Rapid synthesis of poly(methyl methacrylate) particles with high molecular weight by soap-free emulsion polymerization using water-in-oil slug flow

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Abstract

We propose a flow process for the production of poly(methyl methacrylate) (PMMA) particles by soap-free emulsion polymerization using a water-in-oil (W/O) slug flow in a microreactor. Thin oil films generated around the dispersed aqueous phase of the W/O slug prevented the prepared particles from adhesion to the microchannel wall, enabling the continuous production of PMMA particles without clogging. The effects of the linear flow rate of the slug flow and the addition of ethanol in the dispersed aqueous phase on the polymerization were evaluated. We found that increasing the linear flow rate of the slug flow or the addition of ethanol in the dispersed aqueous phase resulted in PMMA particles with high molecular weight (~ 1,500 kg mol^{-1}) in 20 min reaction time. We believe that this process would be a promising way to prepare polymer particles with high molecular weight in a short reaction time.

Introduction

Soap-free emulsion polymerization is an environmentally-friendly process that does not use hazardous solvent or surfactants for the production of submicron-sized polymer particles with a narrow size distribution [1,2]. In general, soap-free emulsion polymerization takes place in the system consisting of a sparingly water-soluble monomer, an ionic water-soluble initiator, and water. In the polymerization, the ionic water-soluble initiator molecules first decompose and react with sparingly water-soluble monomers dissolved in water. The resulting oligomer containing an ionic end group becomes immiscible in water as growing their lengths, which serves as a surfactant and aggregates into micelles (nucleation). The polymerization takes place mostly in the micelles and monomer is supplied from large monomer droplets by diffusion through the water phase, resulting in polymer particles dispersed in water [3]. Although soap-free emulsion polymerization has been generally conducted in batch reactors (batch process), there is still room for improvement in the reactor from the viewpoint of process intensification such as mixing and insufficient heat and mass transfer.

In the last two decades, microreactors have attracted considerable attentions in the field of chemistry and chemical engineering as interesting reaction fields, since they have advantages in facilitating heat and mass transfer [4-6] and providing precise temperature and reaction time [7-10]. These characteristics of microreactors are derived from their large surface to volume ratio and short diffusion path. In recent years, microreactors have been also applied to both homogeneous and heterogeneous polymerization processes. Homogeneous polymerization including radical polymerization [11] and controlled/living polymerization [12,13] with the use of microreactors provides polymers with controlled molecular weight and narrow molecular weight distribution. Heterogeneous polymerization using liquid-liquid multiphase systems such as emulsion polymerization [14], miniemulsion photopolymerization [15] and suspension polymerization [16] has been shown to be a robust way to prepare polymer particles with various sizes and structures. However, these polymerization processes have a potential risk of clogging due to uncontrollable adhering of polymer solutions or droplets to the microchannel wall [17,18].

To overcome the clogging issue, liquid-liquid slug flow has recently attracted a great deal of attention as a new type of polymerization field. Different from aforementioned emulsion droplets, the segmented liquid-liquid slug flow is formed without surfactant and thus collection of products after polymerization can be achieved easily by spontaneous phase separation at the exit of microreactors. Moreover, because of different wettability of the channel wall for two immiscible liquid phases (*i.e.* organic phase and aqueous phase), adhesion of polymerization phase to the channel wall can be mitigated by selecting the material compositions of tubing and thin liquid films are formed between the dispersed phase slugs and the inner wall of microreactor [19]. The thin liquid films prevent the viscous polymer solution from adhering to the channel wall and clogging of the channel [20, 21]. Furthermore, it is well-known that internal circulation flow generated in a slug flow enhances the mixing of reactants in each slug and facilitates mass transfer between the liquid-liquid interfaces [19, 22-24]. Although a few studies using a slug flow for polymerization have been reported, to the best of our knowledge, there are no studies showing the production of polymer particles using a slug flow.

In this study, we propose a soap-free emulsion polymerization using a water-in-oil (W/O) slug flow (slug flow process). Different from aforementioned typical soap-free emulsion polymerization using an oil-in-water (O/W) system in a batch process, we use a W/O system in the slug flow process to limit the polymerization field in the dispersed aqueous phase and prevent the produced polymer particles from adhering to the microchannel wall. Moreover, internal circulation in the slug flow contributes to efficient mixing in each segment as well as promotion of monomer diffusion from oil to aqueous phase. We expect that the internal circulation in the slug flow would increase the rate of polymerization. For a model monomer in this study, we chose methylmethacryate (MMA) because of its high solubility in water (~15.9 g/L at 20 °C) [25] and relatively high polymerization rate, which should be suitable for flow process with limited lengths of reaction tubing (residence time ~ 30 min). We first compare the reaction performance of soap-free emulsion polymerization of MMA in the slug process with that in the batch process. Then, we evaluate the effects of the linear flow rate of the slug flow and the addition of ethanol in the dispersed aqueous phase on the characteristics of the polymerization as well as the resulting polymer particles.

Experimental Section

Materials

Methyl methacrylate (MMA, FUJIFILM Wako) was used after purification by distillation under a reduced pressure to remove polymerization inhibitors. Deionized water used in all experiments was obtained from an Elix UV (Millipore, Japan) purification system. Sodium persulfate (NaPS), dodecane, *N,N*-dimethylformamide (DMF), and ethanol were purchased from FUJIFILM Wako and used without further purification.

Fabrication of a microreactor system

The microfluidic device was fabricated by assembling a T-shaped poly(1,1,2,2-tetrafluoroethylene) (PTFE) union (o.d. 1/16”, GL science) and PTFE tubing (i.d. 1 mm and o.d. 1/16”, GL science). The inlet PTFE tubing was connected to syringes (HSW NORM -JECT® Syringe, Henke-Sass, Wolf) placed on syringe pumps (Harvard Pump 33

Dual Syringe Pump, Harvard Apparatus). The outlet PTFE tubing was coiled helically and dipped in an oil bath (PAIRSTIRRER PS-1000, EYELA) at 70 °C.

Soap-free emulsion polymerization of MMA in a microreactor (Slug flow process)

Soap-free emulsion polymerization was carried out using a W/O slug flow in the microreactor. For the initiator solution (W), an aqueous solution dissolving 5.0 mmol L^{-1} of sodium persulfate (NaPS) was used. For the organic solution (O), a mixture of MMA and dodecane (MMA/dodecane = 1/4 (v/v)) was used. Both solutions were pumped into the microreactor using syringe pumps (Harvard Pump 33 Dual Syringe Pump, Harvard Apparatus) with a total flow rate in the range of 92.3 to 274.8 $\mu L\ min^{-1}$, while keeping the volume ratio of organic to aqueous phase constant at 1.0. W/O type slug flow was formed at the T-shaped union and it passed through the reaction tubing placed in an oil bath (PAIRSTIRRER PS-1000, EYELA) at 70 °C. The residence time of heating zone was controlled from 5 to 20 min by changing the length of the tubing. After the polymerization, the sample solution was collected in a sample bottle (10 mL, LABORAN) and the polymerization was quenched by cooling it in an ice bath. The resulting polymer particles were washed with pure water 3 times and collected by centrifugation (himac CF 15R, HITACHI, 15,000 rpm for 10 min).

Soap-free emulsion polymerization of MMA in a batch reactor (Batch process)

Soap-free emulsion polymerization of MMA using a batch reactor was conducted in a glass two-neck flask at 70 °C for 5 to 20 min under a nitrogen atmosphere. A mixture of MMA and dodecane (MMA/dodecane = 1/4 (v/v), total: 10 mL) and NaPS (5.0 mmol L^{-1}) aqueous solution (10 mL) were first added to a glass three-neck flask, and the mixture (organic phase : aqueous phase = 10 mL : 10 mL) was stirred with a magnetic stirrer at 800 rpm under a nitrogen atmosphere to prepare O/W emulsion. The O/W emulsion was then poured into the glass two-neck flask preheated at 70 °C under a nitrogen atmosphere to initiate the polymerization. After the predetermined reaction time was reached, the polymerization was quenched by cooling the reactor in an ice bath. The resulting polymer particles were washed with pure water 3 times and collected by centrifugation (himac CF 15R, HITACHI, 15,000 rpm for 10 min). The collected sample was freeze-dried overnight before characterization.

Characterization

The morphology of the prepared particles after drying was observed by means of a scanning electron microscope (SEM, S-4700, Hitachi Ltd., Japan) at a voltage intensity of 2 kV. Before SEM observation, the prepared particle samples were sputter-coated (E-1030 Ion-Sputter, Hitachi Ltd., Japan) with Pd/Pt in order to reduce the sample charging. Average particle diameter and the size distribution were determined from SEM images by using an image analysis software (WinROOF, Mitani Co., Ltd., Japan). In the analysis, the size distribution was evaluated as the coefficient of variation (*CV*) that is defined as the ratio of the standard deviation to the average diameter. The *CV* values were calculated from the average diameter of 200 particles. The conversion of monomer was determined by means of a gas chromatography (GC-14A, Shimadzu Ltd., Japan). The weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution ($M_\mathrm{w}/M_\mathrm{n}$) were characterized by using a gel permeation chromatography (HLC-8120 GPC, Tosoh Ltd., Japan), equipped with a refractive index detector and columns. DMF was used as the eluent at a flow rate of 0.3 mL min^{-1}.

(Figure 1)

Results and Discussion

Figure 1a shows a schematic image of the microfluidic system for the soap-free emulsion polymerization of MMA using a W/O slug flow. In this system, we used a mixture of 20 vol% MMA and 80 vol% dodecane as the organic phase and an initiator aqueous solution as the aqueous phase. The dodecane in the organic phase was served as an inert oil to keep the slug flow stable during polymerization. When feeding the organic and aqueous phases at the volume ratio of 1.0 into the microfluidic device, W/O type slug flow was spontaneously formed at the T-junction because the wall of the microchannel is made of PTFE and intrinsic hydrophobic. The slug flow then entered the reaction zone, where the temperature was fixed at 70 °C. Because of the narrow channel width, the temperature of each slug reached to 70 °C soon after entering the heating zone and then polymerization took place in the dispersed aqueous phase. We macroscopically confirmed that the color of the dispersed aqueous phase gradually turned from transparent to white during polymerization, indicating that polymer particles formed only in the dispersed aqueous phase (**Figure 1b**). We also found that the microreactor can be operated without clogging at least for 30 min. Based upon these results, we consider that the dispersed aqueous phase of the W/O slug flow can be served as micron-sized reaction field for the soap-free emulsion polymerization of MMA and that the mechanism of nucleation and growth in the slug flow process is analogue to that in the batch process, as shown in **Figure. 1c**. In the slug flow process, initiation reaction first occurs by the decomposition of the ionic water-soluble initiators in the dispersed aqueous phase. Then, the ionic radicals react with dissolved MMA molecules in the aqueous phase to form surface-active oligomeric radicals which generate micelles. After the formation of the micelles, particle growth is achieved by monomer supply from the continuous organic phase to the micelles in the dispersed aqueous phase *via* internal circulation flow, which finally leads to the formation of PMMA particles in the dispersed aqueous phase.

To compare the reaction performance between slug flow and batch processes, we conducted the soap-free emulsion polymerization of MMA using W/O slug flow and batch processes and investigated the effect of the types of the reactor systems on the particle diameter, monomer conversion, weight-averaged molecular weight (M_w), and molecular weight distribution (M_w/M_n). It is noted here that in the batch process, we used the organic phase consisting of MMA and inert oil (dodecane) (1/4, v/v) and fixed the volume ratio of organic to aqueous phase at 1.0 to ensure a rationale comparison between slug flow and batch processes, although soap-free emulsion polymerization of MMA using a batch process is generally performed in the conditions where inert oil does not exist and the volume ratio of organic to aqueous phase is less than 1.0. In both the systems, the particle diameter became bigger as increasing the reaction time and the particle growth in the slug flow was faster than that in the batch process (**Figure 2a**). The monomer conversion in the slug flow was higher than that in the batch process at each reaction time, suggesting that the rate of polymerization in the slug flow is higher than that in the batch process (**Figure 2b**). Moreover, the M_w of PMMA particles prepared using the slug flow showed a marked increase as increasing the reaction time and reached about 600 kg mol^{-1} in 20 min, which was approximately three times larger value than that using the batch reactor in 20 min (**Figure 2c**). On the other hand, the M_w/M_n values between the both systems were in the range of 1.5 to 2.0, regardless of the reaction time

(**Table 1**). We consider that the high polymerization rate and high molecular weight in the slug flow would attribute to two effects: high heat transfer efficiency in the microreactor [26] and high mass transfer efficiency induced by the internal circulation flow in the slug flow [19]. Because of high heat transfer efficiency in the microreactor, the reaction temperature in slugs reaches to a fixed temperature soon after they entered the reaction zone and thus the decomposition of initiator molecules occurs in a more uniform manner. This increases the numbers of ionic radicals and growing chains in the dispersed phase, leading to high rate of polymerization. Another factor is the internal circulation flow in slug flow, providing high mass transfer efficiency through liquid-liquid interfaces. The internal circulation flow continuously provides the dispersed aqueous phase with monomer from the continuous phase and maintains the concentration of the dissolved monomer in the dispersed aqueous phase high, which facilitates the propagation of polymer.

However, in the case of the slug flow, unexpectedly, the *CV* value of the resulting PMMA particles gradually increased from 10.7 to 15.7% with increasing the reaction time from 10 min to 20 min (**Figure 2d**). Although we have not elucidated the detailed mechanism yet, the broader particle size distribution in the slug flow process compared to that in the batch process would be due to non-uniform mixing by internal circulation flow in each slug [27]. We consider that the non-uniform mixing in each slug at the particle growth stage may broaden the particle size distribution. These findings suggest that soap-free emulsion polymerization using a W/O slug flow can be effective to rapidly synthesize polymer particles with higher molecular weight, although the particle size distribution increases as a function of reaction time.

(Figure 2)

(Table 1)

We next evaluated the effect of internal circulation in the slug flow on the soap-free polymerization of MMA by using a W/O slug flow with three different linear flow rates (2.0, 3.9, and 5.8 cm s^{-1}). **Figure 3a** shows the effect of the linear flow rate on the particle diameter as a function of time. It is noted that we could not obtain enough amount of polymer particles to observe at 10 min in the case of linear flow rate at 2.0 cm s^{-1}. When compared at each reaction time, the particle diameter increased with increasing the linear flow rate. However, there was no significant difference in the particle diameter between 3.9 and 5.8 cm s^{-1} conditions (**Table 2**). Similar trend was confirmed from the monomer conversion plots as depicted in **Figure 3b**. Moreover, we found that when increasing the linear flow rate, the M_w of the PMMA particles significantly increased as increasing the reaction time (**Figure 3c**). We consider that when the linear flow rate is at 2.0 cm s^{-1}, the internal circulation flow is too weak to promote MMA diffusion to the dispersed aqueous phase, which gives "diffusion-limited" condition and results in a relatively slow rate of polymerization. When the linear flow rate is increased from 2.0 to 3.9 cm s^{-1}, the reaction regime changes from "diffusion-limited" to "reaction-limited" condition and the enhanced internal circulation flow continuously provides sufficient amount of MMA to the dispersed aqueous phase, which saturates the aqueous phase with MMA. Hence, the rate of polymerization increased with increasing the linear flow rate from 2.0 to 3.9 cm s^{-1} and then became almost constant over 3.9 cm s^{-1}. These results suggest that the internal circulation flow generated in a W/O slug flow intensify the rate of polymerization.

(Figure 3)

(Table 2)

It is well known that particle nucleation in soap-free emulsion polymerization takes place in the aqueous phase and the solvent quality of the aqueous phase can affect the characteristics of the polymerization as well as the resultant polymer particles [28]. To investigate whether increasing MMA solubility in the dispersed aqueous phase of the W/O slug affects the rate of polymerization, we performed the soap-free emulsion polymerization of MMA using a W/O slug flow in the presence of 20 vol% ethanol as a cosolvent in the dispersed aqueous phase. Before the experiment, we confirmed that the presence of ethanol in the dispersed aqueous phase up to 20 vol% did not affect the flow pattern in the microreactor. **Figure 4** shows the comparison of the soap-free emulsion polymerization of MMA using the W/O slug flow with and without 20 vol% ethanol. We found that the particle diameter in the presence of ethanol became larger than that in the absence of ethanol (**Figure 4a**). This is because ethanol in the aqueous phase decreases electrostatic repulsive forces between the prepared particles and causes the promotion of their coagulation [29]. Regarding monomer conversion, there was no significant difference in monomer conversion between the systems with and without ethanol, indicating that the addition of ethanol has a low impact on the rate of polymerization

(**Figure 4b**). On the other hand, we found that the M_w of PMMA particles in the presence of ethanol was considerably higher than that in the absence of ethanol when compared at each reaction time. Specifically, the M_w of PMMA particles in the presence of ethanol at 20 min was about 1,500 kg mol^{-1}, while that in the absence of ethanol was about 600 kg mol^{-1} (**Figure 4c**). We speculate that these results would be due to the effect of ethanol on the critical chain length of PMMA oligomers. Because ethanol is a good solvent for MMA, the addition of ethanol into the reaction medium increases the solubility of MMA in the dispersed aqueous phase, which makes the critical chain length of PMMA oligomers longer. The longer critical chain length of the PMMA oligomers reduce the required number of polymer molecules to form a single particle nucleus, which increases the amount of monomer to be incorporated in a single particle, thus resulting in PMMA with high molecular weight in a short reaction time, when compared with the case without ethanol. Based upon these results, we concluded that the addition of ethanol in the dispersed aqueous phase of W/O slug flow for the soap-free emulsion polymerization of MMA significantly increases the molecular weight of PMMA particles and that PMMA particles with million molecular weight is obtained in 20 min using this system.

(Figure 4)

(Table 3)

Conclusion

We developed a continuous flow process for the production of PMMA particles by soap-free emulsion polymerization using a W/O slug flow in a microreactor. Because of high heat/mass transfer efficiency in the W/O slug flow, the soap-free emulsion polymerization using the W/O slug flow showed higher polymerization rate than that using the conventional batch process. We also found that the increase of the linear flow rate of the slug flow or the addition of ethanol in the dispersed aqueous phase increased the particle diameter and the molecular weight of PMMA particles. Using the slug flow process, we succeeded in the continuous production of PMMA particles with high molecular weight (~ 1,500 kg mol^{-1}) in 20 min reaction time.

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Figure Captions

Figure 1 (a) Schematic image of the experimental setup for soap-free emulsion polymerization using a water-in-oil (W/O) slug flow. (b) A photograph of the W/O slug flow during polymerization at 70 °C. (c) Schematic image of particle formation in W/O slug.

Figure 2 Comparison of the characteristics of the soap-free emulsion polymerization of MMA using W/O slug flow and batch reactor regarding (a) particle diameter, (b) conversion of MMA and (c) weight-averaged molecular weight of PMMA. (d) SEM images of PMMA particles at different reaction times. The *CV* was defined as the ratio of the standard deviation to the average diameter. NA means not available.

Figure 3 Effect of the linear flow rate of a W/O slug flow on the soap-free emulsion polymerization of MMA (a) particle diameter, (b) conversion of MMA and (c) weight-averaged molecular weight of PMMA. (d) SEM images of PMMA particles prepared at different linear flow rates. The *CV* was defined as the ratio of the standard deviation to the average diameter.

Figure 4 Effect of the addition of ethanol to the aqueous phase on soap-free emulsion polymerization (a) particle diameter, (b) conversion of MMA and (c) weight-averaged molecular weight of PMMA. The linear flow rate was kept constant at 3.9 cm s^{-1}. (d)

SEM images of PMMA particles prepared with or without ethanol in the aqueous phase.

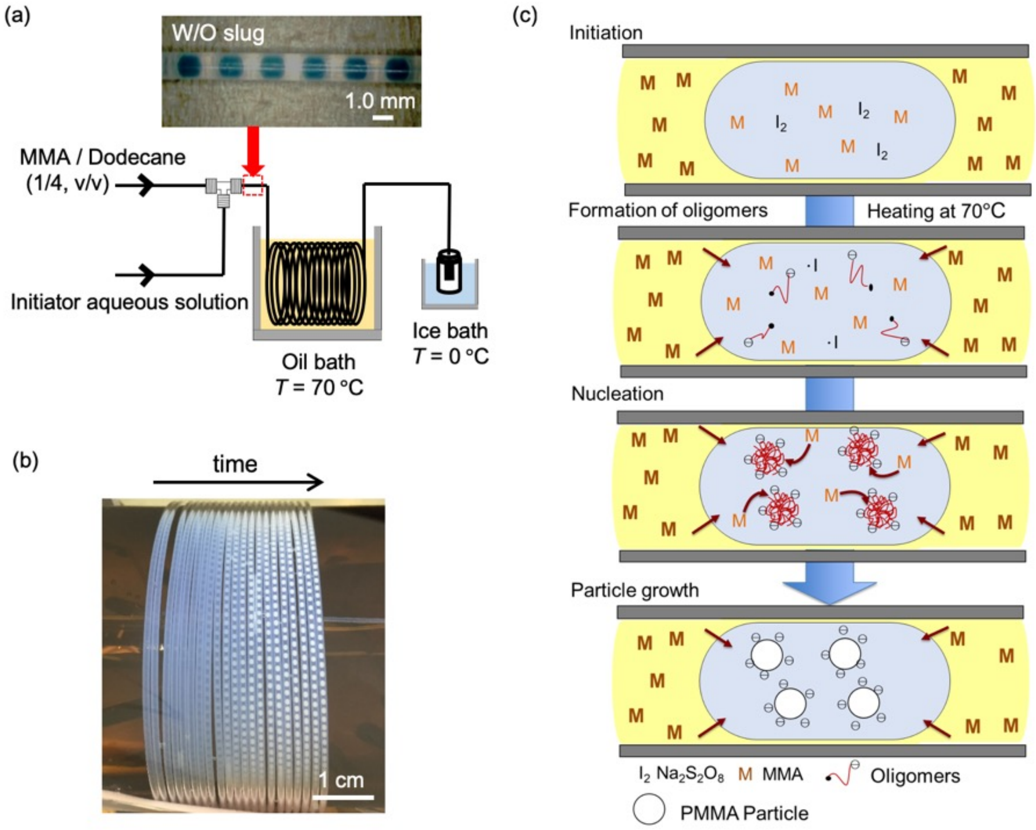
The *CV* was defined as the ratio of the standard deviation to the average diameter.

Table captions

Table 1 Characteristics of PMMA particles prepared using W/O slug flow and batch processes.

Table 2 Effect of the linear flow rate of a slug flow on the characteristics of PMMA particles prepared using a W/O slug flow.

Table 3 Effect of the addition of ethanol in the dispersed aqueous phase on the characteristics of PMMA particles prepared using a W/O slug flow.



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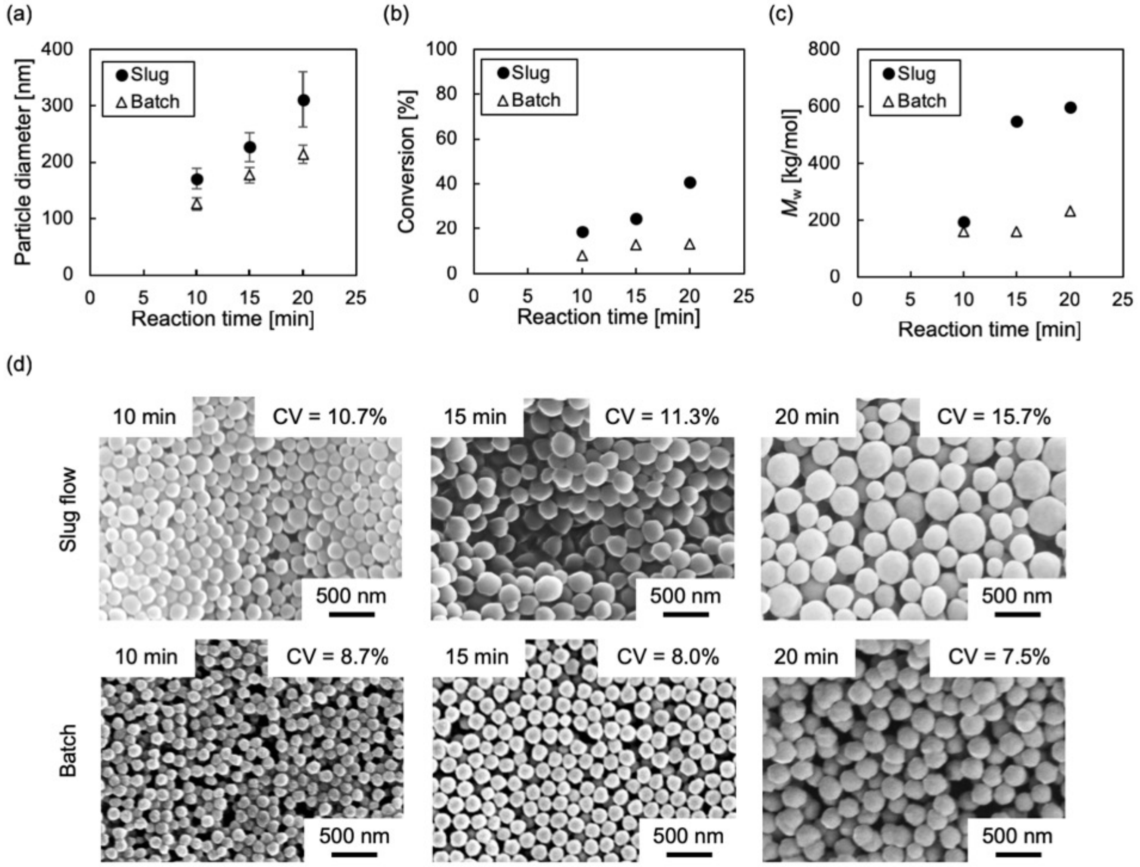

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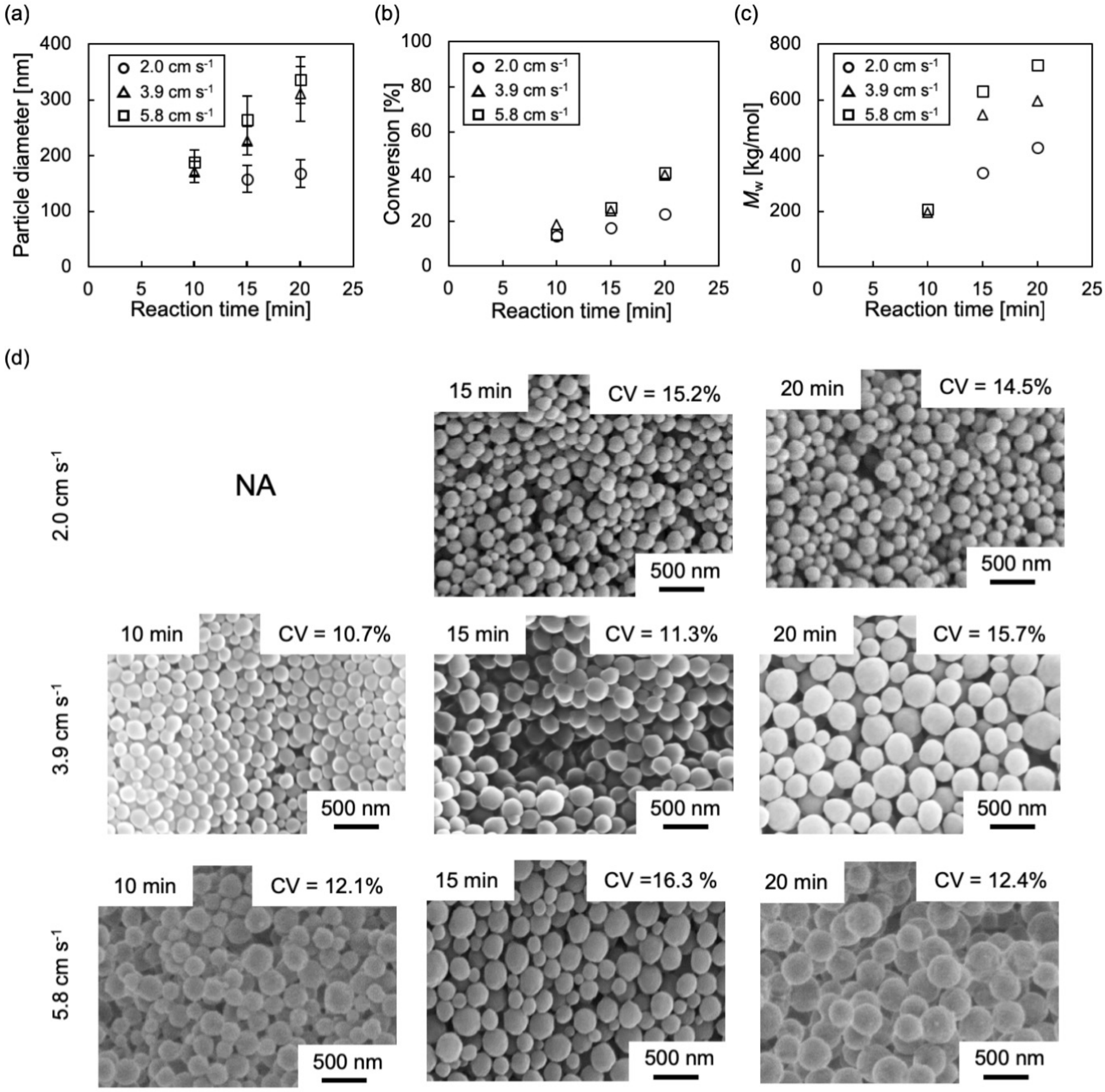

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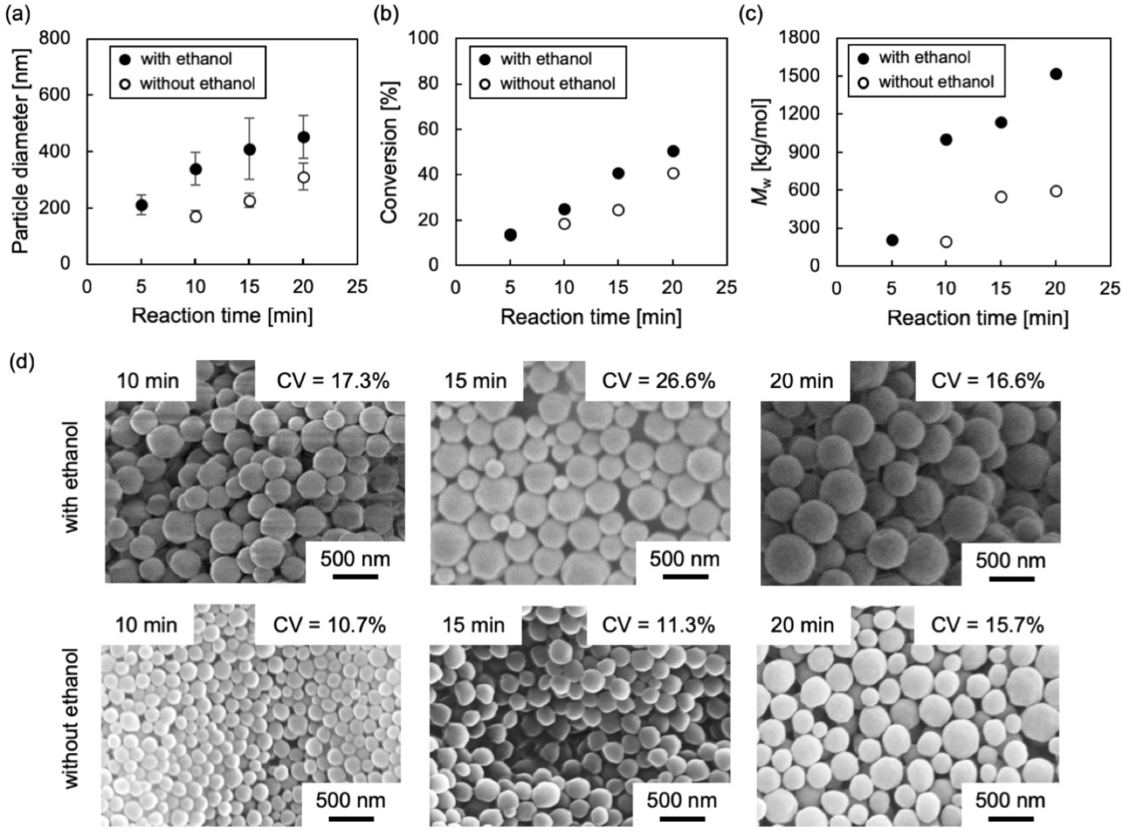

Figure 4 Effect of the addition of ethanol to the aqueous phase on the soap-free emulsion polymerization (a) particle diameter, (b) conversion of MMA and (c) weight-averaged molecular weight of PMMA. The linear flow rate was kept constant at 3.9 cm s^{-1}. (d) SEM images of PMMA particles prepared with or without ethanol in the aqueous phase. The *CV* was defined as the ratio of the standard deviation to the average diameter.

Table 1 Characteristics of PMMA particles prepared using W/O slug flow and batch processes.

Process	Time [min]	Diameter [nm]	*CV* [%]	Conversion [%]	M_w [kg mol^{-1}]	M_n [kg mol^{-1}]	$M_\mathrm{w}/M_\mathrm{n}$ [-]
Slug flow	10	171	10.7	18.6	195	129	1.5
Slug flow	15	227	11.3	24.7	546	310	1.8
Slug flow	20	311	15.7	40.8	596	303	2.0
Batch	10	126	8.7	8.1	159	101	1.6
Batch	15	177	8.0	12.8	159	91	1.8
Batch	20	214	7.5	13.1	232	148	1.6

Table 2 Effect of the linear flow rate of a slug flow on the characteristics of PMMA particles prepared using a W/O slug flow.

Linear flow rate [cm s^{-1}]	Time [min]	Diameter [nm]	*CV* [%]	Conversion [%]	M_w [kg mol^{-1}]	M_n [kg mol^{-1}]	M_w/M_n [-]
2.0	10	-	-	13.6	-	-	-
2.0	15	158	15.2	17.1	340	163	2.1
2.0	20	168	14.5	23.2	431	202	2.1
3.9	10	171	10.7	18.6	195	129	1.5
3.9	15	227	11.3	24.7	546	310	1.8
3.9	20	311	15.7	40.8	596	303	2.0
5.8	10	188	12.1	14.3	206	140	1.5
5.8	15	264	16.3	26.1	630	226	2.8
5.8	20	336	12.4	41.9	725	302	2.4

Table 3 Effect of the addition of ethanol in the dispersed aqueous phase on the characteristics of PMMA particles prepared using a W/O slug flow.

Solvent quality	Time [min]	Diameter [nm]	*CV* [%]	Conversion [%]	M_w [kg mol^{-1}]	M_n [kg mol^{-1}]	M_w/M_n [-]
With 20 vol% ethanol	5	210	16.5	13.5	208	152	1.4
With 20 vol% ethanol	10	338	17.3	25.0	1005	409	2.5
With 20 vol% ethanol	15	410	26.6	40.8	1136	425	2.7
With 20 vol% ethanol	20	453	16.6	50.8	1519	631	2.4
Without ethanol	5	-	-	13.9	-	-	-
Without ethanol	10	171	10.7	18.6	195	129	1.5
Without ethanol	15	227	11.3	24.7	546	310	1.8
Without ethanol	20	311	15.7	40.8	596	303	2.0

Table of Contents

Soap-free emulsion polymerization of methyl methacrylate (MMA) in a microreactor was demonstrated using a water-in-oil slug flow. It was found that the rate of polymerization in the slug flow was higher than that in the conventional batch process, which consequently resulted in polymer particles with million molecular weight in 20 min reaction time.