



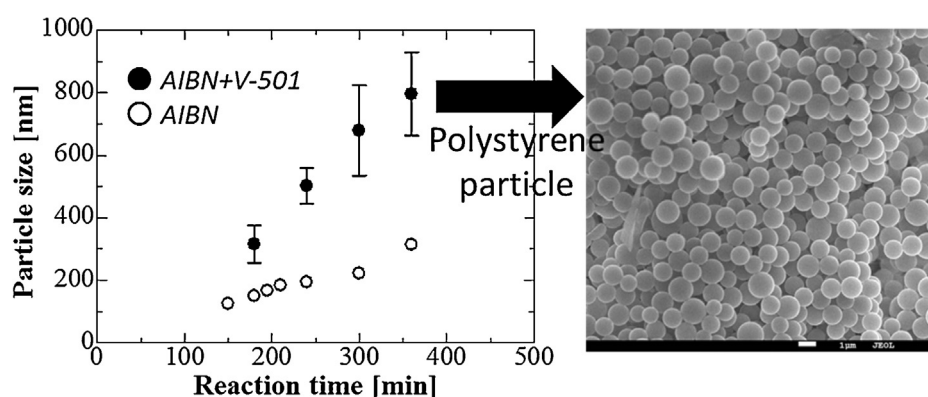
Particle size control in the soap-free emulsion polymerization of styrene by an oil-soluble initiator with a weakly acidic water-soluble initiator



HIGHLIGHTS

- Polystyrene particles were able to be synthesized by oil- and water-soluble initiators.
- V-501 worked as radical initiators and weak acid to promote the particle growth.
- Particle size was enabled to be controlled by the concentration of V-501.
- Number concentration of particle was maintained by V-501.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Soap-free emulsion polymerization
Size control
Oil-soluble initiator
Water-soluble initiator

ABSTRACT

The soap-free emulsion polymerization of styrene by an oil-soluble initiator, 2,2'-azobis(2-methylpropionitrile) (AIBN), with a water-soluble initiator, 4,4'-azobis(4-cyanovaleic acid) (V-501), was conducted in water to control the size of the synthesized polymeric particles. The particle size and surface potential were monitored as concentration of V-501 used for the polymerization was varied. When the V-501 concentration was increased, the particle size increased because V-501 was a weak acid and reduced the surface potential, thereby promoting particle growth through coagulation. Additionally, V-501 can also function as a radical initiator, increasing the efficiency of the polymerization reaction and, thus, the number concentration of the particles.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Emulsion polymerization [1,2] is generally used to prepare polymeric particles with a minimum size of 33 nm [3,4]. Such particles can also be synthesized in water based on the surface activation effect derived from an ionic water-soluble initiator without the need for a surfactant [5,6]. This environmentally-friendly polymerization method, which is known as soap-free emulsion polymerization, is suitable to prepare particles with clean surfaces and the sizes up to the micron scale. For example, surfactant-free micron-sized particles can be easily handled and utilized as toner particles [7]. In our recent work, the soap-free emulsion polymerization of aromatic vinyl monomers using an oil-soluble initiator in aqueous solution was developed as a method to prepare polymeric particles [8,9]. The negative charges of the synthesized particles,

which support their good dispersion stabilities in water, can be attributed to the phenyl ring of the monomer used in the polymerization [10,11]. Adding an electrolyte to this system promoted the particle growth through coagulation by reducing the thickness of the electrical double layer. This method was efficient for the production of enlarged particles in a short reaction time [8,12]. Thus, surface potential of the particle is a very important factor determining the particle size [12–16]. In the conventional soap-free emulsion polymerization of styrene using a water-soluble initiator, increasing the initiator concentration increases [5,17]. However, when using an oil-soluble initiator for soap-free emulsion polymerization, the initiator partially dissolves into the monomer phase, causing the monomers to solidify. Hence, attempting to increase the particle size by increasing the concentration of the oil-soluble initiator could lead to wasting monomers, which solid-

Nomenclature

C Mole concentration (mmol/L)

ify and become unavailable for making particles. Additionally, the electrolytes added to the system to control the particle size remain in the bulk as impurities. In the present study, to prevent monomer solidification and the introduction of impurities and to increase of the number of initiator radicals in the bulk solution, a weakly acidic water-soluble initiator, which does not dissolve in the monomer phase and contributes to reducing the surface potential, was added to the soap-free emulsion polymerization reaction of styrene by an oil-soluble initiator to promote 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 bubbled with nitrogen gas to remove any dissolved oxygen. The 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 is a well-known oil-soluble initiator (Fig. 1a), and 4,4'-azobis(4-cyanovaleric acid) (V-501, Wako Pure Chemical Industries, Ltd.), a water-soluble initiator containing carboxyl groups (Fig. 1b), were used in the polymerization without further purification. V-501 ($pK_a = 3.85$) is a weak acid. Acetic acid (Kanto Chemical Co., Inc.), a weak acid, was used to control the concentration of carboxyl groups in the reactor to investigate the function of V-501, which contains carboxyl groups.

2.2. Polymerization reaction

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

The polymerization experiments were conducted as follows. The appropriate amounts of pure water, AIBN, and V-501 were added to the reactor, and followed by the monomers. 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 this solution

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] | C |
| Temperature [°C] | 70 |
| Rotation speed of impeller [rpm] | 130 |

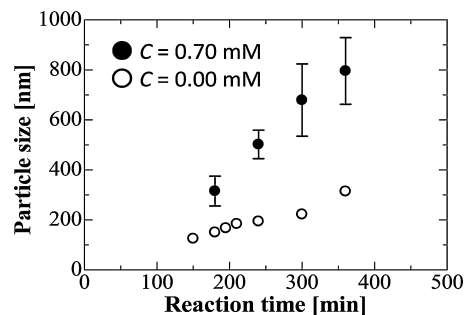


Fig. 2. Growth plots of polystyrene particles using AIBN and V-501.

was placed on a freshly cleaved mica plate. The specimen was dried, and then coated with a thin osmium oxide film via the chemical vapor deposition (CVD) (Osmium Plasma Coater OPC60A, Filgen). The number-averaged particle size was calculated by averaging the data from more than 200 particles in SEM photographs. The zeta potential of the particles in the suspension was measured using a ZETASIZER Nano-ZS (MALVERN Co., Ltd.). The number concentration of the particles in the suspension was determined using the electric pulsed resistance method with a qNano instrument (Izon Science Ltd.) [18].

3. Results and discussion

3.1. Promotion of particle growth by V-501

The growth plots recorded with $C = 0.0$ and 0.70 mM were compared as shown in Fig. 2. When using only AIBN, the particle size increased gradually. In contrast, the particle growth was rapid in the presence of both AIBN and V-501. Thus, V-501 promoted particle growth. To clarify why V-501 exerted this effect, the zeta potential of the particles synthesized at $C = 0.70$ mM was measured in solutions with various concentrations of V-501 by ZETASIZER. The influence of the V-501 concentration in medium on the zeta potential is shown in Fig. 3. As the V-501 concentration increased, the surface potential decreased and the pH ranged from 3.56 to 4.05, as determined by a pH meter (LAQUA F-74, Horiba). Based on Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, particle coagulation was expected to occur during the growth processes because of the decreased surface potential at low pH [19]. This is why the particle size grew so rapidly. This phenomenon was very similar to that observed during the soap-free emulsion polymerization of styrene by AIBN with an electrolyte. Thus, V-501 can reduce the surface potential reduced plays the same role as the electrolyte in the polymerization of styrene using AIBN [8,12].

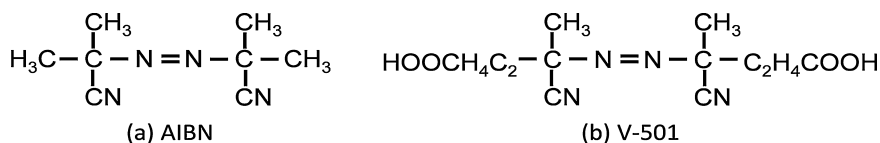


Fig. 1. Chemical structures of the initiators: (a) AIBN and (b) V-501.

Download English Version:

<https://daneshyari.com/en/article/591578>

Download Persian Version:

<https://daneshyari.com/article/591578>

[Daneshyari.com](https://daneshyari.com)