



# Advanced soap-free emulsion polymerization for highly pure, micron-sized, monodisperse polymer particles



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## ABSTRACT

A previously proposed method of soap-free emulsion polymerization employing an amphoteric initiator, 2,2'-azobis[N-(2-carboxyethyl)-2-methylpropionamidine] (VA-057), was extended to synthesize micron-sized, monodisperse polystyrene (PSt) particles at low impurity levels. Initial pH values of solutions in which anionic PSt particles were formed were adjusted between neutral pH and 8.9 with a tiny amount of strong base such as NaOH to constitute a low-impurity polymerization system. Micron-sized polymer particles with a narrow size distribution were obtained in a pH range of 8.1–8.9. Different strong bases of KOH, Ca(OH)<sub>2</sub> and tetramethylammonium hydroxide were also added to examine electrostatic interaction between PSt particles formed in the low-impurity system, indicating that surface charge density of PSt particles is an important factor to determine size distributions of PSt particles formed. Polymerizations at high styrene concentrations and an appropriate VA-057 concentration succeeded in preparation of highly pure, monodisperse PSt particles with an average size of 1.86 μm.

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## 1. Introduction

Applications of monodisperse polymer particles to various fields including drug delivery carriers [1], disease diagnosis [2] and selective sorbent beads [3] have become increasingly widespread because of easy controls over their characteristics such as average sizes, surface charge densities and surface functional groups [4–6]. Monodisperse polymer particles in a particle size range of micrometers have often been employed in biomedical applications such as protein separation, antibody and enzyme immobilization, and protein purification [7–9]. In the applications where functional molecules are chemically or physically bound to surfaces of the polymer particles, non-specific adsorptions of functional molecules to the polymer surface should be minimized for obtaining desired compounds in sufficient purity and concentration. To prevent such non-specific adsorptions, intensive washings to remove impurities and unreacted monomers should be applied to the polymer particles before their use [10,11]. Thus the preparation of micron-sized, monodisperse polymer particles at low impurity levels is a practical issue to further develop the applications.

Dispersion polymerization is a suitable method for preparation of monodisperse polymer particles in a size range of micrometers.

In the dispersion polymerization, polymer particles are formed in the presence of stabilizers in media containing organic solvents such as alcohols. To explore preparation of polymer particles at high purity, Kim et al. examined polymerization of methyl-methacrylate (MMA) in mixed solvents of water and methanol without any surfactants and stabilizers [12]. They could prepare micron-sized PMMA particles in a high methanol content of 60 wt%. Recently, Chou et al. have succeeded preparation of 4.1 μm monodisperse polystyrene (PSt) particles via alcoholic dispersion polymerization with a combination of ionic and nonionic initiators in the absence of stabilizers [13]. The uses of alcoholic solvents described above, however, are not environmentally friendly and need additional costs to treat waste solution after the polymerization.

A surfactant-free heterogeneous polymerization in water solvent [14,15], which is called soap-free emulsion polymerization, is an environmentally desirable choice for preparation of monodisperse polymer particles at low impurity levels. Polymer particles formed in the aqueous polymerization are generally stabilized with electrostatic interaction between particles. The conventional soap-free emulsion polymerization has been applied mainly to production of submicron-sized polymer particles [16–18]. Previously, the authors developed a novel method to prepare micron-sized, monodisperse polymer particles in soap-free emulsion polymerization where weak-electrolyte initiator is employed in aqueous buffer solution [19–23]. Dissociation of the weak-

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electrolyte initiator depends on solution pH dominated by components of the buffer solutions. Due to the pH dependence of dissociation, surface charge density of polymer particles can be controlled by solution pH. The controllability is allowed to extend the size range of PSt particles up to 6  $\mu\text{m}$  with a weak-electrolyte initiator of 2, 2'-azobis [*N*-(2-carboxyethyl)-2-methylpropionamide] (VA-057) [22]. Electrolytes added as pH control agents to the polymerization in a concentration range of 10–100 mM, however, have a possibility to be contaminants in the biomedical applications where precise separation and purification of biomolecules are required.

In the present work, we examined VA-057 initiated soap-free emulsion polymerization to which a strong base was added as a pH control agent at extremely low concentrations (<3 mM) to constitute low-impurity polymerization systems for preparation of micron-sized, monodisperse PSt particles. Different strong bases of NaOH, KOH,  $\text{Ca}(\text{OH})_2$  and tetramethylammonium hydroxide (TMAH) were also used as pH controllers in the polymerization to understand electrostatic interactions between PSt particles formed in the polymerization. Polymerizations at high styrene concentrations were also performed to explore the possible size range of PSt particles prepared and also to enhance the amount of PSt products (PSt yields) in the polymerization.

## 2. Experimental

### 2.1. Chemicals

All the chemicals used were purchased from Wako Pure Chemical Industries (Osaka, Japan). Inhibitor for styrene monomer (St, 99%) was removed by inhibitor removal column. The initiator of 2, 2'-azobis [*N*-(2-carboxyethyl)-2-methylpropionamide] (VA-057), basic pH controllers of NaOH, KOH,  $\text{Ca}(\text{OH})_2$  and tetramethylammonium hydroxide (TMAH), and an electrolyte of NaCl were used as received. Water was deionized to have an electric resistance higher than 18.2 M $\Omega$  cm.

### 2.2. Polymerization

A batch reactor (11 cm I.D. and 12 cm height) equipped with four baffles and a six-blade pitched paddle impeller was used for the polymerization. The width of the baffles was 1 cm, and the diameter and width of the impeller were 6 and 1 cm, respectively.

Deionized water dissolving a basic pH controller was charged into the reactor and then deoxygenated at 65 °C by bubbling with nitrogen for 30 min under stirring. After addition of styrene (St) monomer, the bubbling was stopped, and the mixture was further stirred for 30 min under a nitrogen atmosphere. The polymerization of St was initiated by adding an aqueous solution of VA-057 to the polymerization in the pH controller concentrations of 0.1–3.0 mM. The initial pH values and VA-057 concentrations were in ranges of 7.5–8.9 and 5–30 mM, respectively. All the concentrations are based on the volume of the aqueous phase. All runs were conducted under nitrogen atmosphere at an impeller speed of 300 rpm.

### 2.3. Characterization

In the polymerization, small amounts of reaction mixture (less than 20  $\text{cm}^3$ ) were withdrawn to measure particle size distributions and polymer content in the mixture. Hydroquinone was added to the samples to terminate the polymerization. More than two hundred particle diameters were measured for each reaction mixture with a transmission electron microscope (TEM mode on FE-SEM Hitachi S-4800) to determine the volume-averaged

diameter,  $d_V$  and the coefficient of variation of particle size distribution,  $C_V$ . Monomer conversion was defined as the percentage of the polymer weight relative to the weight of monomer added, because almost no adhesion of polymer precipitate to the reactor walls and impeller was observed after polymerization. The polymer weights in the samples were measured after removal of volatile components with freeze-drying.

## 3. Result and discussion

### 3.1. Preparation of monodisperse polymer particles at low pH controller concentrations

To examine dependence of solution pH on base concentrations in the presence of initiator, a strong base of NaOH at different concentrations was added to deionized water dissolving 10 mM VA-057. The increase in solution pH with NaOH addition at 65 °C is shown in Fig. 1. In our previous work, we reported an appropriate pH range of 8.1–8.8 for monodisperse PSt particles formed in the VA-057 initiated soap-free emulsion polymerization [19]. The pH curve drawn in Fig. 1 shows that solution pH can be raised up to approximately 9.0 by NaOH addition at concentrations less than 3 mM.

Fig. 2 shows averaged sizes and their coefficients of variation for PSt particles formed in an initial pH range of 7.5–8.9 that was adjusted with NaOH addition at [VA-057] = 10 mM. Although a low pH value of 7.5 formed PSt particles with an average size of 2.1  $\mu\text{m}$ , their size distribution was considerably broad ( $C_V = 15\%$ ). The broad size distribution was probably due to insufficient electrostatic stabilization that was caused by high protonation of VA-057 amidino groups on particle surfaces. On the other hand, in the pH range of 8.1–8.9, micron-sized PSt particles with narrow size distributions were obtained with monomer conversions higher than 90% (see Table S1 in Supporting Information).

At an initial pH 8.3 suitable for monodisperse particles, the effect of VA-057 initiator concentration on particle size distribution was examined. Fig. 3 shows TEM images and size distributions of PSt particles formed in the VA-057 concentration range of 5–30 mM. At all the VA-057 concentrations, micron-sized, monodisperse PSt particles were obtained with monomer conversions higher than 85% (see Table S2). In Fig. 3, a minimum average size of monodisperse PSt particles was observed at VA-057 10 mM, which suggests that both increasing and decreasing factors for particle sizes should be simultaneously considered to explain the average sizes of particles formed at different VA-057 concentrations. A possible factor to decrease particle sizes with an increase in VA-057 concentration in the range of 5–10 mM is the rate of radical formation. The decomposition rate of VA-057 initiator at a pH range of

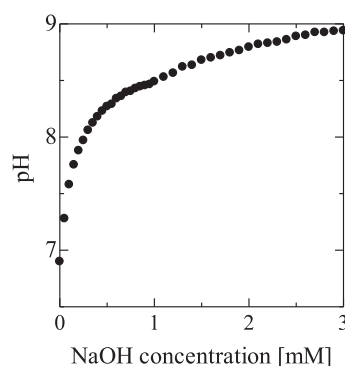


Fig. 1. Solution pH values measured at 65 °C, a fixed VA-057 concentration of 10 mM and different NaOH concentrations.

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