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Radical Polymerization Using Microflow System: Numbering-up of Microreactors and Continuous Operation

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Abstract:

A microchemical pilot plant for radical polymerization of methyl methacrylate (MMA) was constructed by numbering up eight microtube reactors. Continuous operation was accomplished for 6 days without any problems, indicating that microflow systems can be applied to relatively large-scale production of polymers.

1. Introduction

Recently, chemical processes using microreactors (reactors having micro structures)[1−3] have received significant interest because they are expected to make an innovative and revolutionary change for chemical synthesis by virtue of their advantages over conventional macroscale batch reactors, such as effective mass transfer and heat transfer,[4] extremely fast mixing,[5] and precise residence time control.[6]

Polymerization[7] is an important process for the synthesis of macromolecules, and polymerization using microreactors has received significant research interest.[8] We have reported controlled/living cationic polymerization using microsystems initiated by the "cation pool" method.[9] The combination of a highly reactive carbocationic initiator and an extremely fast mixing device enables cationic polymerization in a highly controlled manner even in the absence of the dynamic equilibrium between active and dormant species.

As for radical polymerizations, AXIVA group reported that the premixing of a monomer with an initiator using a micromixer is quite effective for radical polymerization of acrylates.[10] The amounts of high-molecular-weight polymer fractions decreased significantly by the use of the micromixer in the premixing process before being fed into a millimeter-scale tube reactor for polymerization. Beers and co-workers reported atom transfer radical polymerization by using a microchip system to achieve precise molecular weight distribution control.[11]

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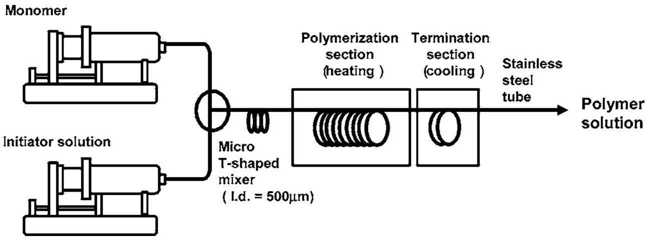


Figure 1. **Schematic diagram of a microflow system for laboratory-scale polymerization.**

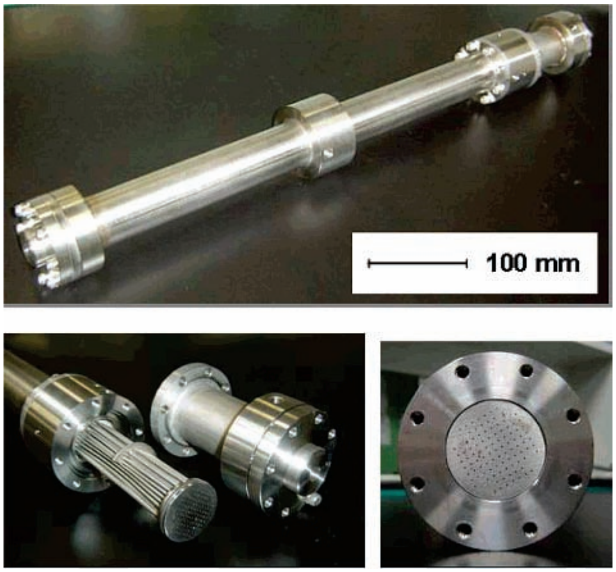
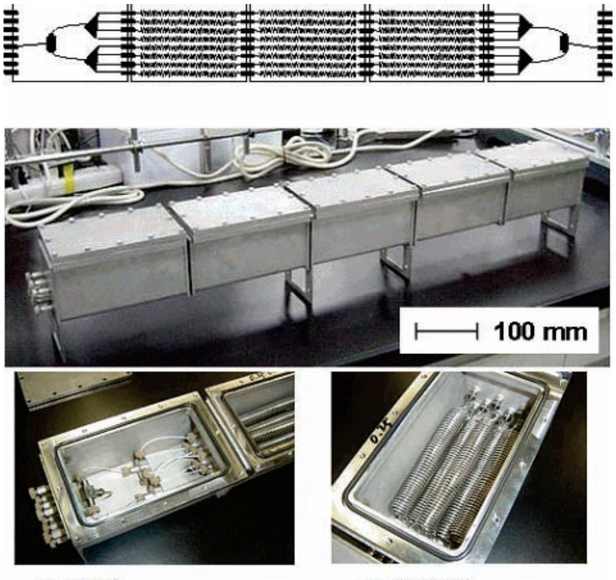


Figure 2. **Outside and inside of type-1 numbering-up reactor.**



#1 Shell
(Tube divided section)

#2~4 Shell
(Reactor section)

Figure 3. **Schematic diagram and pictures of type-2 numbering-up reactor.**

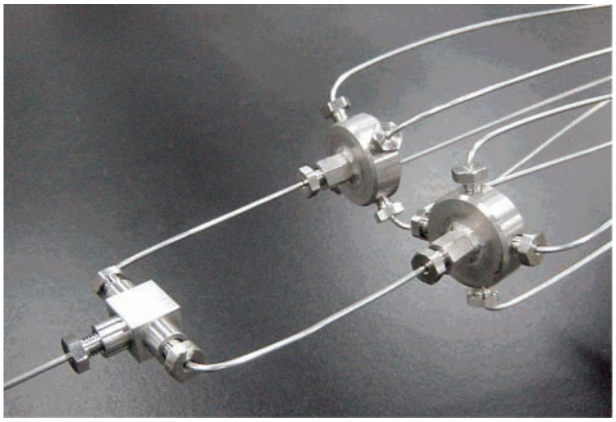


Figure 4. **Tube branch structure using simple couplers.**

Recently, we have reported that the use of microreactors leads to a significant improvement in the control of molecular weight distribution in free radical polymerization by virtue of superior heat-transfer efficiency.[12] Because free radical polymerization reactions are usually highly exothermic, precise temperature control is essential for carrying out free radical polymerization in a highly controlled manner. Thus, from both academic and industrial viewpoints, a major concern with free radical polymerization is the controllability of the reaction temperature.

A temperature-control problem often arises as a serious problem during the scale-up from a bench process to an industrial production. The use of conventional macroscale reactors and microchemical plants, in which the increase of the production scale can be achieved by the numbering up of microreactors without changing the size of each of them, is expected to solve this problem.[13] Thus, we initiated our project aiming at the large-scale production of polymers using numbering-up microreactors. Herein we report the results of this study.

2. Experimental Section

Materials. Methyl methacrylate (MMA) and butyl acrylate (BA) used in the laboratory were washed with 1 N NaOH three times, washed with water three times, and dried over Na_2SO_4. In the case of the polymerization in a pilot plant, MMA was used as obtained commercially without purification. 2,2-Azobis(isobutyronitrile) (AIBN) was used as obtained commercially. Argon gas was bubbled through monomers and toluene as solvent for 1 h before use.

GPC Analysis. GPC analysis was carried out with GPC-101 (Shodex) equipped with two LF-804 columns (Shodex) and an RI detector. The molecular weight (M_n) and the polydispersity index (PDI $= M_w/M_n$) of synthesized polymers were determined at 40 °C in THF using poly(methyl methacrylate) standard samples for calibration.

Laboratory-Scale Polymerization Procedure. Polymerization reactions were carried out using the microflow system reported in the previous paper,[12] which consists of two syringe pumps, a T-shaped micromixer, and a single microtube reactor. A schematic diagram of the system is shown in Figure 1. A monomer (neat, flow rate 0.2−4.0 mL/min) and a solution of AIBN in toluene (0.07−0.09 mol/L, flow rate 0.2−4.0 mL/min, 1 mol % based on the monomer)

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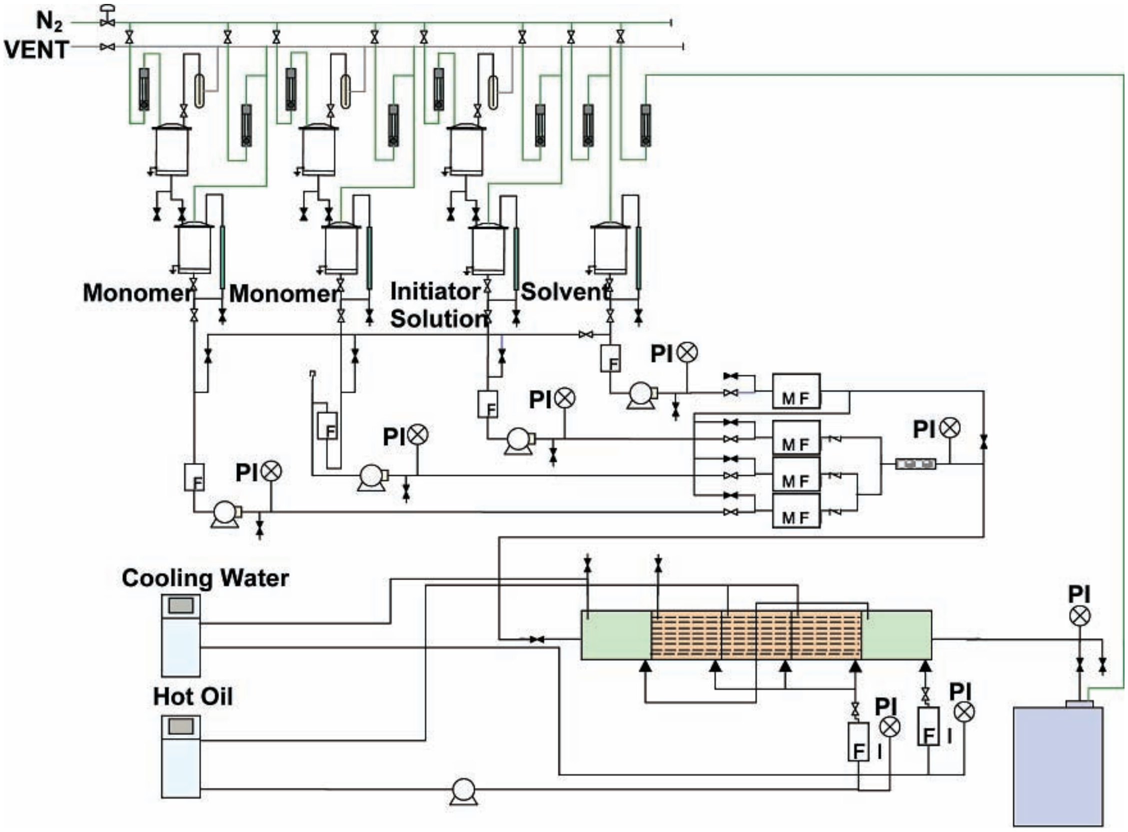

Figure 5. **Schematic diagram of the pilot plant.**

Table 1. **Polymerization of MMA and BA using the laboratory-scale single microtube reactor and type-1 numbering-up reactor**[a]

monomer	reactor type	reactor volume (mL)	monomer flow rate (mL/min)	AIBN flow rate (mL/min)	residence time (min)	yield (%)	M_n	PDI (M_w/M_n)
MMA	laboratory-scale single microtube reactor	1.8	0.9	0.9	1.0	12.4	8600	1.80
			0.4	0.4	2.3	25.9	8400	1.82
	type-1 numbering-up reactor	9.6	4.1	4.1	1.2	12.8	9300	1.84
			1.9	1.9	2.5	21.2	9800	1.85
BA	laboratory-scale single microtube reactor	1.8	0.6	0.6	1.5	70.7	33000	3.63
			0.3	0.3	3.0	84.5	22800	3.14
	type-1 numbering-up reactor	9.6	2.4	2.4	2.0	66.8	34500	3.21
			1.6	1.6	3.0	73.2	32000	3.26

[a] Polymerization temperature 100 °C, cooling temperature 0 °C, [MMA] = 9.4 mol/L (neat), [BA] = 7.0 mol/L (neat), [AIBN] = 0.094 mol/L (MMA conditions), 0.070 mol/L (BA conditions) in toluene, numbering-up reactor i.d. = 510 μm, 500 mm, 94 pieces, single tube i.d. = 500 μm, 9 m (cooling tube i.d. = 500 μm, 1 m)

were introduced into the T-shaped micromixer (stainless, i.d. = 500 μm), and the resulting solution was passed through a microtube (stainless, i.d. = 250 μm, 2 m) at room temperature in order to achieve complete mixing. Then, the solution was introduced into a microtube reactor (stainless, i.d. = 250−1000 μm, 2.5−10 m) heated at 100 °C, where the polymerization takes place. The polymerization was stopped by passing the reaction mixture through a microtube reactor (stainless, i.d. = 500−1000 μm, 0.5−1.0 m) cooled at 0 °C.

The obtained polymer solution was concentrated under reduced pressure at room temperature. The solid materials were analyzed by GPC.

Type-1 Numbering-up Reactor. A shell and tube microreactor shown in Figure 2 was developed to increase the throughput. The reactor consists of 94 microtubes (stainless, i.d. = 510 μm, 600 mm) in a shell (i.d. = 60 mm, 600 mm). The total volume of all of the microtubes is 9.6 mL. The shell is divided into two sections. Hot oil is introduced to

Table 2. **Polymerization of BA using the single microtube reactor and type-2 numbering-up reactor**[a]

reactor type	reactor volume (mL)	monomer flow rate (mL/min)	AIBN flow rate (mL/min)	residence time (min)	yield (%)	M_n	PDI (M_w/M_n)
single tube 500 μm ϕ	2.0	0.5	0.5	2.0	81.4	40900	2.98
		0.33	0.33	3.0	89.5	35000	2.71
		0.2	0.2	5.0	95.5	28400	2.74
single tube 1000 μm ϕ	2.0	0.5	0.5	2.0	71.3	43700	3.36
		0.33	0.33	3.0	79.4	37300	2.96
		0.2	0.2	5.0	86.3	29000	2.91
single tube 250 μm ϕ + 500 μm ϕ + 1000 μm ϕ	2.0	0.5	0.5	2.0	73.5	40500	2.44
		0.35	0.35	2.9	86.5	36300	2.48
		0.2	0.2	5.0	87.1	31500	2.57
type-2 numbering-up reactor 250 μm ϕ + 500 μm ϕ + 1000 μm ϕ	16.1	4.0	4.0	2.0	78.0	37000	2.26
		2.7	2.7	3.0	84.7	33600	2.44
		1.6	1.6	5.0	93.5	31000	2.61

[a] Polymerization temperature 100 °C, cooling temperature 0 °C, [BA] = 7.0 mol/L (neat), [AIBN] = 0.070 mol/L in toluene, single microtube reactor i.d. = 500 m, 10 m (cooling tube i.d = 500 μm, 0.5 m); single microtube reactor i.d. = 1000 μm, 2.5 m (cooling tube i.d. = 1000 μm, 0.5 m); single microtube reactor i.d. = 250 μm, 1950 mm + 500 μm, 1950 mm + 1000 μm, 1950 mm (cooling tube i.d. = 1000 μm, 0.5 m); type-2 numbering-up reactor (i.d. = 250 μm, 1950 mm + 500 μm, 1950 mm + 1000 μm, 1950 mm) × 8 pieces.

the first part of the shell (length = 500 mm), and a coolant is introduced to the second part (length = 100 mm).

Type-2 Numbering-up Reactor. Another shell and tube microreactor shown in Figure 3 was also developed. The reactor consists of five shells, which are coupled by tube connectors. The length of each shell is 178 mm, and the total length of the reactor is 904 mm. In the first shell, a single inlet tube branched into eight tubes under cooling conditions. Figure 4 shows the tube-branch structure that used simple couplers. Polymerization was carried out in shells 2 through 4 , in which eight coiled microtubes (stainless, i.d. = 250 μm, 500 μm, 1000 μm; length = 1950 mm) were placed. The microtubes were heated by hot oil circulating in the shells. In the final shell, the microtubes were combined into a single tube, and polymerization was terminated by cooling.

Pilot Plant for Continuous Operation. A pilot plant consisting of a T-shaped micromixer (i.d. = 250 μm) and a type-2 shell and tube numbering-up reactor was constructed. A schematic diagram of the pilot plant is shown in Figure 5. Polymerization was carried out in the microtubes. The inner diameters of the microtubes in the second, third, and fourth shells were 500, 500, and 1000 μm, respectively (the total volume of eight microtubes = 18.4 mL) Plunger pumps (Nihon-seimtsu-kagaku) were used for introducing the monomer (MMA, neat, 9.4 mol/L) from a 10-L stainless steel tank at the flow rate of 30 or 55 mL/h and for introducing an initiator solution (AIBN in toluene, 0.05 or 0.09 mol/L) from a 10-L stainless steel tank at the flow rate of 30 or 55 mL/h. The residence time was 18.4 or 10 min. The reaction temperature was automatically controlled at 100 °C by circulating hot oil in the shells, and the cooling temperature was also automatically controlled at 25 °C by circulating water in the shells. The product solution was introduced to a 10-L stainless steel tank. For the determination of the yield, molecular weight, and molecular weight distribution, aliquots of the product solution were taken and analyzed. Workup procedure was same as that for the laboratory-scale experiments described in the previous section.

3. Results and Discussion

Polymerization Using Type-1 Numbering-up Reactor. The radical polymerization of BA and MMA initiated by AIBN was carried out with type-1 numbering-up reactor (94 microtubes) described in the Experimental Section, and the results were compared with those obtained with a laboratory-scale single microtube system. The results are summarized in Table 1. The residence time was varied by changing the flow rate. The yield, molecular weight, and polydispersity index (PDI) for the polymerization of MMA in the type-1 numbering-up reactor were similar to those obtained with the single microtube reactor. In the case of the polymerization of BA, however, the yield obtained with the numbering-up reactor was smaller than that obtained with the single microtube reactor in the same reaction time.

The viscosity of the solution did not vary under the conditions of polymerization of MMA, in which the yield of the polymer was low. On the other hand, in the case of BA polymerization, the viscosity of the solution increased remarkably because the polymerization rate of BA was very fast. It seems reasonable to consider that the decrease of polymerization yield for BA in the numbering-up reactor could be attributed to the lack of flow uniformity. Some channels, presumably those located in the outer part of the reactor shell were clogged because of viscosity increase. Thus, the number of effective channels decreased, and the average residence time decreased, leading to the lower yield of the polymer.

Polymerization Using Type-2 Numbering-up Reactor. Uniformity of the flow rate is one of the most important factors for the design of numbering-up reactors. Therefore,

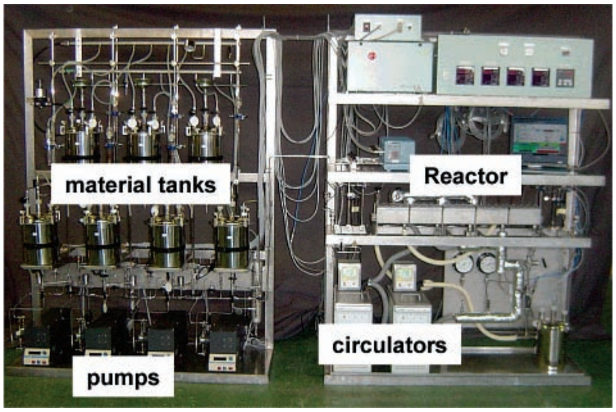

Figure 6. **Photograph of the pilot plant.**

Table 3. **Yield, molecular weight, and PDI of poly-MMA obtained in every channel in the type-2 numbering-up reactor**[a]

channel no.	yield (%)	M_n	PDI (M_w/M_n)
1	52	17900	1.68
2	50	17500	1.71
3	49	17000	1.73
4	50	17700	1.67
5	51	17900	1.66
6	46	17800	1.72
7	55	18400	1.66
8	54	18000	1.70

[a] Polymerization temperature 100 °C, cooling temperature 25 °C, [MMA] = 9.4 mol/L (neat), [AIBN] = 0.050 mol/L, flow rate = 30 + 30 mL/h, residence time = 18.4 min.

we designed and fabricated another numbering-up reactor (type-2) containing eight microtubes in order to attain the uniformity of the flow rate. The reactor has the following excellent features from a viewpoint of industrial application. First, the number of parallel microtubes is only eight, and the uniformity of the flow rate can be easily verified by measuring the outcoming flows if all of the microtube reactors are not combined into a single tube in the final shell. The second feature is that the inner diameter of the microtubes can be easily varied. Microtube reactors of different inner diameters can be used for the polymerization in each shell. Generally, high heat-transfer efficiency is needed at the early stage of the polymerization because the concentration of the monomer is high and a large amount of heat of polymerization is liberated at this stage. Microtubes of small inner diameter have excellent heat-transfer ability because of high surface-to-volume ratio. Such microtubes of small inner diameter, however, suffer from high pressure drop. Thus, it is reasonable to use microtube reactors of small inner diameter only at the early stage of the polymerization, and at the later stage of the polymerization microtubes of larger inner diameter should be used to minimize the pressure drop and to increase the reactor volume to attain high throughput. The third feature is the simplicity of the structure of the device. Complex fabrication is not required at all for the construction of the present reactor, leading to minimizing the cost of fabrication. It is also noteworthy that each microtube is easily replaced in the case of clogging.

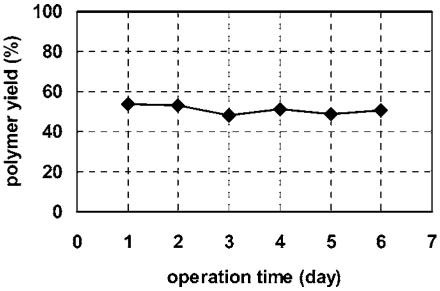

Figure 7. **Plots of the yield of poly-MMA against the operation time for 6 days continuous operation of the pilot plant. Polymerization temperature: 100 °C, cooling temperature: 25 °C, [MMA] = 9.4 mol/L (neat), [AIBN] = 0.050 mol/L, flow rate 30 + 30 mL/h, residence time = 18.4 min.**

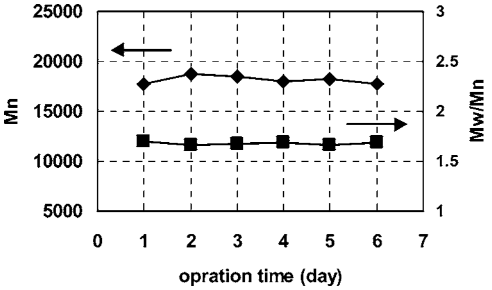

Figure 8. **Plots of the molecular weight and PDI of poly-MMA against the operation time for 6 days continuous operation of the pilot plant. Polymerization temperature: 100 °C, cooling temperature: 25 °C, [MMA] = 9.4 mol/L (neat), [AIBN] = 0.050 mol/L, flow rate = 30 + 30 mL/h, residence time = 18.4 min.**

The polymerization of BA was carried out with the type-2 numbering-up reactor, and the results are compared to those obtained with the single microtube system. The results are summarized in Table 2. The combination of microtubes (i.d. = 250 μm, 1950 mm × 8 + i.d. = 500 μm, 1950 mm × 8 + i.d. = 1000 μm, 1950 mm × 8, total reactor volume = 16.1 mL) was used. The polydispersity index (PDI) for the polymerization with the single microtube reactor of varied inner diameters (250 μm + 500 μm + 1000 μm) was smaller than those obtained with the single microtube reactors of fixed inner diameter (500 μm or 1000 μm). Presumably, high heat-exchange ability of the first microtube (250 μm) is responsible for controlling the early stage of polymerization, which may be highly exothermic. The later part of polymerization is not so exothermic because the monomer concentration is low. Therefore, microtubes of larger inner diameter are sufficient for controlling the polymerization. A large reactor volume of microtubes of larger inner diameter is advantageous because a relatively long residence time is needed for the completion of the polymerization. The yield and molecular weight and PDI for the polymerization of BA in the type-2 numbering-up reactor of varied inner diameter (8 microtubes) was similar to those obtained with the single microtube reactor of varied inner diameter. Thus, the type-2 numbering-up reactor did not suffer from the problem of the lack of flow uniformity, which was a significant problem in the case of the type-1 numbering-up reactor.

Continuous Polymerization Using the Pilot Plant. The most important technical point for commercialization of

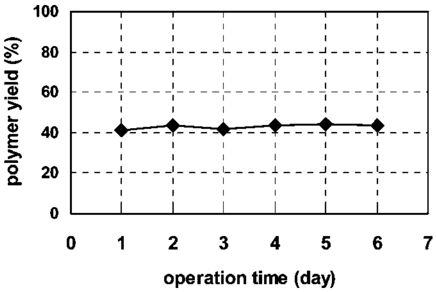

Figure 9. **Plots of the yield of poly-MMA against the operation time for 6 days continuous operation of the pilot plant. Polymerization temperature: 100 °C, cooling temperature: 25 °C, [MMA] = 9.4 mol/L (neat), [AIBN] = 0.094 mol/L, flow rate = 55 + 55 mL/h, residence time = 10.0 min.**

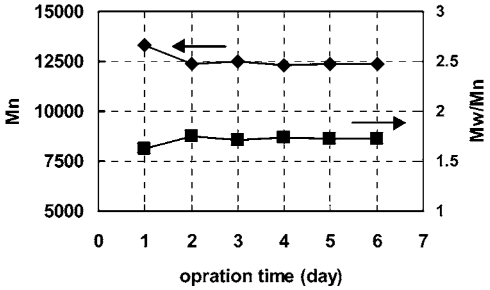

Figure 10. **Plots of the molecular weight and PDI of poly-MMA against the operation time for 6 days continuous operation of the pilot plant. Polymerization temperature: 100 °C, cooling temperature: 25 °C, [MMA] = 9.4 mol/L (neat), [AIBN] = 0.094 mol/L, flow rate = 55 + 55 mL/h, residence time = 10.0 min.**

microreactor polymerization is stable continuous operation without any troubles such as clogging. A pilot plant consisting of the type-2 numbering-up reactor was constructed. As shown in Figure 6, the width of the pilot plant was 3.5 m, and the depth was 0.9 m. The continuous operation of polymerization using the pilot plant was carried out for a week.

Polymerization of MMA was carried out using microtube reactors of varied inner diameter (i.d. = 500 μm, 1950 mm $\times$ 8 + i.d. = 500 μm, 1950 mm $\times$ 8 + i.d. = 1000 μm, 1950 mm $\times$ 8, total reactor volume = 18.4 mL).

The uniformity of the flow in eight tubes was examined by collecting samples from eight microtube reactors at the flow rate of 30 mL/h (MMA) + 30 mL/h (AIBN). The yield, molecular weight, and PDI of polymers synthesized in eight channels are shown in Table 3. Very similar values were obtained for all of the microtubes, indicating the uniformity of the flow.

Continuous operation was carried out for 6 days without increase of the pressure and the reactor temperature. The yield, molecular weight, and PDI of synthesized polymers obtained every 24 h are shown in Figures 7 and 8 and Figures 9 and 10. The total volume of fluid passed through the process was 10 L, and the weight of product was estimated 2.5 kg for a week.

The productivity can be increased by increasing the flow rate (55 mL/h + 55 mL/h). The total volume of fluid passed through the process was 19 L, and the weight of product was 4.0 kg for a week. Thus, it was proved that the continuous operation of polymerization with high productivity can be attained in the present pilot plant.

4. Conclusion

The results described above indicate that a microflow system consisting of several microtube reactors is quite effective for conducting radical polymerization. Precise temperature control by effective heat transfer, which is an inherent advantage of microflow systems, seems to be responsible for the effective control of the molecular weight distribution. Obtaining the data with the continuous operation of the pilot plant demonstrates that the microflow system can be applied to relatively large-scale production and speaks well of the potentiality of microchemical plants in the polymer industry.

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