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Free Radical Polymerization in Microreactors. Significant Improvement in Molecular Weight Distribution Control

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ABSTRACT: The thermal decomposition of a radical initiator, AIBN in a microreactor was examined. The plots of unchanged AIBN against the residence time fitted well to the calculated one based on the bath temperature, indicating the efficient heat transfer through the wall of the microreactor by virtue of a high surface-to-volume ratio. The effectiveness of the microreactor on the molecular weight distribution control was then examined. For the polymerization of butyl acrylate (BA), the polydispersity index (PDI) of the polymer obtained using the microreactor was much smaller than that obtained with a macroscale batch reactor. The result can be explained in terms of much higher heat removal efficiency of the microreactor compared with the macroscale batch reactor. For the polymerization of benzyl methacrylate (BMA) and methyl methacrylate (MMA), the effect of the microreactor on PDI was smaller than in the case of BA. For the polymerization of vinyl benzoate (VBz) and styrene (St), no appreciable effect of microreactor on PDI was observed. These experimental results indicate that the microreactor is quite effective to the molecular weight distribution control for highly exothermic free radical polymerizations (BA, BMA, and MMA) but that it is not so effective for less exothermic polymerizations (VBz and St).

Introduction

Free radical polymerization is an important process for the synthesis of macromolecules since free-radicals are compatible with a wide variety of functional groups, which are not compatible with ionic and metal-catalyzed polymerization.[1] It is important to note that the precise temperature control is essential for carrying out free radical polymerization in highly controlled manner, because free radical polymerization reactions are usually highly exothermic. Therefore, polymerization reactions in conventional macroscale bath reactors often suffer from inefficient heat removal and the lack of homogeneity of the reactor temperature, which eventually give rise to low level of molecular weight distribution control. Thus, a major concern with free radical polymerization is the controllability of the reaction temperature from both academic and industrial viewpoints.

Recently, chemical processes using microreactors (reactors having microstructures)[2,3] 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] Among these inherent advantages of microreactors, efficient heat transfer seems to be one of the most important features for free radical polymerization. Generally, the heat generation rate in polymerization increases in proportion to the reactor volume, while the heat removal capacity decreases with the increase of the reactor volume. Because the heat of polymerization is removed through the wall of the reactor, a wall-surface area/reactor-volume ratio, which decreases with the increase of the size of the reactor, plays a crucial role. Thus, in polymerizations in macroscale reactors, heat removal capacity often becomes a limiting factor. Therefore, the advantage of the polymerization in microreactors is obvious. As the reactor size decreases, heat transfer becomes faster and the temperature control becomes more efficient, leading to better control of molecular weight distribution (Figure 1).

It is important to note that the temperature control problem described above may arise as a serious problem during the scale-up from a bench process to an industrial production using conventional macroscale reactors. 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, are expected to solve this problem. The advantages of microreactors of easy modulation and the possibility of combining reactors in parallel promise a quick means for making chemical plants for large scale production.

It has been reported that the premixing using a micromixer is quite effective for radical[7] and anionic[8] polymerization of acrylates. The amount of high-molecular-weight polymer fractions decreased significantly by the use of the micromixer in premixing process before being fed into a millimeter-scale tube reactor for polymerization. There are only a few reports, however, on the polymerization in microreactors. Most of the reports concern with the formation of a solid polymer product in micro channels[9] or the synthesis of polymer particles.[10] Thus, we initiated our study on the solution phase free radical polymerization in a microreactor from a viewpoint of the control of molecular weight distribution, and report here our findings.

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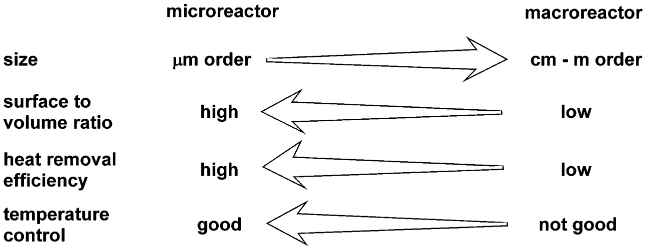

Figure 1. Characteristic features of microreactors and macroraeactors

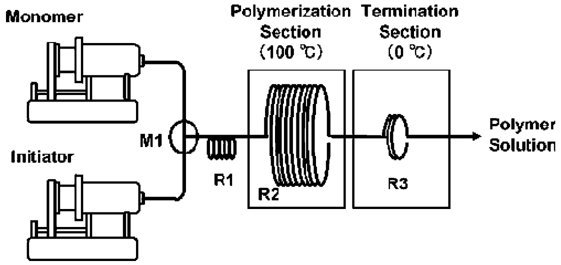

Figure 2. Microreactor system for polymerization. Key: **M1**, T-shape micromixer, **R1**, **R2**, and **R3**, microtube reactors.

Experimental Section

General Data. HPLC analysis was carried out with Shimadu LC−VP equipped with a CD-C18 column (Imtact) and UV detector. GPC analysis was carried out with Shimadu LC-10 equipped with a K-804L + K-805L column (Shodex) and an RI detector.

Materials. Butyl acrylate (BA), methyl methacrylate (MMA), and styrene (St) were washed with 1 N NaOH three times, washed with water three times, and dried over Na_2SO_4. Benzyl methacrylate (BMA) and vinyl benzoate (VBz) were filtered through an inhibitor remover disposable column (Aldrich) in order to remove a radical inhibitor. 2,2-Azobis(isobutylronitrile) (AIBN) was used as obtained commercially. Argon gas was bubbled through these monomers and toluene as solvent for 1 h before use.

Temperature Evaluation in a Microreactor. A solution of AIBN (0.02 mol/L) in toluene was passed through a microreactor (stainless tube, i.d. 500 μm × 1 m, thickness of wall = 540 μm) dipped in an oil bath (80 or 100 °C). The decomposition was stopped by cooling at 0 °C in a subsequent tube reactor. The flow rate was 0.2−1.0 mL/min. The decomposition of AIBN in the presence of MMA was carried out using a premixed solution of AIBN (0.02 mol/L) and MMA (2.0 mol/L) in toluene. The unchanged AIBN was analyzed by HPLC at 20 °C.

Polymerization in a Microreactor. As shown in Figure 2, a monomer (neat, flow rate 0.06−1.8 mL/min) and a solution of AIBN in toluene (0.03−0.05 mol/L, 0.06−1.8 mL/min, 1 mol % based on the monomer) were introduced into a T-shape micromixer **M1** (stainless, i.d. = 800 μm) and the resulting solution was passed through microreactor **R1** (stainless tube, i.d. 250 μm, 2 m) at room temperature in order to achieve complete mixing. Then, the solution was introduced to microreactor **R2** (stainless tube, i.d. 500 μm × 9 m, thickness of wall = 540 μm) heated at 100 °C (oil bath), where the polymerization takes place. The polymerization was stopped by cooling at 0 °C in microreactor **R3** (stainless tube, i.d. 500 μm × 1 m, thickness of wall = 540 μm).

For the polymerization of BA, MMA, and St, the obtained polymer solution was concentrated under reduced pressure at room temperature. The solid material was analyzed by GPC. For the polymerizatoin of BMA and VBz, the obtained polymer solution was mixed with methanol. The solid material thus precipitated was collected by filtration and analyzed by GPC.

Polymerization in a Macroscale Batch Reactor. The polymerization was carried out in a stainless steel vessel (i.d. = 10.2 mm × 20 cm, thickness of wall = 1.24 mm, 16.5 mL) under an atmosphere of argon at 100 °C. The polymerization was stopped by cooling of the vessel at 0 °C.

Table 1. Thermal Decomposition of AIBN in the Microreactor

	percentage of unchanged AIBN		
residence time (min)	bath temp 80 °C	bath temp 100 °C	bath temp 100 °C in the presence of MMA
0.2	99.2	94.8	95.7
0.5	99.6	91.5	92.8
1.0	99.8	90.7	87.1
2.0	99.2	81.1	81.1
5.0	97.5	63.6	63.0

Molecular Weight and Molecular Weight Distribution. The molecular weight (M_n) and the polydispersity index (PDI = M_w/M_n) were determined at 40 °C in $CHCl_3$ using a poly(methyl methacrylate) standard sample or a polystyrene standard sample for calibration.

Results and Discussion

Temperature Evaluation in a Microreactor. In the present study, it is important to evaluate the inside temperature of a microreactor, but this is not a trivial task. Physical methods for temperature measurement seem to be problematic. The introduction of a thermometer inside of the microreactor might change the nature of the flow, because the thermometer is usually relatively large in comparison with the volume of the microreactor. It is also important to note that the heat capacity of the thermometer and heat transfer through the thermometer cannot be ignored because the volume of the solution in the microreactor is very small. Therefore, we have searched for a chemical method for the measurement of the inside temperature of microreactors. Although a fluorescent molecular thermometer using temperature-induced phase transitions seems to be quite attractive,[11] it needs a transparent window on the wall of the microreactor for the optical measurement. Eventually, we found that the thermal decomposition of radical initiators serves as a good indicator of the temperature in the microreactor. Although it is impossible to measure the inside temperature directly, this method seems to be useful and convenient for the evaluation of the effective temperature in the microreactor under the polymerization condition.

Thus, a solution of AIBN in toluene was introduced to a microreactor (stainless tube, i.d. 500 μm), which was heated in an oil bath (80 or 100 °C), and the amount of unchanged AIBN in the outlet solution was determined by HPLC. The experiments were carried out with different flow rates, and the results are summarized in Table 1. We also carried out the experiment in the presence of MMA. In this case, MMA should polymerize, and the heat of polymerization might cause the temperature increase in the microreactor.

The percentage of unchanged AIBN is plotted against the residence time in Figure 3. The plots fitted well to the calculated values based on the bath temperature according to eq 1, which was reported in the literature,[12] indicating that the inside temperature of the microreactor was very close to the bath temperature.

$$k_d\,(\mathrm{s}^{-1}) = 1.58 \times 10^{15} \exp(-129/RT) \qquad (1)$$

The present results demonstrate superior heat transfer ability of the microreactor. It is also noteworthy that the temperature is controllable even in the case where

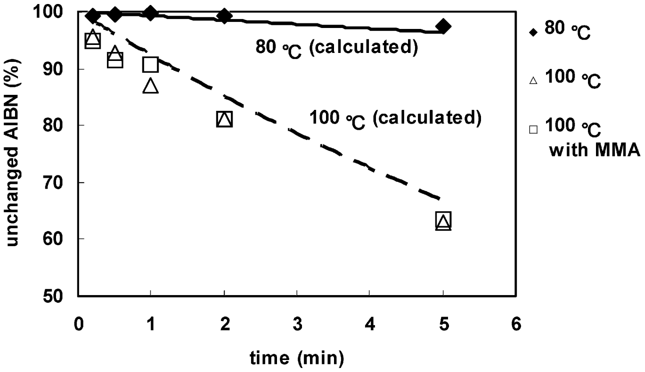

Figure 3. Thermal decomposition of AIBN in the microreactor.

Table 2. Polymerization of Butyl Acrylate (BA)

reactor	residence time or reaction time (min)	yield (%)	M_n ($\times 10^3$)	PDI (M_w/M_n)
microreactor	1.5	72.4	33.0	3.63
	2.0	86.5	26.1	3.59
	3.0	86.5	22.8	3.14
	4.0	89.6	20.8	3.16
	5.0	89.3	19.2	3.35
macro-scale batch reactor	2.0	50.0	27.1	212
	3.0	82.1	10.0	9.61
	3.5	86.0	9.3	10.0
	4.0	88.0	9.3	10.3

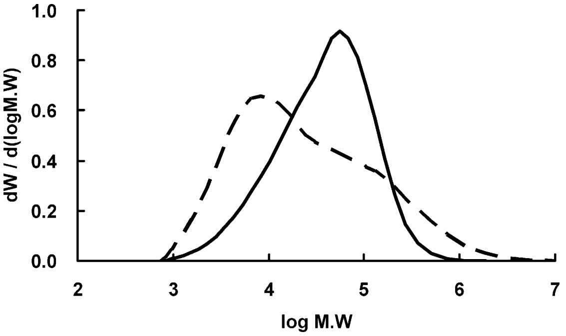

Figure 4. Molecular weight distribution of poly(butyl acrylate) produced by the microreactor polymerization and that produced by the macroscale batch reactor polymerization (residence time or reaction time was 4 min). Key: (—) polymer obtained in the microreactor; (- - -) polymer obtained in the macroscale batch reactor.

polymerization of MMA takes place simultaneously. The heat generated by the polymerization seemed to be efficiently removed through the wall of the microreactor.

Polymerization of Butyl Acrylate (BA). We first examined the polymerization of butyl acrylate (BA) in the microreactor. The experiments were carried out with different flow rates. The effect of flow rate on the polymerization is not simple. Not only the residence time but also other factors such as the nature of the flow may change with the flow rate. The results of the polymerization, however, were summarized only in terms of the residence time in order to avoid overcomplication. The polymerization was very fast and was almost finished within the residence time of 2−3 min (Table 2). The polydispersity index (PDI) for the polymerization in the microreactor was much smaller than that obtained by the polymerization in a macroscale batch reactor (Table 2). Figure 4 also shows the superior molecular weight distribution control in the microreactor. It is well-known that the polymerization of BA is highly exothermic. Significant increase of the temperature seems to be responsible for large PDI observed for the polymerization in a macroscale batch reactor. In the case of the polymerization in the microreactor, however, the efficient heat transfer through the wall of the reactor presumably diminished temperature increase caused by the polymerization, and consequently yielded the polymer of smaller PDI. Smaller local deviation of the temperature in the microreactor also seems to be responsible for narrower molecular weight distribution. Not only the local heterogeneity of temperature but also the cooling rate to stop the polymerization may also responsible for smaller PDI. A significant improvement of the molecular weight distribution might be ascribed to the suppression of transfer reactions, although more data should be accumulated before discussing the mechanism in detail.

Table 3. Polymerization of Benzyl Methacryalte (BMA)

reactor	residence time or reaction time (min)	yield (%)	M_n ($\times 10^3$)	PDI (M_w/M_n)
microreactor	3.0	42.8	15.6	2.05
	5.0	58.1	15.3	1.98
	7.5	70.7	14.1	2.03
	9.9	78.7	14.4	2.01
	12.0	83.1	13.2	2.06
macroscale batch reactor	5.0	27.8	25.7	2.71
	7.5	51.1	17.5	2.52
	10.0	65.9	14.3	2.71
	15.0	79.0	13.4	2.66

Table 4. Polymerizatoin of Methyl Methacrylate (MMA)

reactor	residence time or reaction time (min)	yield (%)	M_n ($\times 10^3$)	PDI (M_w/M_n)
microreactor	0.5	8.6	8.6	1.84
	1	14.1	8.6	1.80
	2	27.1	8.4	1.82
	5	51.1	8.5	1.83
	10	75	9.1	1.84
macroscale batch reactor	3	8.1	18	2.51
	5	21.9	13.1	2.21
	7.5	50.5	7.8	2.26
	10	68.5	7.0	2.26
	15	77.1	7.4	2.14

Polymerization of Benzyl Methacrylate (BMA). The polymerization of BMA was much slower than that of BA as shown in Table 3. Although the yield of the polymer increased with the increase of the residence time, the polymerization did not complete within 12 min. The PDI was much smaller than that of BA both in the microreactor and the macroreactor. Probably, temperature control for BMA polymerization was better than that for BA, even in the macroreactor, because heat generation for BMA polymerization seemed to be much less than that for BA polymerization. It is noteworthy that the PDI of the polymer obtained with the microscale batch reactor was smaller than that obtained with a batch reactor. The result also indicates superior heat removal ability of the microreactor in comparison with the macroreactor.

Polymerization of Methyl Methacryalte (MMA). The polymerization of MMA was similar to that of BMA. Although the yield of the polymer increased with the increase of the residence time, the polymerization did not complete within 10 min (Table 4). PDI was slightly smaller than that for BMA in both the microreactor and the macroscale batch reactor. Similar to the case of BMA, PDI of the polymer obtained with the microreactor was smaller than that obtained with the batch reactor.

Table 5. Polymerization of Vinyl Benzoate (VBz)

reactor	residence time or reaction time (min)	yield (%)	M_n ($\times 10^3$)	PDI (M_w/M_n)
microreactor	5.0	35.9	11.6	1.93
	7.5	46.1	10.9	2.05
	9.9	51.7	11.1	2.12
	15.0	69.3	10.8	2.16
macroscale batch reactor	5.0	11.3	14	1.83
	10.0	43.7	10.9	2.07
	12.5	53.7	10.5	2.13
	15.0	58.3	10.4	2.16

Table 6. Polymerization of Styrene (St)

reactor	residence time or reaction time (min)	yield (%)	M_n ($\times 10^3$)	PDI (M_w/M_n)
microreactor	5.0	14.4	4.7	1.74
	7.5	24.8	4.8	1.70
	9.9	27.3	5	1.76
	11.9	31.1	5.1	1.69
	15.0	34.2	5.3	1.74
macroscale batch reactor	5.0	5.7	5.6	2.05
	7.5	10.9	5.5	1.79
	10.0	18	5.3	1.76
	15.0	29.4	5.5	1.72
	20.0	38.6	5.6	1.70

Polymerization of Vinyl Benzoate (VBz). The polymerization of vinyl benzoate (VBz) was slower than the polymerizations of MMA and BMA. It is noteworthy that PDI of the polymer obtained in the microreactor was very similar to that obtained in the macroscale batch reactor. This result suggests that the superior heat removal ability of the microreactor is not important for the molecular weight distribution control. This is presumably because the heat generation of VBz polymerization is smaller and controllable even in the macroscale batch reactor for laboratory use.

Polymerization of Styrene (St). The polymerization of styrene was much slower than VBz. A significant amount of the monomer remained unchanged even after the residence time of 15 min. PDI of the monomer obtained in the microreactor was similar to that obtained in the macroscale batch reactor, indicating that the heat removal ability of the reactor is not important in this case.

The Rate of Polymerization and Effect of Microreactor. To get deeper insight into the effect of the microreactor on the molecular weight distribution control, the relative rates of the polymerization in the microreactor were studied. In Figure 5, the yield of the polymer was plotted against the reaction time (residence time) for each monomer. It can be easily seen from Figure 5 that the rate of polymerization increases in the order of St < VBz < MMA < BMA < BA. It is reasonable to consider that similar order is applicable for the heat of polymerization, because faster reactions are usually more exothermic.[13] The polymerization of BA is the fastest among the examined, and therefore BA polymerization seems to be the most exothermic among the examined. On the other hand, the polymerization of St is the slowest, and therefore the St polymerization is considered to be least exothermic. As a matter of fact, the effect of the microreactor on the molecular weight distribution control was found to be the greatest for the BA polymerization and the effect for St polymerization was not appreciable.

Continuous Operation. The fouling problems during continuous polymerization for a long period of time are important from a viewpoint of industrial application. Although the present reactions were carried out in a laboratory scale, the continuous polymerization was accomplished without suffered by significant pressure increase due to adhesion of polymers at the reactor wall for at lest several hours (BA, 70 min; BMA, 280 min; MMA, 130 min; VBz, 270 min; St, 360 min). Therefore, it is hoped that the present method can be used for industrial synthesis of polymers.

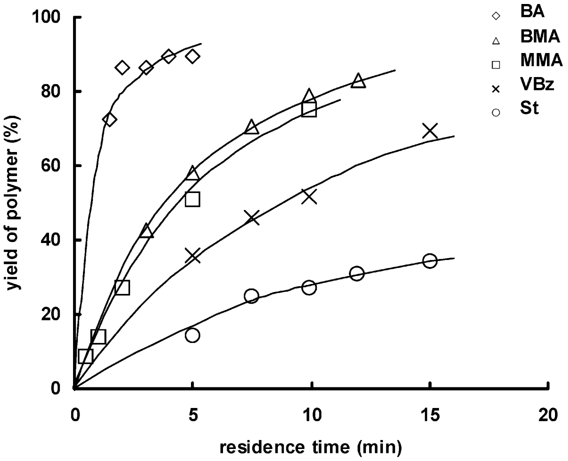

Figure 5. Relative rate of the polymerization in the microreactor.

Conclusion

A general conclusion from the experimental results described above is that microreactors are quite effective for molecular weight distribution control for highly exothermic free radical polymerization. The superior heat transfer ability of the microreactor in comparison with conventional macroscale batch reactors seems to be responsible for the high controllability. It is also noteworthy that the more exothermic the polymerization is, the more effective the microreactor is to the control of molecular weight distribution. The present observations speak well for the potentiality of microreactors in control of highly exothermic free radical polymerization.

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