Large-Scale Polycondensation of Lactic Acid Using Microwave Batch Reactors

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Abstract:

Chemical processes assisted by microwave heating are attractive energy-saving processes. We applied microwave heating to the polycondensation of lactic acid, which conventionally is known as a high-energy-consuming process. We herein studied the microwave-assisted reaction at scales ranging from several tens of milliliters to several tens of liters. Poly(lactic acid) polymers with average molecular weights exceeding 10,000 were obtained after 5 h of microwave heating. Analysis of the consumed microwave power also showed that the energy used by the polycondensation per mole of substrate was saved by scaling up the reaction.

1. Introduction

In recent years, microwave (MW) heating has attracted considerable attention of chemical engineers as a new heating tool for chemical reactions as an alternative to conventional conductive heating tools such as steam, electric heaters, and so on.[1] Because MW can directly heat materials via a dielectric interaction between materials and MW, MW heating has a high potential to strikingly accelerate the chemical reaction and drastically reduce the production energy when compared with the conventional conductive heating processes.

MW-assisted chemical synthesis was first reported by the groups of Gedye[2] and Giguere[3] in 1986. Thus far, more than 4,000 articles have been published in this field. MW heating especially at the 2.45 GHz frequency band has been widely applied to organic,[4–6] inorganic,[7] and polymer synthese,[8–10] and has demonstrated significantly reduced reaction times and improved product yields.

From the beginning of the MW chemistry in the middle of 1980s to the 1990s, the MW-assisted organic synthesis was exclusively carried out in domestic MW ovens. Typical domestic MW ovens are equipped with a 2.45 GHz magnetron as a MW generator and the irradiation power typically between 500 W and 1 kW. The organic syntheses with this household appliance were generally carried out in a beaker or a glass vessel with a reflux condenser, and the size of the reactant was at most around gram scale. After the 2000s, some MW reactors dedicated for organic synthesis have been released by CEM, Biotage, Milestone, Shikoku Instrumentation Co. Ltd., and others. These MW synthesizers were equipped with a temperature controller, a magnetic stirrer, a continuous power controller, etc. However, the reaction size was practically still gram- to at most a few hundred grams-scale.

By using these important small-scale results, scale-ups of reaction volumes have been designed for industrial uses to create a new industry "MW-assisted chemical industry" based on MW heating. Thus far, some MW heating instrument suppliers have developed larger MW synthesizers which were applicable to reactions of some liters. For example, CEM[11] released MARS,[12] a scale-up batch reactor; MicroSYNTH released by Milestone[13,14] was applicable for 5- and 4- L volume reactions. Voyager,[15] a continuous-flow process released by CEM, and FlowSYNTH, by Milestone, could treat reaction mixtures at 20 mL/min (1.2 L/h) and 100 mL/min (6 L/h), respectively. SAIREM reportedly put a MW-assisted flow-type reactor into a practical use to synthesize an ester compound, Laurydone.[5,16] This flow-type reactor was reported to consist of a 1 m³ raw material storage tank and a circulating pipeline for MW heating, and succeeded in reducing more than 60% of the production energy compared to that of a conventional heating process. These "large" reactors could be applicable to some industrial use only for chemicals of small production.

When MWs interact dielectric materials such as organic compounds, MW is absorbed by the material and leads to a rapid heating, depending on the dielectric properties (dielectric constant, ε', and dielectric loss, ε'') of the material.[17,18] The range in the material heated by MW is dependent on the penetration

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(11) CEM Corporation Home Page. http://cem.com/ (accessed May 2010).
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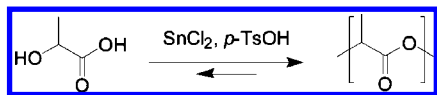(13) Milestone Inc. Home Page. http://www.milestonesci.com (accessed May 2010).
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Scheme 1

depth which is defined as the depth into a material where the power falls to one-half of its value. The penetration depth is another important parameter in the design of a MW experiment. An approximate relationship for penetration depth D_p when ε'' is small, is given by:

$$D_p \propto \lambda_0 \sqrt{\varepsilon'/\varepsilon''} \qquad (1)$$

where λ_0 is the wavelength of the MW. When 2.45 GHz MW is irradiated into water, the penetration depth is calculated only around 1 cm. Hence, a reaction conducted in a small flask in a domestic MW oven may not proceed to any appreciable extent when performed in a larger MW reactor.

As reported previously, we have found the MW irradiation drastically accelerated the polycondensation of lactic acid to produce poly(lactic acid) (PLA) in the gram-scale reaction size (Scheme 1).[19] However, there were some difficulties to estimate the energy efficiency in the MW reaction because of the small size of the reaction. We have also estimated the dielectric properties (ε' and ε'') under the real conditions of the MW-assisted polycondensation of lactic acid.[20] As a result, we confirmed that MWs penetrate into the PLA with depths of approximately 30 cm. On the basis of this result, we have designed a large-scale MW instrument. Here we examined polycondensation by using three different-scale MW reactors and analyzed the scale effects of the energy efficiency in the reaction.

2. Results and Discussion

2.1. Controllability of Reaction Temperature and Consumed MW Power As a Function of Heating Time. *Polycondensation of LA by Use of SMW-087 (μReactor).* The reaction temperature and total MW power profiles as a function of time obtained using μReactor are shown in Figure 1. From the start of heating to 8 min, MWs were irradiated at 700 W at maximum MW power to remove contained water and to increase the temperature. After 10 min from the start of heating, MWs were irradiated at 200−300 W to sustain reaction temperature at 180 °C.

Polycondensation of LA by Use of SMW-101. The reaction temperature and total MW power profiles as a function of time obtained using SMW-101 are shown in Figure 2. The ratio of incident MW power to reflected MW power was calculated to estimate the MW power consumed through heat and polycondensation (incident and reflected MW power are described in the Experimental Section). Dissipation of energy by reaction system P_{dis} is written by using incident P_{in} and reflected power P_{ref} as follows:

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(18) Metaxas, A. C.; Meredith, R. J. *Industrial Microwave Heating*; Peter Peregrinus Ltd.: London, 1983.
(19) Nagahata, R.; Sano, D.; Suzuki, H.; Takeuchi, K. *Macromol. Rapid Commun.* **2007**, *28*, 437.
(20) Nakamura, T.; Nagahata, R.; Suemitsu, S.; Takeuchi, K. *Polymer* **2010**, *51*, 329.

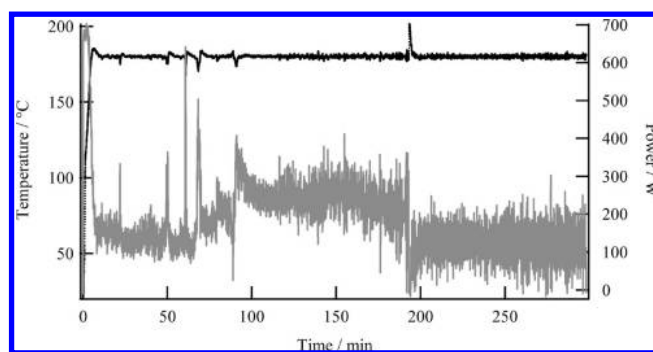$$P_{dis} = P_{in} - P_{ref} \qquad (2)$$

Ratio of the dissipation to the incident power is estimated by following equation.

$$\frac{P_{dis}}{P_{in}} = \frac{P_{in} - P_{ref}}{P_{in}} = 1 - \frac{P_{ref}}{P_{in}} \qquad (3)$$
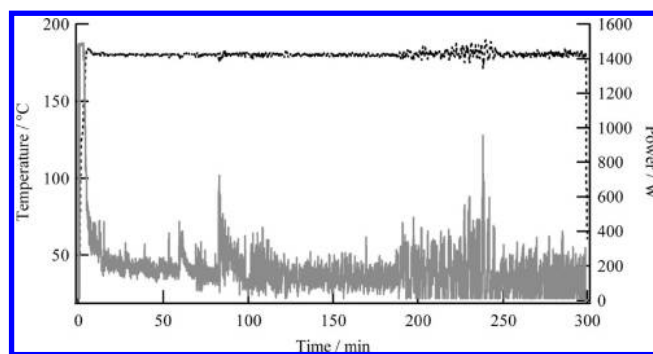
The ratio on percentage as a function of time is shown in Figure 3. MW power of 80−100% with dispersion was dissipated by the reaction system until 180 min of reaction time. After 180 min, the dispersion of the ratio increased. It may be that controllability of temperature decreased due to the decreased MW absorption property of the reaction system caused by progressing polycondensation.[20]

The reaction temperature reached 180 °C within 10 min and was held constant with high controllability. This high controllability is an advantage of MW heating. The MW power chart indirectly shows energy consumed by endotherm and reaction in the whole reaction system. From the start of heating until 10 min of reaction have elapsed, MW power was incident at 1400 W due to rising reaction temperature and endothermic energy by evaporation of contained water. After 90 min, operation of the vacuum was carried out. MW power temporarily increased to cover the decreasing temperature by endothermic energy of evaporation. The MW power involved in maintaining the temperature was approximately 200 W, which is 13% of the maximum total MW power.

Polycondensation of LA by Use of SMW-114. The reaction temperature and the total MW power profiles as a function of time obtained using SMW-114 are shown in Figure 4. In the

Figure 1. Temperature (black dots) and power (gray) profiles obtained using μReactor (0.06 mol % catalyst concentration).
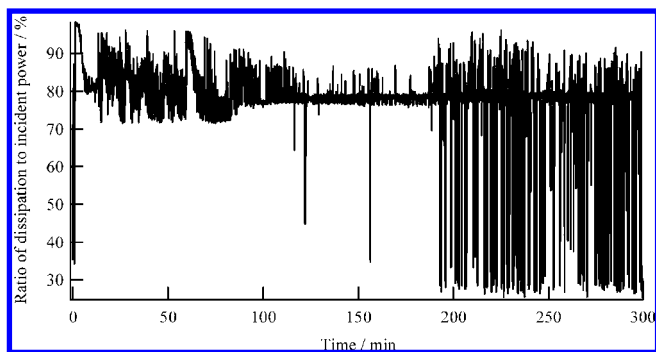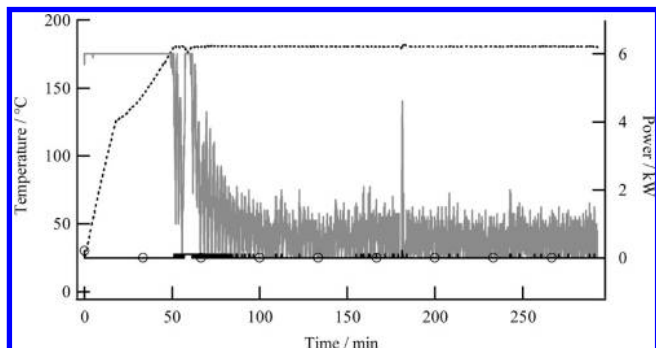

Figure 2. Temperature (black dots) and power (gray) profiles obtained using SMW-101 (0.06 mol % catalyst concentration).
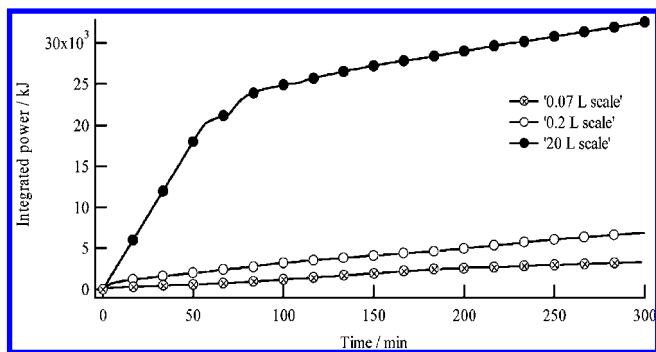
Figure 3. Ratio of dissipation power to incident power over time carried out by the use of SMW-101 (0.06 mol % catalyst concentration).
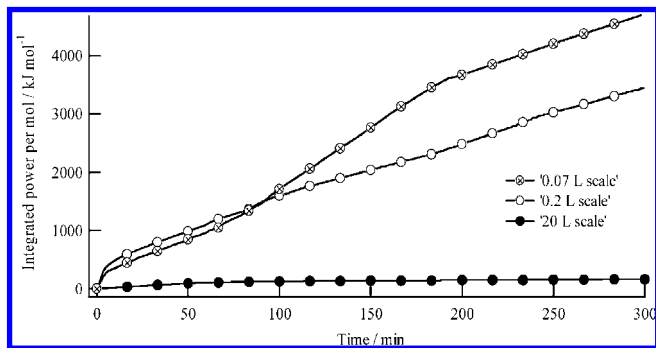

Figure 4. Temperature (black dots), incident power (gray), and reflected power (black circles) profiles obtained using SMW-114 (0.06 mol % catalyst concentration).

Figure 5. Total power consumed by MW irradiation as a function of time. Polycondensations were carried out using a 0.06 mol % catalyst concentration.

Figure 6. Total power consumption by MW irradiation per mole of raw lactic acid. Polycondensations were carried out using a 0.06 mol % catalyst concentration.

temperature profile, the rate of the temperature increase was slow and took over 60 min. This is caused by the large amount of evaporated water which originates from the aqueous lactic acid solution and from the polycondensation. The incident MW energy was insufficient to increase the temperature along the programmed temperature. After 60 min of reaction time, the reaction temperature was adequately regulated along the programmed temperature. SMW-114 could directly monitor incident and reflected MW powers. Analysis of these MW powers indicated that the MW power that was used for heating amounted to 100% of the total MW power. For this large-scale polycondensation, 6 kW of MW power was necessary to increase the reaction temperature and evaporate water. However, 1 kW of MW power, which corresponds to 17% of the maximum total MW power, was enough to irradiate the reactor to keep the reaction temperature at 180 °C under atmosphere pressure. After 75 min of reaction time, the vacuum began to operate in the reaction system, causing a decrease in the reaction mixture temperature. This temperature drop was concomitant with a vigorous boiling of the mixture due to the endothermic nature of evaporation. To prevent this drop in the temperature, MW energy was quickly supplied into the reaction mixture, stabilizing the reaction temperature. This quick MW energy supply enabled a precise reaction-temperature control.

Analysis of Efficiency of MW Power. We analyzed MW power, which is consumed in the reaction, versus reaction

volume. Power dissipation by MW energy is given by the following equation:[18]

$$P = \omega\varepsilon_0\varepsilon''E^2V \qquad (4)$$

where ω is the angular frequency, ε_0 is the permittivity of free space, E is the electric field strength and V is the volume. For generating heat by dissipation of MW energy, large-volume material adds an advantage under same the frequency, dielectric loss, and electric field strength. Namely, energy efficiency of MWs is increased by larger reaction volume.

The total MW power and the energy per mol of substrate consumed as a function of time are shown in Figure 5 and 6, respectively. The MW power generated by the magnetron was used to determine the consumption. Energy per mole of substrate consumed is calculated by dividing total energy by mole of raw lactic acid. The total MW power consumed by SMW-114 was greater than that for μReactor and SMW-101 because of reaction-scale differences. SMW-114 consumed 5.6 times as much MW power as SMW-101 for the entire reaction. However, when the MW power consumptions per mole were compared, SMW-114 used $^1/_{18}$th as much MW power as SMW-101 over 5 h. This analysis showed that the energy efficiency was enhanced by scaling up the reaction volumes.

We also confirmed that MW-assisted synthesis reduced energy consumption compared to conventional heating in case of polycondensation of lactic acid without catalyst. Energy consumption by MW heating was calculated to reduce ap-

Table 1. Large-scale MW-accelerated direct polycondensation of LA

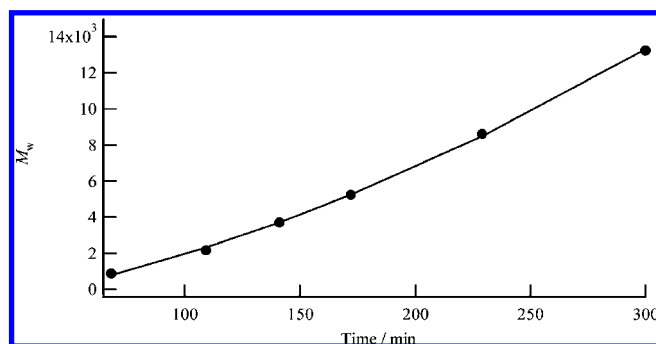| LA/L	catalyst/mol %[a]	heating time/h	press/Pa	M_w[b]	M_w/M_n[b]	yield/%	power consumption/ $\times 10^3$ kJ[c]	power consumption per mol/ $\times 10^3$ kJ mol^{-1}
0.07	0.06	5	1000	18 300	1.8	85	3.3	4.66
0.07	0.008	5	400	5 000	1.8	88	3.2	4.57
0.2	0.6	5	100	9 550	1.9	98	5.9	2.95
0.2	0.06	5	100	9 000	2.0	87	6.7	3.35
0.2	0.008	5	400	5 900	1.9	88	5.8	2.90
20	0.6	5	800	13 200	2.1	77	32.9	0.16
20	0.06	5	700	7 700	2.1	74	32.5	0.16
20	0.008	5	1000	3 600	1.7	72	31.2	0.16

[a] Catalyst: SnCl$_2$ and p-TsOH (1:1). [b] Molecular weight was measured using SEC (standard = poly(styrene)). [c] The power consumption was estimated from data recorded by a power monitor linked to the MW instruments.

proximately 70% compared to that in a conventional conductive heating process with an electric mantle heater.[21]

2.2. Chemical Characterizations of Resultant PLA. The chemical structures of polymers formed by the MW-assisted polycondensation were characterized by ^{1}H and ^{13}C NMR. The obtained polymers gave similar spectra. The ^{1}H and ^{13}C NMR spectra for a PLA synthesized using a 0.6 mol % catalyst concentration on a 20-L scale are mainly described as follows. The ^{13}C NMR spectrum was composed of three peaks located at 16.6, 68.9, and 169.5 ppm, which corresponded to the methyl, methyne, and carbonyl carbon atoms, respectively. These peaks were clearly distinct from the lactic acid peaks at 20.2, 66.6, and 179.6 ppm and from the lactide peaks at 15.7, 72.3, and 167.6 ppm. The ^{1}H NMR spectrum of the obtained polymer also gave two signals for PLA at 1.6 and 5.2 ppm, which corresponded to methyl and methylene hydrogen atoms, respectively. These were clearly distinct from the lactic acid signals at 1.5 and 4.4 ppm and from the lactide signals 1.7 and 5.1 ppm, respectively.

The reaction conditions, the average molecular weight of the resultants, and the consumed MW powers are listed in Table 1. The MW power consumed depended on the reaction volume, but not on the amount of catalyst used. The minimum pressure of SMW-101 was 100 Pa because of the high airtightness of the reactor structure. On the other hand, the minimum pressure of SMW-114 in the reaction system was 700 Pa. The lower airtightness of SMW-114 is due to the structure of the reactor as a separable flask. In addition, with a reaction volume of approximately 20 L, SMW-114 has a higher vapor pressure than SMW-101 and μReactor which have reaction volumes of approximately 0.2 and 0.07 L, respectively. This may cause a stronger vacuum in SMW-114 than in SMW-101.

By using SMW-101 and SMW-114, PLA polymers with average molecular weights of approximately 10,000 were obtained with a 0.6 mol % catalyst concentration. The average molecular weights of the obtained polymers increased with increasing catalyst concentrations. An increase in the average molecular weight of PLA as a function of heating time on a 20-L scale is shown in Figure 7. The average molecular weight increased with prolonged reaction times. After 5 h of reaction, the average molecular weight had not reached a saturation point. Beyond 5 h of heating, PLA polymers with higher molecular weights are expected.

(21) AIST Home Page. http://www.aist.go.jp/aist_e/latest_research/2009/20091216/20091216.html (accessed May 2010).

Figure 7. Average molecular weight (M_w) as a function of heating time. Polycondensation was carried out on a 20-L scale and used a 0.6 mol % catalyst concentration.

3. Conclusions

PLA was synthesized by MW-assisted polycondensation at 0.07-, 0.2-, and 20-L scales. At these reaction scales, PLA with average molecular weights of approximately 10,000 were obtained using MW heating for 5 h. The percentages of incident MW power used for heating at the 0.2 and 20 L scales, were 80% and 100%, respectively. The total incident MW power per mole consumed by the 20-L scale reaction decreased to $^1/_{18}$th of its value for the 0.2-L scale reaction. Our results suggest that scaling up MW heating processes saves energy for chemical production.

4. Experimental Section

4.1. MW Heating System. In this study, we used three types of MW instruments, SMW-087, SMW-101, and SMW-114, with different reaction sizes as shown in Table 2. These MW instruments were basically designed by Shikoku Instrumentation, Co. Ltd.

The SMW-087, commercially named as μReactor, is a multimode MW instrument with a 2.45 GHz magnetron (max power 700 W) and 21.5 L cavity, but not an impedance control system (Figure 8). We used a glass reaction vessel in the polycondensation. Its maximum reaction volume is 70 mL.

Polycondensation of lactic acid proceeds with dehydration under an equilibrium reaction condition. We have already reported that reducing reaction pressure was strikingly effective to accelerate the polycondensation of lactic acid and to enhance the molecular weight of the PLA.[19] However, in general, MW often discharges a MW plasma which damages the reactants under a reduced pressure lower than around 3000 Pa. Here we could prevent MW from discharging even under reduced

Table 2. Characteristics of the multimode MW reactors

	SMW-087 (μReactor, specialized in polycondensation)	SMW-101	SMW-114
cavity size/W mm × D mm × H mm (volume)	320 × 320 × 210 (21.5 L)	500 × 460 × 300 (69 L)	750 × 750 × 650 (366 L)
max. reaction volume	70 mL	300 mL	30 L
max. output power (W)	700 (1 magnetron)	1500 (1 magnetron)	6000 (1 magnetron)
impedance matching	−	three stub	E-H tuner
temperature controller	fiber-optic thermometer (1 position)	fiber-optic thermometer (1 position)	fiber-optic thermometer (2 positions)
max reaction temperature (°C)	250	400	250
min pressure (without reagent) (Pa)	30	30	100
extra control	temperature control by PID and power constant control		

pressure conditions lower than 30−3000 Pa by designing the reaction cavity to precisely control the distribution of the electromagnetic field of MWs in the reaction cavity.

The SMW-101 has a cylindrical heavy-wall glass reaction vessel placed in a 69-L cavity made of stainless steel. Its maximum reaction volume is 300 mL (expandable to 500 mL), and the maximum MW output power is 1500 W at 2.45 GHz. Impedance matching is carried out using a three-stub tuner. The top of the cylindrical vessel is closed by a stainless steel cover perforated with five holes, allowing overhead stirring, temperature measurements, gas injection, and vacuum pumping to be carried out. The maximum reaction temperature is 400 °C. This vessel allows reactions under vacuum to be carried out without discharge plasma. Vacuum conditions correspond to a 100 Pa minimum pressure. Pictures of SMW-101 are shown in Figure 9.

With a 366 L maximum cavity size, SMW-114 is a bench-scale MW reactor in anticipation of a pilot plant (Figure 10). Its maximum reaction volume is 30 L. Its maximum MW power output is 6000 W. Impedance matching is carried out using an automated E-H tuner. The reaction vessel is a five-neck separation flask equipped with a bottom outlet which is used to extract the resulting polymer. Overhead stirring, temperature and pressure measurements, and vacuum pumping are carried out through these necks. This vessel allows reactions under vacuum to be carried out without discharge plasma. Vacuum conditions correspond to a 100 Pa minimum pressure.

The SMW-101 and SMW-114 are consisted of components shown in Figure 11. A magnetron is powered by an electric source to generate MW radiation. The MW power generated is set as the

Figure 8. Picture of the *μ*Reactor showing the entire instrument.

total MW power. The generated MW radiation passes through a waveguide and is input into a cavity which comprises a heated target. The MW energy is used for heating and for chemical reactions. Some MW energy returns to the magnetron. These reflected MWs are driven to a load by a circulator to protect the magnetron from heat damage. Forward and reflected MW energies, which set the incident and reflected MW powers, respectively, are detected by power monitors and recorded by a PC. Differences between the incident and the reflected MW powers are used to determine heating and reaction energies. For high-efficient heating this reflected MW power is suppressed by using a tuner.

4.2. Polycondensation of Lactic Acid. A 90% aqueous lactic acid solution (LA) was purchased from Musashino Chemical Laboratory, Ltd. and used as received. Tin(II) chloride ($SnCl_2$) and *p*-toluenesulfonic (*p*-TsOH) acid were purchased from Wako Pure Chemical Industries, Ltd. These reagents were used as received.

A typical experiment using μReactor was carried out as follows. LA (0.7 mol), $SnCl_2$ (0.42 mmol), and *p*-TsOH (0.42 mmol) were charged in a glass tubular reaction vessel, and the vessel was placed in the cavity of μReactor. Reaction temperature of the LA mixture was increased from room temperature to 180 °C in 5 min and then kept at that temperature for 55 min under atmospheric pressure. Then the pressure was gradually decreased from atmospheric pressure to 1000 Pa in 30 min, and was additionally heated at 180 °C for 240 min under vacuum at 1000 Pa. Reaction temperature and pressure were measured using a fiber-optic thermometer (AMOTH FL-2000, Anritsu) and a Pirani gauge (PG-D5A, Sato Vac Inc.), respectively. Temperature, vacuum, and MW power were recorded with a PC by use of a NI 9215 with BNC (National Instruments Co.)

A typical experiment using the SMW-101 MW reactor was carried out as follows. LA (2 mol), $SnCl_2$ (12 mmol), and *p*-TsOH (12 mmol) were put into a cylindrical reaction vessel, and the vessel was placed in the cavity of SMW-101. Reaction temperature of the LA mixture was increased from room temperature to 180 °C for 5 min and then kept at that temperature for 55 min under atmospheric pressure. Then the pressure was gradually decreased from atmospheric pressure to 100 Pa in 30 min and was additionally heated at 180 °C for 240 min under 100 Pa. Reaction temperature and pressure were measured using a fiber-optic thermometer (AMOTH FL-2000, Anritsu) and an absolute pressure transmitter (KL79, Nagano Keiki Co., Ltd.), respectively. Temperature, vacuum, and

Figure 9. Pictures of the SMW-101 MW reactor showing the entire instrument (left) and the reaction cavity (right).

Figure 10. Pictures of the SMW-114 MW reactor showing the entire instrument (left) and the reaction cavity (right).
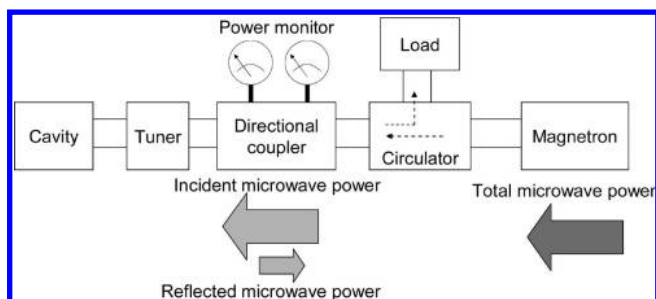

Figure 11. Diagram of the MW heating system components.

incident and reflected MW power were recorded with a PC by use of a R1M-GH (M-System Co., Ltd.).

A typical experiment using the SMW-114 MW heating system was carried out as follows. LA (200 mol), SnCl₂ (1.2 mol), and *p*-TsOH (1.2 mol) were put into a five-neck separation reaction vessel loaded in the cavity of SMW-114. Reaction temperature of the LA mixture was increased from room temperature to 180 °C in 60 min and kept at 180 °C for 15 min under atmospheric pressure. Then the pressure was gradually decreased to 800 Pa in 30 min and was additionally heated at 180 °C for 225 min at 800 Pa. Reaction temperature and pressure were measured using a fiber-optic thermometer (Reflex, Neoptix) and a vacuum manometer, respectively. Temperature

and incident and reflected MW powers were recorded with a PC by use of a NR-500 interface (Keyence).

4.3. Characterizations. Molecular weights of the obtained polymers were measured by the use of a size-exclusion chromatograph (SEC) system (Tosoh Bioscience 8020 SEC series) equipped with two columns (K-805 L, K-802; Shodex) using poly(styrene) as a standard. The temperature of the column oven was set at 40 °C, and chloroform was used as an eluent.

The resulting polymers were analyzed by use of ^{1}H NMR and ^{13}C NMR spectroscopy. NMR spectra were recorded with an AVANCE 400 spectrometer (Bruker Co.) using tetramethylsilane (TMS) as internal standard in CDCl₃.

Supporting Information Available

This material is available free of charge via the Internet at http://pubs.acs.org.