**, particle size was enlarged as  $C$  was increased because of the reduction of surface potential as shown in Fig. 3. Similarly, the particle size became larger through the hetero coagulation mechanism even increasing the concentration of initiator in the conventional soap-free emulsion polymerization of styrene by water-soluble initiator, such as 2,2'-azobis(2-methylpropionamide) dihydrochloride and potassium persulfate [5, 17, 20]. This kind of growth promotion by the addition of V-501 could also be explained by the hetero coagulation. There, tiny secondary particles generated from the bulk, the number of particles was increased as the radical initiators increased, made a contribution to particle growth adsorption of particle surface [17]. Increase of the concentration of oil-soluble initiator brought about the further solidification of the monomer phase. Hence, the addition of water-soluble initiator to the soap-free emulsion polymerization using oil-soluble initiator was effective for making the particle size enlarged. Furthermore, **Fig. 5** showed the relationship between the particle size and number concentration. It was clear that the number concentration of particle was decreased as the

particle size became larger according to the general coagulation theory. From these above experimental results, it was possible to think that particle grew rapidly through the coagulation between particles.



**Fig. 4.** Effect of concentration of V-501 in the polymerization using AIBN on particle size: a)  $C = 0.7$  mM; b)  $C = 1.4$  mM; c)  $C = 2.0$  mM; d) relationship between concentration of V-501 and particle size.



**Fig. 5.** Relationship between particle size and number concentration of particle in the polymerizations under various concentrations of V-501.

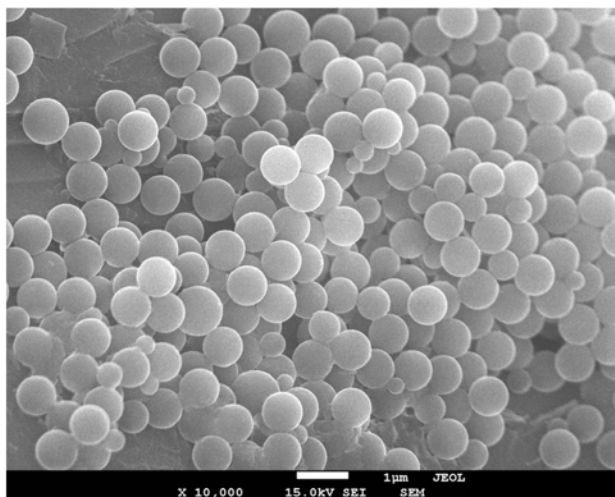
### 3.3 Effect of acetic acid on particle properties

To investigate the effect of radical initiator of V-501 on particle properties, the particle were synthesized by AIBN at the concentration of acetic acid, 1.4 mM, replacing of V-501, where the concentration of carboxyl group was the same as that of  $C = 0.70$  mM. **Fig. 6** shows SEM image of the

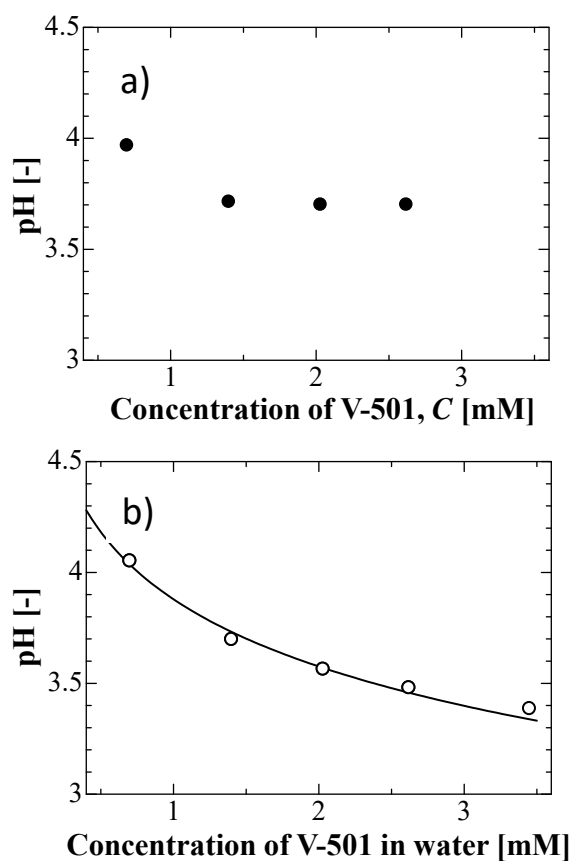


particles. It was found that the number averaged particle size was calculated to be 736 nm from SEM observations and the number concentration of particles was measured to be  $1.3 \times 10^7 \text{ mL}^{-1}$  by qNano. Low pH by acetic acid could make the particles coagulated with each other for their growth. In the case of  $C = 0.70 \text{ mM}$  in the polymerization by AIBN, the particle size and number concentration were 796 nm and  $1.8 \times 10^9 \text{ mL}^{-1}$ , respectively. Compared with these data, it was possible to say that V-501 could work as not only weak acid but also initiator and promote the polymerization reaction efficiently for increase of particle size and number. The pH of V-501 water solution and the synthesized polystyrene colloids prepared under the various concentrations of V-501 was measured by pH meter, as shown in **Fig. 7**. As  $C$  and the concentration of V-501 in water were increased, the pHs were decreased. However, the pH of the polymer colloids in **Fig. 7a** was not changed largely compared with that of V-501 water solution in **Fig. 7b**. These results indicated that V-501 was consumed for making particle in the polymerization and not remained in the bulk. This point was an advantage in the present synthesis method for controlling the size of the particle because all of chemicals were components of the synthesized particles.

The experimental results so far suggested that particle would be formed in the polymerization using only V-501 without AIBN. To investigate this possibility, the polymerizations by V-501 without AIBN were carried out in water. However, particle was hardly generated by V-501. In the previous works, the particles were synthesized in the soap-free emulsion polymerization using water-soluble initiator with carboxyl groups, such as V-501 and 2,2'-azobis[*N*-(2-carboxyethyl)-2-methylpropionamide]tetrahydrate, at high pH because of ionized initiator radicals derived from the initiators [14, 15, 21]. Hence, particles were not able to be formed by V-501 in normal water. AIBN had an indispensable role for the generation of particle in the present polymerization.



**Fig. 6.** SEM image of the particle synthesized by AIBN without V-501 under the condition of the concentration of acetic acid, 1.4 mM.



**Fig. 7.** pH of synthesized polymer colloid and V-501 water solution under the various V-501 concentrations: a) the effect of C on pH of the synthesized polymer colloid; b) the effect of concentration of V-501 on pH of water.

## Conclusions

To control particle size in the soap-free emulsion polymerization of styrene using oil-soluble initiator, water-soluble initiator, V-501, was added to the system. As the concentration of V-501 was increased, the particle size became larger due to the growth promotion through coagulation between particles because of the reduction of surface potential by weak acid of V-501. In the soap free emulsion polymerization of styrene using the ionic water-soluble initiator, particle size was generally enlarged with the increase of the initiator concentration. This growth mechanism could make a contribution to the enhancement of particle size and polymerization reaction. Hence, the number concentration of the particles synthesized by AIBN with the help of V-501 was improved as compared with the polymerization by only AIBN under the same concentration of carboxyl group derived from acetic acid.

### **Acknowledgement**

This study was financially supported in part by Scientific Research (C) from the Ministry of Education, Culture, Sports, Science and Technology of Japan, (No. 25420817).

### **References**

- [1] W.D. Harkins, A general theory of the mechanism of emulsion polymerization, *Journal of the American Chemical Society*, 69 (1947) 1428-1444.
- [2] W.V. Smith, The kinetics of styrene emulsion polymerization, *Journal of the American Chemical Society*, 70 (1948) 3695-3702.
- [3] H. Ishii, N. Kuwasaki, D. Nagao, M. Konno, Environmentally adaptable pathway to emulsion polymerization for monodisperse polymer nanoparticle synthesis, *Polymer*, 77 (2015) 64-69.
- [4] H. Ishii, M. Ishii, D. Nagao, M. Konno, Advanced synthesis for monodisperse polymer nanoparticles in aqueous media with sub-millimolar surfactants, *Polymer*, 55 (2014) 2772-2779.
- [5] A.R. Goodall, M.C. Wilkinson, J. Hearn, Mechanism of Emulsion Polymerization of Styrene in Soap-Free Systems, *J Polym Sci Pol Chem*, 15 (1977) 2193-2218.
- [6] M. Arai, K. Arai, S. Saito, POLYMER PARTICLE FORMATION IN SOAPLESS EMULSION POLYMERIZATION, *J Polym Sci Pol Chem*, 17 (1979) 3655-3665.
- [7] Y. Higashiyama, G.S.P. Castle, I.I. Inculet, J.D. Brown, The Effect of an Externally Added Charge Control Agent on Contact Charging between Polymers, *Journal of Electrostatics*, 30 (1993) 203-212.
- [8] T. Yamamoto, Synthesis of micron-sized polymeric particles in soap-free emulsion polymerization using oil-soluble initiators and electrolytes, *Colloid Polym Sci*, 290 (2012) 1023-1031.
- [9] T. Yamamoto, Synthesis of nearly micron-sized particles by soap-free emulsion polymerization of methacrylic monomer using an oil-soluble initiator, *Colloid Polym Sci*, 291 (2013) 2741-2744.
- [10] T. Yamamoto, Soap-free emulsion polymerization of aromatic vinyl monomer using AIBN, *Colloid Polym Sci*, 290 (2012) 1833-1835.

- [11] T. Yamamoto, 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 (2015) 1555-1556.
- [12] T. Yamamoto, K. Kawaguchi, Effect of electrolyte species on size of particle through soap-free emulsion polymerization of styrene using AIBN and electrolyte, *Colloid Polym Sci*, 293 (2015) 1003-1006.
- [13] S.C. Gu, S. Inukai, M. Konno, Preparation of monodisperse, micron-sized polystyrene particles with an amphoteric initiator in soapfree polymerization, *J. Chem. Eng. Jpn.*, 35 (2002) 977-981.
- [14] S. Gu, H. Akama, D. Nagao, Y. Kobayashi, M. Konno, Preparation of micrometer-sized poly(methyl methacrylate) particles with amphoteric initiator in aqueous media, *Langmuir*, 20 (2004) 7948-7951.
- [15] Y. Yamada, T. Sakamoto, S. Gu, M. Konno, Soap-free synthesis for producing highly monodisperse, micrometer-sized polystyrene particles up to 6 microm, *J Colloid Interface Sci*, 281 (2005) 249-252.
- [16] T. Yamamoto, K. Kawaguchi, Relationship between surface potential and particle size in soap-free emulsion copolymerization of styrene and methyl methacrylate using a water- or oil-soluble initiator, *Colloid Polym Sci*, (2015).
- [17] T. Yamamoto, M. Nakayama, Y. Kanda, K. Higashitani, Growth mechanism of soap-free polymerization of styrene investigated by AFM, *J Colloid Interface Sci*, 297 (2006) 112-121.
- [18] D. Kozak, W. Anderson, R. Vogel, S. Chen, F. Antaw, M. Trau, Simultaneous size and zeta-potential measurements of individual nanoparticles in dispersion using size-tunable pore sensors, *ACS Nano*, 6 (2012) 6990-6997.
- [19] E.J.W. Verwey, J.T.G. Overbeek, "Theory of the stability of lyophobic colloids", (1948).
- [20] D. Munro, A.R. Goodall, M.C. Wilkinson, K. Randle, J. Hearn, Study of particle nucleation, flocculation, and growth in the emulsifier-free polymerization of styrene in water by total intensity light scattering and photon correlation spectroscopy, *Journal of Colloid and Interface Science*, 68 (1979) 1-13.
- [21] H. Moribe, Y. Kitayama, T. Suzuki, M. Okubo, Effect of stirring rate on particle formation in emulsifier-free, organotellurium-mediated living radical emulsion polymerization (emulsion TERP) of styrene, *Polym J*, 44 (2011) 205-210.

## Nomenclature

$C$  mole concentration (mmol/L)