

Synthesis of Hydrocolloid through Polymerization of Styrene and *N*-Vinyl Acetamide by AIBN

AUTHOR NAME. Tetsuya Yamamoto, 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 with hydrophilic monomer, *N*-vinyl acetamide (NVA), using oil-soluble initiator was carried out to synthesize polymeric particles with good dispersion stability and improve the polymer yield. As a result, it was found that the polymer yield and dispersion stability were enhanced by the promotion of polymerization by the dissolved monomers and hydrogen bonding between NVA on the particle surface and water molecules in the bulk. Accordingly, this polymer colloid showed the nature of hydrocolloid by their hydration layers because its dispersion stability was kept even when the electrolytes were added to the system. In the conventional soap-free emulsion polymerization, the counter ions including the water-soluble initiators were remained in the water phase. However, because all of chemical components in the present study were consumed for the polymerization, the impurities except polymers were hardly remained in the bulk.

Keywords. Soap-free Emulsion Polymerization, *N*-Vinyl Acetamide, Hydrocolloid, Solvation Layer

1. Introduction

Polymerization using more than two kinds of monomers was often utilized to develop new functional materials. This was also applied to the emulsion polymerization and methyl methacrylate (MMA) was well known monomer in this polymerization because it gave the materials hydrophilicity to enhance the dispersion stability in the aqueous phase [1-3]. Especially, soap-free emulsion copolymerization can be used to investigate functional polymer colloids because it was easy to design without taking an influence of surfactant into consideration [4-6]. Conventionally, this kind of polymerization in water was carried out using an ionic initiator, hence, the surface properties, such as zeta potential, were affected by the ionic functional groups decomposed from the initiator and the corresponding counter ions [7-13]. Therefore, it was too difficult to give the only monomer properties on surface characters of the particle.

Recently, it was found that even nonionic initiators, such as 2,2'-azobis(2-methylpropionitrile) (AIBN), were also able to be used to carry out the soap-free emulsion polymerization of styrene to prepare polystyrene particles [14]. The surface potentials of the synthesized particles were enough negative to keep good colloidal dispersion, and this was probably due to not initiator radical but the phenyl rings of the aromatic monomers used in the polymerization [15, 16]. Additionally, the surface properties of the synthesized particle through the copolymerization by AIBN was controllable by the molar fraction of MMA to styrene [17]. In this study, we used the nonionic and hydrophilic monomer, *N*-vinyl acetamide (NVA), which created hydrogen bonding easily, in the soap-free emulsion polymerization of styrene by AIBN to investigate the effect of NVA on the polymer yield and surface properties.

2. Experimental

2.1. Materials

The water used in the 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. NVA (SHOWA DENKO K.K.) was used in the polymerization as received. 2,2'-azobis(2-methylpropionitrile) (AIBN, Sigma Aldrich Co. LLC.) or 2,2'-azobis(2-methylpropionamide) dihydrochloride (V-50, Sigma Aldrich Co. LLC.), which was a water-soluble initiator, was used as an initiator without further purification.

Either ethanol (Wako Pure Chemical industry) or 1-propanol (Nacalai Tesque) was used as a medium to measure the apparent size of the particle synthesized by the polymerization in each organic solvent by ZETASIZER Nano-ZS (MALVERN Co., Ltd.).

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 quantities used for the polymerization reaction [14] are listed in **Table 1**. The reaction time was set to 6 hours because the previous studies have shown that the polymerization has mostly completed after this time [13-15, 18].

The polymerization experiments were carried out as follows. The given amounts of pure water and initiator (Table 1) were poured into the reactor, and the monomers were added. The reactor was sealed with a cap and heated to 70 °C using an electric heater. The reaction mixture was agitated at 130 rpm with an impeller using a magnetic stirrer.

To calculate the yield of polymer by the polymerization against the total monomers in the polymerization, the weight of the solid content of the synthesized particle dispersed in the aqueous phase was measured using the centrifugal method (3700, KUBOTA).

Table 1. Experimental conditions of the present polymerization.

Water [g]	15
Styrene [mmol/l]	320
NVA [mmol/l]	0 ~ 1570
Initiator [mmol/l]	2.03
Temperature [°C]	70
Rotation speed of impeller [rpm]	130

2.3. Characterization

The size of the polymerized particles was measured using scanning electron microscopy (SEM) (JSM-7500FA, JEOL). SEM samples were prepared as follows: a small amount of solution was sampled from the reactor, and a drop of this solution was placed on a freshly cleaved mica plate. The specimen was dried and coated with a thin osmium tetroxide film using chemical vapor deposition (CVD) (Osmium Plasma Coater OPC60A, Filgen). The number-averaged particle size was calculated by averaging the sizes of more than 200 particles in the SEM photographs. The zeta potential of the particles in the suspension was measured using a ZETASIZER Nano-ZS (MALVERN Co., Ltd.) after diluting the sample slurry with deionized water. The number of particles in the suspension and apparent particle size in the NVA solution were measured using the electric pulsed resistance method using a qNano (Izon Science Ltd.) [19].

To estimate the thickness of solvation layer of the particle synthesized by styrene and NVA in the solvent, ZETASIZER Nano-ZS (MALVERN Co., Ltd.) was operated using alcohols as medium.

3. Results and discussion

3.1. Effect of NVA on polymer yield and particle size in soap-free emulsion polymerization by AIBN

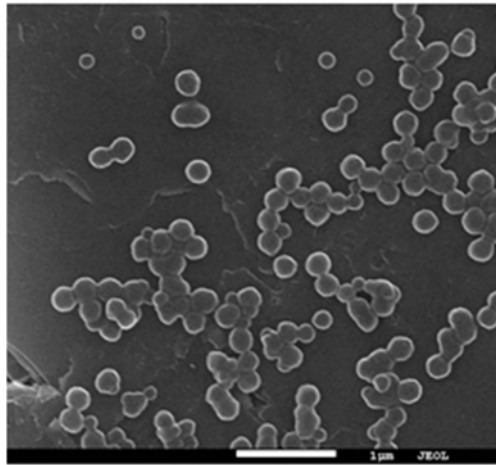


Fig. 1 SEM image of the synthesized particle at NVA of 392 mM according to the experimental conditions shown in Table 1. Scalebar means 1 μm .

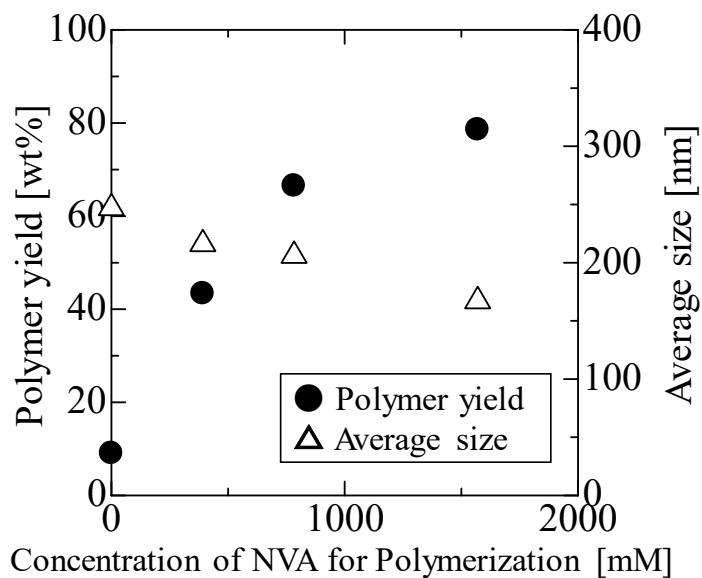


Fig. 2 Effect of concentration of NVA in the polymerization condition on yield and average size of the particle. Polymer yield and average size were calculated by the centrifugal method and from the observations by SEM, respectively.

Fig. 1 showed SEM image of the synthesized particles at the concentration of NVA, 392 mM. The morphologies of the particles seemed to be non-spherical probably because the particle surfaces were covered with the NVA polymers. This covering effect by NVA polymers was discussed in the latter sections. The effect of concentration of NVA in the polymerization on the polymer yield and average size of the particle was shown in **Fig. 2**. When using AIBN as an

initiator, the initiator was partially dissolved in the monomer phase to make it solidified to lead low polymer yield. Increasing of the concentration of NVA, the polymer yield was enhanced because the NVA monomers were dissolved in the aqueous phase and the polymerization reaction was promoted. On the other hand, the particle size was decreased gradually. To clarify the reason of the decrease of the particle size, the zeta potential of each particle was measured by ZETASIZER as shown in **Fig. 3**. As the concentration of NVA in the polymerization was increased, the absolute value of the zeta potential was reduced. This tendency of the zeta potential

was very similar with the experimental results of the polymerization of styrene and MMA by AIBN [17]. Because NVA had no phenyl ring like MMA, it would not be involved in the enhancement of surface potential of the synthesized particle by AIBN. In the case of the polymerization of styrene and MMA, however, particle size was increased because of coagulation

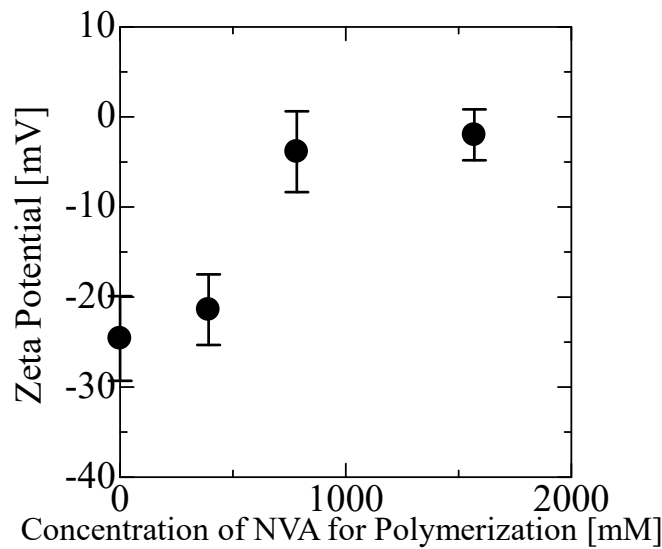


Fig. 3 Effect of concentration of NVA in the polymerization conditions shown in Table 1 on zeta potential. Surface potential were decreased with the concentration of NVA monomer in the polymerization.

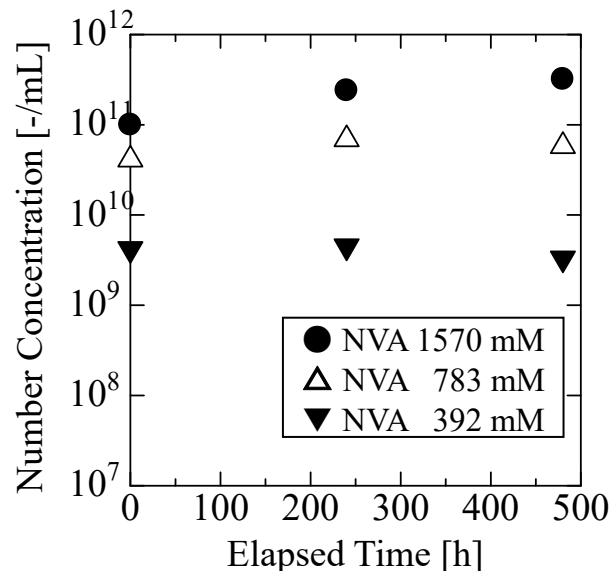


Fig. 4 Evaluation of colloidal stability of the synthesized particle prepared by the various NVA concentrations for the polymerization according to Table 1 by measuring the number of particles. Number concentration of particle synthesized with NVA kept almost constant with the elapsed time.

by the reduction of surface potential. To evaluate the dispersion stability by other method, the particle number concentration was measured with the elapsed time by q-Nano. **Fig. 4** indicated that the particle concentration was almost constant and showed good dispersion stability for long time nevertheless the zeta potential was weakened. The origin of the dispersion stability was studied in the next section.

3.2. Dispersion stability by NVA with hydrogen bonding

It was clear that the surface potential of the synthesized particle was weakened but their dispersion stability was good increasing the concentration of NVA in the polymerization. NVA had a nature to create hydrogen bonding easily in the aqueous phase [20]. In this section, to research the relationship between colloidal dispersion and hydrogen bonding by NVA, the polystyrene particle was synthesized by V-50, which had amino groups to create hydrogen bonding with NVA easily. In contrast, the polystyrene particle was also prepared by AIBN, which was hard to create hydrogen bonding with NVA in the solution. The particle size was measured by q-Nano in the solution of various NVA concentrations. The result was shown in **Fig. 5**. In the case of the polystyrene particle by V-50, the apparent particle size became larger as increasing NVA

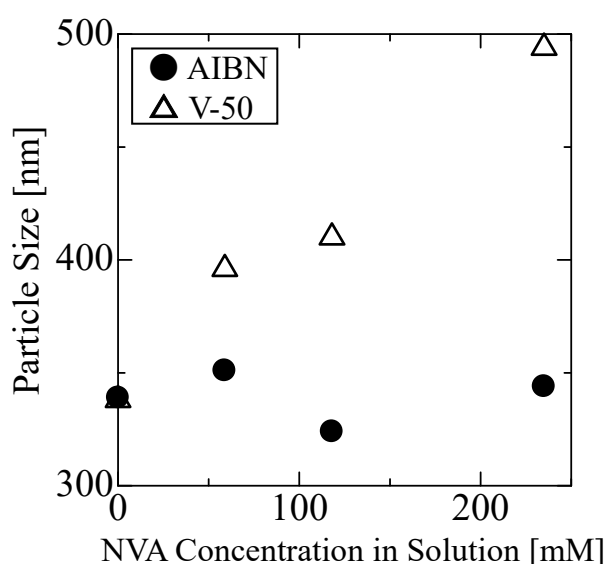


Fig. 5 Effect of NVA concentration in solution on apparent particle size measured by q-Nano. If hydrogen bonding was generated on particle surface in NVA solution, the apparent particle size would increase.

concentration in the solution. Amino groups originated from V-50 on particle surface and NVA molecules in the bulk were bonded through hydrogen bonding, and then the NVA molecules and NVA molecules in the bulk were connected. On the other hand, the polystyrene particle synthesized by AIBN showed almost constant size due to non-construction of hydrogen bonding by NVA in the bulk. In the further investigation, zeta potential of each particle was measured by ZETASIZER as shown in **Fig. 6**. The difference of zeta potential between 0 and 30 mM of NVA concentrations in the solution was much larger in the case of V-50 because the particle surface was covered with NVA molecules to reduce the effect of the amino groups on zeta potential. However, the dispersion in the concentration of NVA, 30 mM, was good. These results suggested that the hydrogen bonding between NVA polymers on particle surface and water molecules would be deeply involved with the dispersion stability of the particle synthesized by the polymerization by NVA.

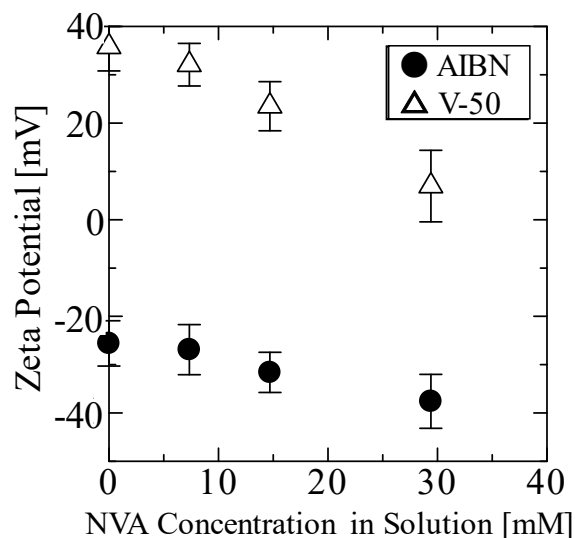


Fig. 6 Effect of NVA concentration in solution on zeta potential of the synthesized particle.

If hydrogen bonding was generated on particle surface in NVA solution, the zeta

Furthermore, the effect of electrolyte, the addition of aluminium chloride (Wako Pure Chemical Industry), on the dispersion stability of colloid prepared under the various NVA concentrations for the polymerization in Table 1 was investigated to measure the particle

concentration by q-Nano. As a result, it was found that polystyrene particle synthesized by AIBN without NVA monomer was influenced by the electrolyte because it was dispersed by the electrical double layer from our recent work [14]. On the other hand, the polymer colloids by the polymerization with NVA were not affected by the electrolyte as shown in Fig. 7. In the previous study, hydrophilic components concentrated to the exterior of the particle in the soap-free emulsion copolymerization [21]. Hence, particle synthesized by the polymerization of styrene and NVA was covered with hydrogen bonding between the NVA polymers located on the particle surface and water molecules in the bulk to show good dispersion stability. Although surface potential was weakened, the colloidal stability was improved by the steric effect of the hydration layer consisted of the water molecules connected through hydrogen bonds [22, 23]. Hence, particle size was decreased gradually as increasing NVA concentration in the polymerization

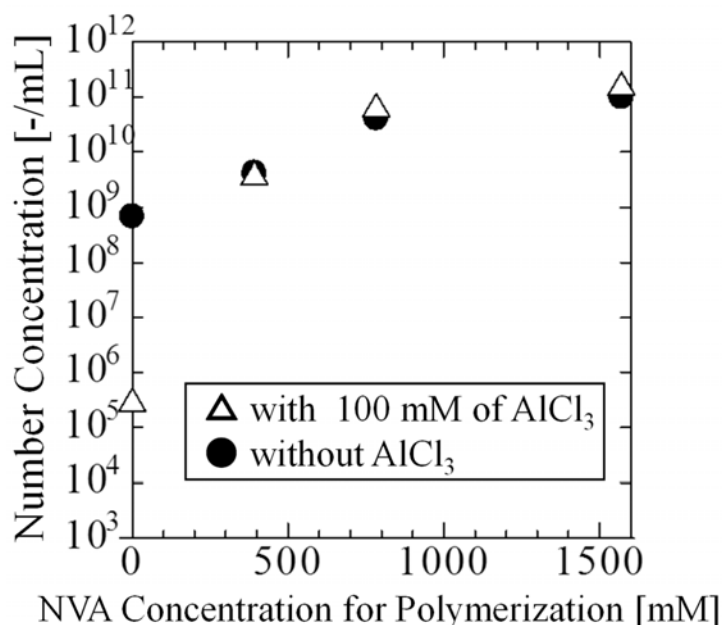


Fig. 7 Effect of electrolyte on dispersion stability of the particle synthesized under the various concentrations of NVA. Particles synthesized with NVA showed good dispersion stability.

condition as shown in Table. 1.

Additionally, to investigate hydration layer of the synthesized particles using styrene, NVA whose concentration was 392 mM and AIBN in water, the solid synthesized particles were obtained by the centrifugal method and dispersed again in organic solvent. Table 2 shows the

effect of medium on the apparent size of the particle in each solvent by ZETASIZER. Each size distribution showed a single peak. As the hydrophobicity of the solvent increased and the hydrogen bonding ability of the solvent decreased, the apparent particle size was decreased. The measurements indicated that the hydration layer was existed on the surface of the synthesized particle, whose size was 216 nm by SEM in Fig. 1, in water and the thickness of the solvation layer was reduced as the alkyl chain length in alcohol became longer. The phenomena were consistent with the previous work in the case of solvation of the silica particle using some alcohols [24].

Table 2. Effect of length of alkyl chain in medium on the apparent size of the particle synthesized by styrene, NVA and AIBN. PdI means polydispersity index.

Medium	Average size [nm]	PdI
Water	364.5	0.167
Ethanol	338.8	0.002
1-Propanol	318.5	0.070

4. Conclusions

Soap-free emulsion polymerization of styrene and NVA using AIBN were carried out to investigate the effect of NVA on the polymer yield and the surface characters. As a result, it was found that the polymer yield and dispersion stability were enhanced by the promotion of polymerization by the dissolved monomers and hydrogen bonding between NVA on the particle surface and water molecules in the bulk. It was clear that these polymer colloids showed the nature of hydrocolloid from the evaluation of the colloidal stability using electrolyte. In the case of water-soluble initiator used in the conventional soap-free emulsion polymerization to synthesize the polymer colloid with good dispersion stability on the basis of the DLVO theory, the counter ion including the initiator was remained in the colloid. However, because almost all of

chemical reagents in the present polymerization were consumed to make the particle, the impurities except polymers were hardly remained in the bulk.

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). The NVA monomers were given from SHOWA DENKO K.K..

References

- [1] S. Zhu, Y. Tian, A.E. Hamielec, D.R. Eaton, Radical concentrations in free radical copolymerization of MMA/EGDMA, *Polymer*, 31 (1990) 154-159.
- [2] P. Li, J.M. Zhu, P. Sunintaboon, F.W. Harris, New route to amphiphilic core-shell polymer nanospheres: Graft copolymerization of methyl methacrylate from water-soluble polymer chains containing amino groups, *Langmuir*, 18 (2002) 8641-8646.
- [3] K. Ishizu, N. Tahara, Microsphere synthesis by emulsion copolymerization of methyl methacrylate with poly(methacrylic acid) macromonomers, *Polymer*, 37 (1996) 2853-2856.
- [4] C.Y.K. Kai Kang, Yi Du, De Shan Liu, Control of Particle Size and Carboxyl Group Distribution in Soap-Free Emulsion Copolymerization of Methyl Methacrylate–Ethyl Acrylate–Acrylic Acid, *Journal of Applied Polymer Science*, 92 (2004) 433-438.
- [5] J.Z. Zhang, Q.C. Zou, X.Q. Li, S.Y. Cheng, Soap-free cationic emulsion copolymerization of styrene and butyl acrylate with comonomer in the presence of alcohols, *Journal of Applied Polymer Science*, 89 (2003) 2791-2797.
- [6] D. Suzuki, H. Kawaguchi, Stimuli-sensitive core/shell template particles for immobilizing inorganic nanoparticles in the core, *Colloid Polym Sci*, 284 (2006) 1443-1451.
- [7] 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.
- [8] M. Arai, K. Arai, S. Saito, POLYMER PARTICLE FORMATION IN SOAPLESS EMULSION POLYMERIZATION, *J Polym Sci Pol Chem*, 17 (1979) 3655-3665.
- [9] T. Tanrisever, O. Okay, I.C. Sonmezoglu, Kinetics of emulsifier-free emulsion polymerization of methyl methacrylate, *Journal of Applied Polymer Science*, 61 (1996) 485-493.
- [10] G. Guven, A. Tuncel, E. Piskin, Monosized cationic nanoparticles prepared by emulsifier-free emulsion polymerization, *Colloid Polym Sci*, 282 (2004) 708-715.
- [11] T. Yamamoto, T. Fukushima, Y. Kanda, K. Higashitani, Molecular-scale observation of the surface of polystyrene particles by AFM, *J Colloid Interface Sci*, 292 (2005) 392-396.
- [12] T. Yamamoto, M. Inoue, Y. Kanda, K. Higashitani, AFM observation of growing poly isobutyl methacrylate (PiBMA) particles, *Chemistry Letters*, 33 (2004) 1440-1441.
- [13] T. Yamamoto, T. Yokoyama, Effect of Counter Ionic Radius in Initiator on Particle Size in Soap-free Emulsion Polymerization of Styrene, *Chemistry Letters*, 44 (2015) 824-825.
- [14] 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.
- [15] T. Yamamoto, Soap-free emulsion polymerization of aromatic vinyl monomer using AIBN, *Colloid Polym Sci*, 290 (2012) 1833-1835.

- [16] 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.
- [17] 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*, 294 (2016) 281-284.
- [18] 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.
- [19] 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.
- [20] Y. Takemoto, H. Ajiro, M. Akashi, Amphiphilic Poly(N-vinyl acetamide) Gels Strengthened with Swelling Solvent, *Macromolecular Chemistry and Physics*, 215 (2014) 384-390.
- [21] J. Wang, Y. Wen, X. Feng, Y. Song, L. Jiang, Control over the Wettability of Colloidal Crystal Films by Assembly Temperature, *Macromolecular Rapid Communications*, 27 (2006) 188-192.
- [22] P. Bagchi, Theory of stabilization of spherical colloidal particles by nonionic polymers, *Journal of Colloid and Interface Science*, 47 (1974) 86-99.
- [23] G. Klose, S. Eisenblaetter, J. Galle, A. Islamov, U. Dietrich, Hydration and Structural Properties of a Homologous Series of Nonionic Alkyl Oligo(ethylene oxide) Surfactants, *Langmuir*, 11 (1995) 2889-2892.
- [24] L. He, Y. Hu, M. Wang, Y. Yin, Determination of solvation layer thickness by a magnetophotonic approach, *ACS nano*, 6 (2012) 4196-4202.