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**Microwave-Assisted Solution Polycondensation of L-Lactic Acid Using a Dean-Stark Apparatus for a Non-thermal Microwave Polymerization Effect Induced by the Electric Field**

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**Abstract:** We examined the solution polycondensation of L-lactic acid (L-LA) in xylene catalyzed by Sc(OTf)<sub>3</sub> using a Dean-Stark apparatus under various microwave power conditions (100–400 W). At the optimum irradiation power (300 W) and 3 M L-LA, we obtained poly(L-lactic acid) (PLLA) with a weight-average molecular weight ( $M_w$ ) of  $11.6 \times 10^3$ . Using 1.0 mol% SnCl<sub>2</sub> as the catalyst and multi-mode irradiation, the largest PLLA ( $M_w = 46.7 \times 10^3$ ) was obtained, which is an  $M_w$  greater than that obtained by conventional heating at the same temperature. We also performed microwave-assisted polycondensation of L-LA using a single-mode microwave cavity that separates microwave electric and magnetic fields. The PLLA  $M_w$  values decreased as the irradiation power of the magnetic field increased. Conversely, PLLA with an  $M_w > 10,000$  was obtained by increasing the electric-field power despite using the same conditions. The results indicate the existence of a non-thermal microwave effect induced by an electric field.

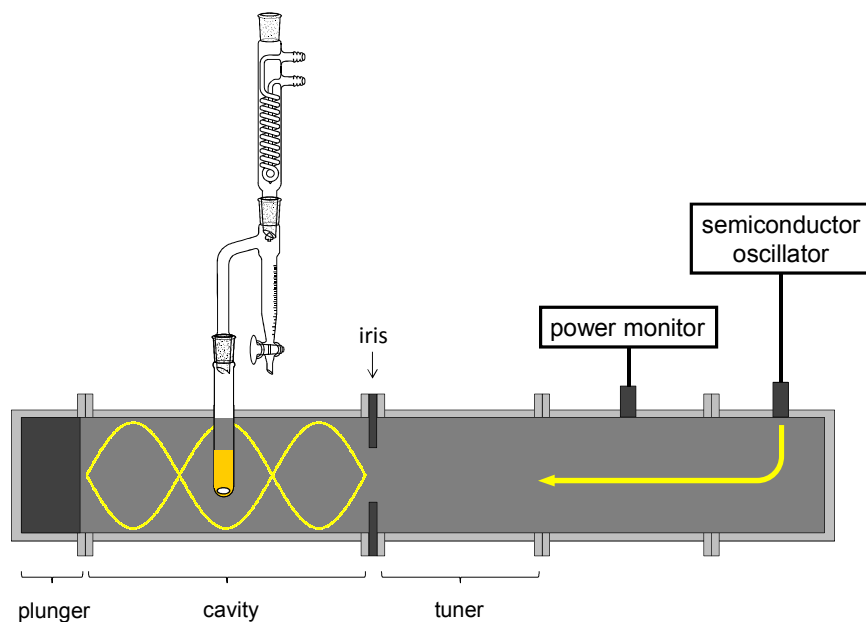
## Introduction

Because of increasing concerns about damage to the environment, the development of new, eco-friendly chemical reactions and materials are being pursued. Aliphatic polyesters have attracted much interest as environmentally benign, biodegradable polymers. Poly(L-lactic acid) (PLLA) is biocompatible and exhibits the same excellent mechanical performance as those of petroleum-based aliphatic polyesters.<sup>1</sup> Currently, PLLA is produced industrially by the ring-opening polymerization of L-lactide, a cyclic dimer of L-lactic acid (L-LA).<sup>2</sup> However, preparation of L-lactide involves two reactions: the condensation of L-LA to oligo(LA), followed by successive ring-closing depolymerizations of oligo(LA) to form L-lactide. Therefore, there have been many attempts made to produce PLLA with a large weight average molecular weight ( $M_w$ ) by a single-step, direct polycondensation of L-LA. Previously, we reported that scandium trifluoromethanesulfonate [ $\text{Sc}(\text{OTf})_3$ ] and scandium trifluoromethanesulfonimide [ $\text{Sc}(\text{NTf}_2)_3$ ] were effective for a one-step dehydration polycondensation of L-LA<sup>3</sup> in the same manner as the syntheses of other aliphatic polyesters.<sup>4</sup> Additionally, Takeuchi and coworkers reported that PLLA with an  $M_w$  of 16,000 could be produced by a single-step direct polycondensation of L-LA in conjunction with microwave irradiation and that the reaction time using those conditions was shortened considerably compared with a conventional polycondensation at the same temperature.<sup>5</sup>

Recently, microwave-enhanced reactions of organic compounds have attracted much attention<sup>6</sup> because, as first reported in 1986,<sup>7,8</sup> irradiation shortens the reaction times. Notably, shorten polymerization times decrease the amounts of by-products, which improves product yield and/or product chemoselectivity (reviewed in refs.<sup>9-11</sup>). Microwave irradiation has been successfully incorporated into chain polymerization procedures—e.g., radical polymerization of methacrylate,<sup>12</sup> anionic polymerization of acrylamide,<sup>13</sup> ring-opening cationic polymerization of 2-oxazoline derivatives,<sup>14</sup> and ring-opening polymerization of cyclic esters,<sup>15</sup>—and into step-growth polymerization procedures—e.g., polycondensation of diols with dicarboxylic acids<sup>16</sup> and polyaddition of dialkynes with diazido via *in situ* azidation of dibromo compounds.<sup>17</sup> The exponentially increasing number of publications concerning

microwave irradiation for polymer syntheses indicates the remarkable interest in and effectiveness of this technique.<sup>18-20</sup> Most of the aforementioned studies are characterized by spectacular polymerization accelerations as a consequence of the heating rate, which cannot be reproduced by classical heating. However, some researchers have postulated the existence of a so-called “microwave effect” that is unrelated to a microwave-induced temperature increase.<sup>9-11</sup> For example, Tompsett and coworkers<sup>21</sup> have proposed a number of scenarios that do not incorporate a heating effect to account for the observed rate increases and Zetterlund and Perrier performed *in silico* experiments to probe the effect of microwave irradiation on the rate enhancement observed for the reversible addition–fragmentation chain-transfer radical polymerization of styrene.<sup>22</sup> We also suggested that a non-thermal microwave effect might affect the rates of polycondensation reactions<sup>16</sup> and that the more favorable  $\Delta G^\ddagger$  values associated with the microwave-assisted polymerizations of  $\epsilon$ -caprolactone mainly reflect the larger  $\Delta S^\ddagger$  values.<sup>23</sup> However, many unresolved issues remain, for example, how the microwave electric and magnetic fields (EF and MF, respectively) individually affect the rates of microwave-subjected reactions.

Herein, we reported microwave-assisted solution polycondensations of L-LA. To the best of our knowledge, no report has dealt with microwave-assisted solution polycondensation of L-LA in a Dean-Stark apparatus. Taking advantage of the constant temperature condition that occurs when a reaction is refluxed at a system’s boiling point, we were able to ask if a non-thermal effect did or did not affect the polycondensation of L-LA. We investigated the relationship between the microwave irradiation power and the reaction conditions e.g., monomer and catalyst concentrations, and the type of catalyst on the PLLA  $M_w$ . Additionally, we investigated the individual effects of a microwave-induced EF and MF produced in a single-mode microwave cavity on the polycondensation of L-LA (Figure 1).



**Figure 1.** Schematic of the single-mode microwave apparatus.<sup>24, 25</sup>

## Results and discussion

### Multi-mode Microwave-Assisted Solution Polycondensation of L-LA Catalyzed by Sc(OTf)<sub>3</sub>.

First, microwave-assisted solution polycondensations of L-LA (85 % aqueous solution) were performed with Sc(OTf)<sub>3</sub> as the catalyst, and under various microwave power levels to optimize the multi-mode microwave reactor-assisted reaction. At 100-W power, polycondensation did not occur (Table 1, run 1). With the power set at 200 or 250 W, we obtained only PLLAs with relatively small  $M_w$  values (Table 1, runs 2 and 3). With 300-W power, PLLA with greater  $M_w$  values was obtained (run 4); the  $M_w$  was larger than that obtained by conventional heating (run 5), which indicated that the thermal effects (e.g., a hot spot or a difference in the heating rate) had been eliminated because for both procedures, the temperature was set to the boiling point of xylene (b.p. 142 °C). From <sup>1</sup>H-NMR spectra for the sample of run4 and 5, we confirmed that these PLLA had the expected structures and that peaks, which could be ascribed to side-reaction products, were absent. Notably, these results support the

existence of a non-thermal microwave effect. In  $\text{CHCl}_3$ ,  $[\alpha]_D^{25}$  is  $-149$  for the sample of run 4, which coincides with the literature value ( $-150$ ).<sup>26</sup> Although we performed the polycondensation of L-LA under  $>400\text{-W}$  power, we could not accurately assess its effect on the polycondensation because the microwaves reflected onto the magnetron, which change the actual power level.

Next, we investigated the effect of the monomer concentration. When the monomer concentration was increased from 3 M to 5 M (300 W; Table 1, runs 4 and 6, respectively), the  $M_w$  of the product PLLA increased. However, PLLA synthesized under this condition (run 6) was black-colored. Because excess microwave was irradiated, we then decreased the power to 200 W (run 7). Although the  $M_w$  of PLLA decreased, the decreased power suppressed formation of the black color. When the monomer concentration was increased to 8 M (keeping at irradiation power of 200 W), the  $M_w$  and  $M_p$  PLLA values (run 8) were greater than those obtained for run 4 and were not colored, although the polydispersity index was broader. Given these results, excessive microwave energy inhibited polycondensation and/or promoted degradation of PLLA.

**Table 1. Microwave-Assisted Solution Polycondensation of L-LA Catalyzed by Sc(OTf)<sub>3</sub>.<sup>a</sup>**

run	heating method		[M] <sub>0</sub>	yield <sup>d</sup> (%)	$M_n^e$ × 10 <sup>-3</sup>	$M_w^e$ × 10 <sup>-3</sup>	$M_p^e$ × 10 <sup>-3</sup>	$M_w/M_n^e$	$T_g^f$ (°C)	$T_m^f$ (°C)	$[\alpha]_D^{25g}$	color
1	MW <sup>b</sup>	100 W	3 M	-	-	-	-	-				
2	MW <sup>b</sup>	200 W	3 M	>99	1.4	2.7	2.4	1.96				
3	MW <sup>b</sup>	250 W	3 M	>99	1.5	3.1	2.1	2.06				
4	MW <sup>b</sup>	300 W	3 M	>99	4.4	11.6	10.6	2.63	40.4	150.4	-149	pale brown
5	CH <sup>c</sup>	160 °C	3 M	>99	3.4	8.8	8.8	2.63	33.1	144.0	-145	pale brown
6	MW <sup>b</sup>	300 W	5 M	>99	6.3	17.2	14.0	2.75				black
7	MW <sup>b</sup>	200 W	5 M	>99	3.1	7.8	7.9	2.49				white
8	MW <sup>b</sup>	200 W	8 M	>99	3.9	16.7	17.6	4.26				white

<sup>a</sup>All runs were performed by a 6-h azeotropic distillation with xylene as the solvent and 0.1 mol% Sc(OTf)<sub>3</sub> as the catalyst. <sup>b</sup>Multi-mode microwave heating. <sup>c</sup>Conventional heating. <sup>d</sup>Without reprecipitation. <sup>e</sup>Without reprecipitation. Determined by SEC with CHCl<sub>3</sub> as the eluent. Values are reported relative to those of poly(styrene) standards. <sup>f</sup> $T_m$  was determined using the first DSC scan, and  $T_g$  was determined using the second scan (heating rate: 10 °C/min). <sup>g</sup>1 g/100 mL CHCl<sub>3</sub>.

### Multi-mode-Microwave-Assisted Solution Polycondensation of L-LA Using Various Catalysts.

We next investigated the effect of various catalysts on the L-LA polycondensation under microwave irradiation. First, we examined the effect of the Sc(OTf)<sub>3</sub> concentration. When the Sc(OTf)<sub>3</sub> concentration was increased to 0.3 mol% (relative to L-LA), the PLLA  $M_w$  was greater than when 0.1 mol% Sc(OTf)<sub>3</sub> was used (Table 2, runs 1 and 2). However, when the Sc(OTf)<sub>3</sub> concentration was 0.5 mol%, the  $M_w$  of the product PLLA decreased (runs 2 and 3). From these results, it seems that the largest Sc(OTf)<sub>3</sub> concentration also inhibited polycondensation and/or promoted the degradation of PLLA. Next, we surveyed the effects of various catalysts on PLLA formation. Previously, we reported

that scandiumbis(nonafluoro-butanesulfonyl)imide  $[\text{Sc}(\text{NNf}_2)_3]$  and Nonafluorobutanesulfonimide  $[\text{Nf}_2\text{NH}]$  are effective catalysts for aliphatic polyester syntheses.<sup>27,28</sup> However,  $\text{Sc}(\text{NNf}_2)_3$  was insoluble in the reaction medium, therefore, could not be used, and when  $\text{Nf}_2\text{NH}$  was used, we obtained only a mixture of oligomers and lactides (data not shown). We also tested the  $\text{SnCl}_2/\text{PTSA}$  binary catalyst system that was reported to be an effective catalyst for direct polymerization of L-LA under microwave irradiation.<sup>5</sup> Although this binary catalyst was effective for microwave-assisted direct polymerization,<sup>5</sup> we did not obtain PLLA with an  $M_w$  similar to that found for run 5 in Table 2. However, we confirmed the existence of a non-thermal microwave effect (runs 4 and 5) similar to that of the  $\text{Sc}(\text{OTf})_3$ -catalyzed experiments. Next, we used  $\text{SnCl}_2$  as the catalyst at various concentrations. When the  $\text{SnCl}_2$  concentration was 0.1 mol%, polymerization hardly occurred (run 6). However, with larger  $\text{SnCl}_2$  concentrations, PLLAs with larger  $M_w$  values were obtained (runs 7 and 9). Particularly, when the  $\text{SnCl}_2$  concentration was 1.0 mol%, PLLA with the largest  $M_w$  ( $46.7 \times 10^3$ ) was obtained for experiments that used multi-mode-microwave irradiation and any of the other tested catalysts. For the  $\text{SnCl}_2$ -catalyzed experiments, a non-thermal microwave effect was also found (runs 8 and 9), because  $M_w$  of run 9 ( $46.7 \times 10^3$ ) was much higher than  $M_w$  of run 8 ( $19.6 \times 10^3$ ).



**Table 2. Microwave-Assisted Solution Polycondensation of L-LA Using Various Catalysts.<sup>a</sup>**

run	catalyst(mol%)	heating method	yield <sup>d</sup> (%)	$M_n^e$ $\times 10^{-3}$	$M_w^e$ $\times 10^{-3}$	$M_p^e$ $\times 10^{-3}$	$M_w/M_n^e$	$T_g^f$ (°C)	$T_m^f$ (°C)	$[\alpha]_D^{25g}$
1	Sc(OTf) <sub>3</sub> (0.1)	MW <sup>b</sup>	>99	4.4	11.6	10.6	2.63	40.4	148.1	-149
2	Sc(OTf) <sub>3</sub> (0.3)	MW <sup>b</sup>	>99	7.0	21.2	16.9	3.04			
3	Sc(OTf) <sub>3</sub> (0.5)	MW <sup>b</sup>	>99	3.8	13.2	14.6	3.45			
4	PTSA (0.6)	CH <sup>c</sup>	>99	2.0	3.8	3.6	1.96			
	SnCl <sub>2</sub> (0.6)									
5	PTSA (0.6)	MW <sup>b</sup>	>99	3.0	8.3	9.1	2.74	33.2	143.9	-139
	SnCl <sub>2</sub> (0.6)									
6	SnCl <sub>2</sub> (0.1)	MW <sup>b</sup>	>99	0.8	1.0	0.8	1.20			
7	SnCl <sub>2</sub> (0.5)	MW <sup>b</sup>	>99	3.1	9.6	10.9	3.08			
8	SnCl <sub>2</sub> (1.0)	CH <sup>c</sup>	>99	3.4	19.6	19.6	5.64			
9	SnCl <sub>2</sub> (1.0)	MW <sup>b</sup>	>99	9.2	46.7	38.9	5.07	54.9	165.4	-146

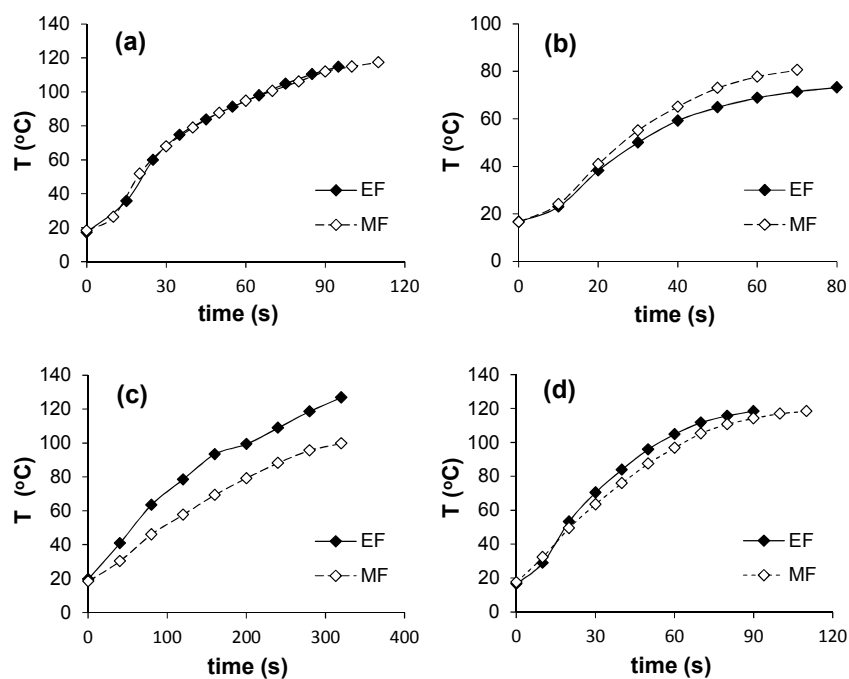
<sup>a</sup>All runs were performed by a 6-h azeotropic distillation with xylene as the solvent ( $[M]_0 = 3$  M).

<sup>b</sup>Microwave heating (300 W). <sup>c</sup>Conventional heating (160 °C) <sup>d</sup>Without reprecipitation. <sup>e</sup>Without reprecipitation. Determined by SEC with CHCl<sub>3</sub> as the eluent. Values are reported relative to those of poly(styrene) standards. <sup>f</sup> $T_m$  was determined using the first DSC scan, and  $T_g$  was determined using the second scan (heating rate: 10 °C/min). <sup>g</sup>1 g/100 mL CHCl<sub>3</sub>.

### Investigation of the Heating Effects Induced by Isolated Electric and Magnetic Fields in the Single-Mode Microwave Cavity on the Reagents Used in PLLA Synthesis.

First, we monitored the changes in the temperature of water, xylene, L-LA<sub>(aq)</sub>, and a mixture of L-LA<sub>(aq)</sub> and xylene when heated by the EF or the MF in the single-mode microwave cavity to evaluate the heating behavior of each reaction component. The temperature behavior of L-LA<sub>(aq)</sub> was the same when subjected to the EF or the MF (Figure 2a). L-LA<sub>(aq)</sub> was heated by the MF more rapidly than by the EF

(Figure 2b). Conversely, the opposite tendency was found for xylene (Figure 2c), i.e., the temperature of xylene increased more rapidly in the presence of the EF than in the presence of the MF. Although there were differences in the heating behaviors of water and xylene under EF and MF irradiation, the heating rate of the mixture (L-LA<sub>(aq)</sub> and xylene) under EF irradiation was similar to that under MF irradiation (Figure 2d).



**Figure 2.** Temperature ( $T$ ) profiles for (a) L-LA<sub>(aq)</sub>, (b) water, (c) xylene, and (d) a mixture of L-LA<sub>(aq)</sub> and xylene (3.18 g and 7.4 mL, respectively, which are the same quantities as used for all reactions) when heated under the EF (diamonds) or the MF (squares) at a power of 50 W. The internal temperatures of the samples were measured by a fiber optic thermometer.

### Solution Polycondensation of L-LA under or EF- or MF-Irradiation in a Single-mode Microwave Cavity.

Next, we performed polycondensation of L-LA catalyzed with 0.1 mol% Sc(OTf)<sub>3</sub> under EF irradiation (Table 3). When the power was 30 W, polycondensation proceeded only to a relatively small extent (Table 3, run 1). PLLA with an  $M_w > 10,000$  was obtained when the power was increased (runs 2-

4). However, when the EF was used with a power of 150 W, the  $M_w$  of the PLLA decreased (run 5). We also performed polycondensations under the MF (runs 6–8). When the power was 50 W, the extent of polycondensation (run 6) was the same as that of the corresponding conventional heating experiment (Table 1, run 5). In contrast to the effects of the EF, the  $M_w$  values of the product PLLAs decreased with increasing power (runs 7 and 8) even though the heating behavior of the reaction mixture in the MF was similar to that in the EF (Figure 2.).  $M_n$  profiles for solution polycondensation of L-LA catalyzed by  $\text{Sc}(\text{OTf})_3$  under EF or MF at 50 W, 80 W, and 100 were also plotted as a function of reaction time (Please see the supporting information: Figure S1). These results show that EF-induced irradiation accelerates the polycondensation and that MF irradiation inhibits it and/or accelerates the degradation, that is, EF-induced irradiation is more effective than microwave irradiation composed of an EF and an MF. In order to check whether depolymerization was induced by MF or not, we also demonstrated alternately irradiate a LA polymerization with EF followed by MF. As the results, not depolymerization but the retardation of the polymerization rate was confirmed compared with EF irradiation (Please see the supporting information: Figure S2).

**Table 3. Solution Polycondensation of L-LA Using a Single Mode Microwave Cavity.<sup>a</sup>**

run	heating method		catalyst (mol%)	yield <sup>d</sup> (%)	$M_n^e$ $\times 10^{-3}$	$M_w^e$ $\times 10^{-3}$	$M_p^e$ $\times 10^{-3}$	$M_w/M_n^e$
1	EF <sup>b</sup>	30 W	Sc(OTf) <sub>3</sub> (0.1)	>99	1.3	2.0	2.0	1.62
2	EF <sup>b</sup>	50 W	Sc(OTf) <sub>3</sub> (0.1)	>99	4.3	12.6	12.4	2.94
3	EF <sup>b</sup>	80 W	Sc(OTf) <sub>3</sub> (0.1)	>99	3.8	10.7	11.2	2.84
4	EF <sup>b</sup>	100 W	Sc(OTf) <sub>3</sub> (0.1)	>99	4.4	11.3	9.2	2.58
5	EF <sup>b</sup>	150 W	Sc(OTf) <sub>3</sub> (0.1)	>99	3.0	7.2	6.9	2.39
6	MF <sup>c</sup>	50 W	Sc(OTf) <sub>3</sub> (0.1)	>99	3.1	9.5	10.5	3.03
7	MF <sup>c</sup>	80 W	Sc(OTf) <sub>3</sub> (0.1)	>99	1.8	4.0	3.8	2.22
8	MF <sup>c</sup>	100 W	Sc(OTf) <sub>3</sub> (0.1)	>99	1.5	2.9	2.1	1.93

<sup>a</sup>All runs were performed by a 6-h azeotropic distillation with xylene as the solvent ( $[M]_0 = 3$  M). <sup>b</sup>Electric field. <sup>c</sup>Magnetic field. <sup>d</sup>Without reprecipitation. <sup>e</sup>Without reprecipitation. Determined by SEC with CHCl<sub>3</sub> as the eluent. Values are reported relative to those of poly(styrene) standards.

To obtain PLLA with a higher  $M_w$ , we performed polycondensations under EF irradiation and catalyzed by 0.3 mol% Sc(OTf)<sub>3</sub> (Table 4 runs 1–3). The  $M_w$  values of PLLA synthesized under these conditions were the same as those for PLLA synthesized in the multi-mode microwave reactor irradiated at 300 W (Table 2, runs 1 and 2). We also performed EF-assisted polycondensations catalyzed by SnCl<sub>2</sub>, which was the most effective catalyst for the multi-mode-microwave-assisted syntheses. When the EF power was 100 W, the PLLA  $M_w$  was the greatest obtained in this study ( $M_w = 60.2 \times 10^3$ ).

**Table 4. Solution Polycondensation of L-LA Under an Electric Field. <sup>a</sup>**

run	heating method	heating power	catalyst (mol%)	yield <sup>c</sup> (%)	$M_n^d$ × 10 <sup>-3</sup>	$M_w^d$ × 10 <sup>-3</sup>	$M_p^d$ × 10 <sup>-3</sup>	$M_w/M_n^d$	$T_g^e$ (°C)	$T_m^e$ (°C)	$[\alpha]_D^{25}$ <sup>f</sup>
1	EF <sup>b</sup>	50 W	Sc(OTf) <sub>3</sub> (0.3)	>99	4.9	11.7	11.0	2.37			
2	EF <sup>b</sup>	80 W	Sc(OTf) <sub>3</sub> (0.3)	>99	6.1	19.9	17.0	3.28	37.7	145.0	-135
3	EF <sup>b</sup>	100 W	Sc(OTf) <sub>3</sub> (0.3)	>99	5.3	15.9	15.3	2.99			
4	EF <sup>b</sup>	50 W	SnCl <sub>2</sub> (1.0)	>99	1.9	4.4	4.8	2.36			
5	EF <sup>b</sup>	80 W	SnCl <sub>2</sub> (1.0)	>99	9.3	53.2	45.3	5.73			
6	EF <sup>b</sup>	100 W	SnCl <sub>2</sub> (1.0)	>99	8.8	60.2	52.8	6.84	50.6	163.8	-147

<sup>a</sup>All runs were performed by a 6-h azeotropic distillation with xylene as the solvent ( $[M]_0 = 3$  M). <sup>b</sup>Electric field. <sup>c</sup>Without reprecipitation. <sup>d</sup>Without reprecipitation. Determined by SEC with CHCl<sub>3</sub> as the eluent. Values are reported relative to those of poly(styrene) standards. <sup>e</sup> $T_m$  was determined using the first DSC scan, and  $T_g$  was determined using the second scan (heating rate: 10 °C/min). <sup>f</sup>1 g/100 mL in CHCl<sub>3</sub>.

## Experimental Section

**Materials.** Aqueous L-LA (85% w/v), anhydrous tin (II) chloride, and xylene were purchased from Wako Pure Chemical Industries (Osaka, Japan). *p*-Toluenesulfonic acid monohydrate was purchased from Kanto Chemical Co., Ins. (Tokyo, Japan). Sc(OTf)<sub>3</sub> was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Nonafluorobutanesulfonimide (Nf<sub>2</sub>NH) was purchased from Mitsubishi Materials Electronic Chemicals (Akita, Japan). scandiumbis(nonafluorobutanesulfonyl)imide [Sc(NNf<sub>2</sub>)<sub>3</sub>] was prepared in our laboratory according to the procedure described in the literature.<sup>27</sup>

**Measurements.** <sup>1</sup>H-NMR spectra were recorded at 27 °C using a 200-MHz DPX200 spectrometer (Bruker Analytik). The number average molecular weight ( $M_n$ ), the  $M_w$ , the molecular weight found for the top of the size-exclusion chromatogram peak ( $M_p$ ), and the polydispersity index

( $M_w/M_n$ ) for each polymer preparation were determined using a size-exclusion-chromatography system that was calibrated with polystyrene standards. The chromatographic system included a pump system (DP-8020; Tosoh), an RI detector (RI-8020; Tosoh), and a TSKgel SuperMultiporeHZ-M column. Chromatography was performed with chloroform as the eluent, at a flow rate of 0.35 mL/min, and at 40 °C. Differential scanning calorimetry (DSC), using a DSC6220S calorimeter (Seiko Instruments Inc., Chiba, Japan), was performed from -20 to +190 to -20 °C, at 10°C/min. The instrument was calibrated with indium and tin. Each polyester sample weighted between 5 and 7 mg and was contained in an aluminum pan that was covered with a lid within the calorimeter. The glass-transition temperature ( $T_g$ ) was taken as the inflection point of the DSC heat-capacity jump. The melting temperature ( $T_m$ ) was defined as the minimum point in the endothermic trough. The specific rotation at 25 °C,  $[\alpha]_D^{25}$ , of each polymer (1 g/dL chloroform) was measured at 589 nm using a P-1010 polarimeter (Jasco).

**Solution Polycondensation of L-Lactic Acid Using Conventional Heating.** A typical procedure was performed as follows. L-LA (3.18 g), a catalyst, and 7.36 mL of xylene were mixed in a flask equipped with a Dean-Stark trap with the heater set at a temperature (160 °C) higher than the boiling point of xylene (b.p. 142 °C) for a 6-h azeotropic dehydration.

**Solution Polycondensation of L-Lactic Acid Using a Multimode Microwave Reactor.** A typical procedure was performed as follows: L-LA (3.18 g), a catalyst, and 7.36 mL of xylene were mixed in a flask equipped with a Dean-Stark trap that was then placed into a multi-mode microwave reactor (MWO-1000S, EYELA, 2.45 GHz, maximum power 500 W) for a 6-h azeotropic dehydration under microwave irradiation.

**Solution Polycondensation of L-Lactic Acid in a Single-mode Microwave Cavity.** Figure 1 shows a schematic of the experimental apparatus that incorporated the 2.45 GHz microwave reactor used to produce an EF or an MF. In a single-mode microwave cavity, there is the standing wave composed of microwave. Microwave is composed of EF and MF shifted by a quarter wavelength each other.<sup>24,25</sup> Therefore, we can divide electric field and magnetic field by choosing the position of a flask. The

microwave power is the difference between the input power and reflex power. Reduction of titanium oxide and sintering of magnetite ( $\text{Fe}_3\text{O}_4$ ) under a microwave MF using this apparatus have been reported.<sup>24,25</sup> A typical procedure was performed as follows. L-LA (3.18 g), a catalyst, and 7.36 mL of xylene were mixed in a flask equipped with a Dean-Stark trap that was then placed into the single-mode microwave cavity (Figure 1) for a 6-h azeotropic dehydration under microwave irradiation. The microwave power was manually controlled.

## Conclusions

Herein, we described solution polycondensation of L-LA using a Dean-Stark apparatus and microwave irradiation. When irradiating at 300-W microwave power, a greater  $M_w$  ( $11.6 \times 10^3$ ) was obtained with 0.1 mol%  $\text{Sc}(\text{OTf})_3$  as the catalyst than when 100–250 W power was employed. For 1.0 mol%  $\text{SnCl}_2$ , the PLLA with the greatest  $M_w$  value ( $46.7 \times 10^3$ ) was obtained for polycondensations that used multi-mode-microwave irradiation. For each catalyst tested, the PLLA  $M_w$  obtained using microwave irradiation was greater than that obtained using conventional heating, indicating that we did not find thermal effects (hot spots or differences in the heating rates) because the reaction temperatures were the same (the boiling point of xylene). Notably, these results support the existence of a non-thermal microwave effect. Additionally, we investigated the individual effects of an EF and an MF on the polycondensation of L-LA using a single-mode microwave cavity. We found that an EF accelerated the polycondensation and that an MF inhibited polycondensation and/or accelerated degradation. The results also support the presence of a non-thermal microwave effect because we could not observe any differences in the heating behavior of the mixture (L-LA<sub>(aq)</sub> and xylene) under EF and MF irradiations. These fundamental results provide new insight into the microwave-assisted, energy-saving production of polymeric materials.

## Acknowledgments

This work was funded by the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Development Scientific Research, no. 24551032).

### Notes and references

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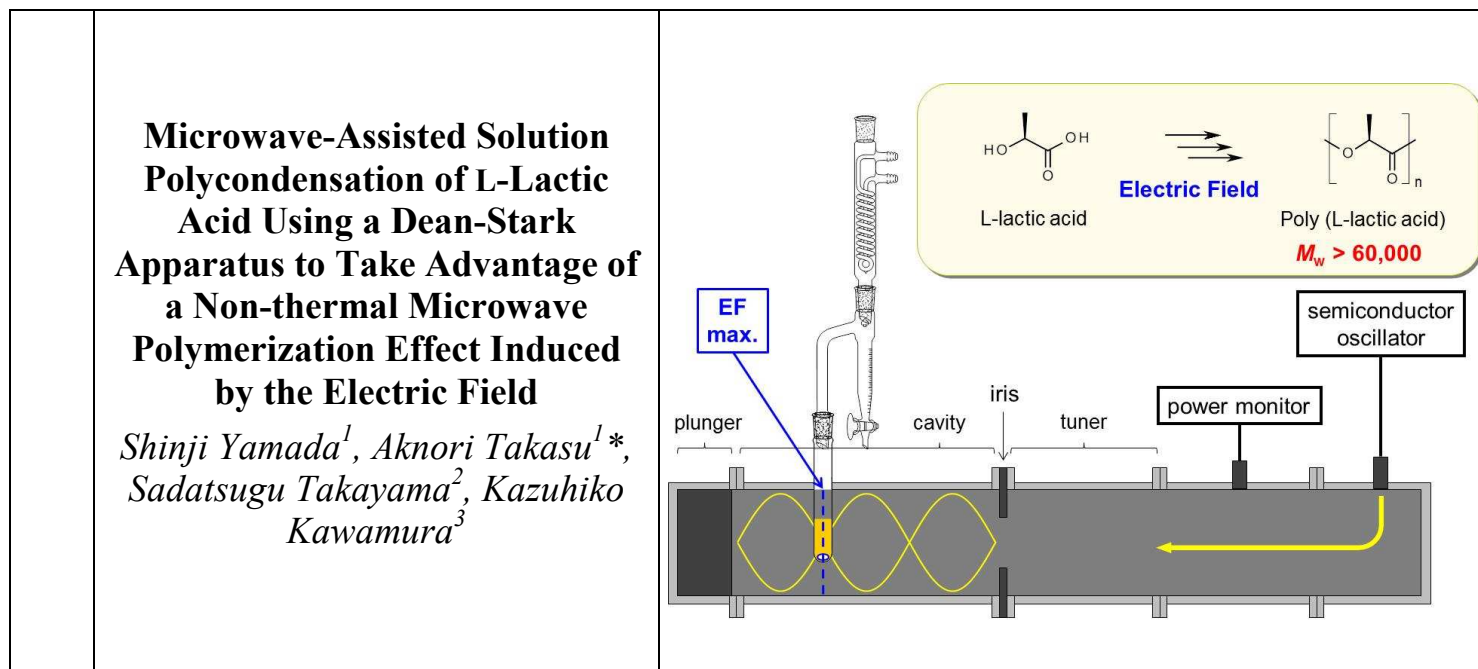
- (1) R. W. Lenz, *Adv. Polym. Sci.* **1993**, *107*, 1.
- (2) T. H. E. Vink, R.K. Ra'bago, A. D. Glassner and R. P. Gruber, *Polym. Degrad. Stab.* **2003**, *80*, 403-419.
- (3) A. Takasu, Y. Narukawa, and T. Hirabayashi, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5247-5253.
- (4) (a) A. Takasu, Y. Oishi, Y. Iio, Y. Inai, and T. Hirabayashi, *Macromolecules* **2003**, *36*, 1772-1774.  
(b) Takasu, A.; Iio, Y.; Oishi, Y.; Narukawa, Y.; Hirabayashi, T. *Macromolecules* **2005**, *38*, 1048-1050. (c) A. Takasu, Y. Iio, T. Mimura, and T. Hirabayashi, *Polym. J.* **2005**, *37*, 946-953.
- (5) R. Nagahata, D. Sano, H. Suzuki, and K. Takeuchi, *Macromol. Rapid Commun.* **2007**, *28*, 437-442.
- (6) D. Adam, *Nature* **2003**, *421*, 571-572.
- (7) R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, and J. Rousell, *Tetrahedron Lett.* **1986**, *27*, 279-282.
- (8) R. J. Giguere, T. L. Bray, S. M. Duncan, and G. Majetich, *Tetrahedron Lett.* **1986**, *27*, 4945-4958.



- (9) C. O. Kappe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6250–6284.
- (10) S. A. Galema, *Chem. Soc. Rev.* **1997**, *26*, 233–238.
- (11) C. O.; Kappe, and D. Dallinger, *Nat. Rev. Drug Discov.* **2006**, *5*, 51–63.
- (12) Y. Kajiwara, A. Nagai, and Y. Chujo, *Polym. J.* **2009**, *41*, 1080–1084.
- (13) T. Iwamura, K. Ashizawa, and M. Sakaguchi, *Macromolecules* **2009**, *42*, 5001–5006.
- (14)(a) R. Hoogenboom, F. Wiesbrock, H. Huang, M. A. M. Leenen, H. M. L. Thijs, S. M. G. F. V. Nispen, M. V. D. Loop, C. -A. Fustin, A. M. Jonas, J.-F. Gohy, and U. S. Schubert, *Macromolecules* **2006**, *39*, 4719–4725; (b) L. Tauhardt, K. Kempe, and U. S. Schubert, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4516–4523.
- (15)(a) H.; Li, L.; Liao, and L. Liu, *Macromol. Rapid Commun.* **2007**, *28*, 411–416. (b) J. Ramier, E. Renard, and D. J. Grande, *Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1445–1455; (c) A. Nan, R. Turcu, and J. Liebscher, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 1485–1490.
- (16) S. Yamada, and A. Takasu, *Polym. J.* **2011**, *43*, 1003–1007.
- (17) Y.; Nagao, and A. Takasu, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 4207–4218.
- (18) F. Wiesbrock, R. Hoogenboom, and U. S. Schubert, *Macromol. Rapid Commun.* **2004**, *25*, 1739–1764.
- (19) R. Hoogenboom, and U. S. Schubert, *Macromol. Rapid Commun.* **2007**, *28*, 368–386.
- (20) K. Kempe, C. R. Becer, and U. S. Schubert, *Macromolecules* **2011**, *44*, 5825–5842.
- (21)(a) G. A. Tompsett, W. C. Conner, and K. S. Yngvesson, *Chem-Phys Chem* **2006**, *7*, 296–319. (b) W. C. Conner, G. A. Tompsett, K.-H. Lee, and K. S. Yngvesson, *J. Phys. Chem. B* **2004**, *108*, 13913–13920.

- (22) P. B. Zetterlund, and S. Perrier, *Macromolecules* **2011**, *44*, 1340–1346.
- (23) S. Yamada, A. Takasu, and K. Kawamura, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 3732–3739.
- (24) J. Fukushima, K. Kashimura, S. Takayama, and M. Sato, *Chem. Lett.* **2012**, *41*, 39–41.
- (25) S. Takayama, J. Fukushima, J. Nishijo, M. Saito, S. Sano, and M. Sato, *Phys. Res. Intern.* **2012**, art. no. 165849.
- (26) A. E. Tonelli, and P. J. Flory, *Macromolecules* **1969**, *2*, 225–227.
- (27) A. Takasu, T. Makino, and S. Yamada, *Macromolecules* **2010**, *43*, 144–149.
- (28) T. Moyori, T. Tang, and A. Takasu, *Biomacromolecules* **2012**, *13*, 1240–1243.

TOC Graphic

*for* Polymer Chemistry

We examined the solution polycondensation of L-lactic acid (L-LA) in xylene catalyzed by  $\text{Sc}(\text{OTf})_3$  using a Dean-Stark apparatus under various microwave power conditions (100–400 W). We also performed microwave-assisted polycondensation of L-LA using a single-mode microwave cavity that separates microwave electric and magnetic fields. The results indicate the existence of a non-thermal microwave effect induced by an electric field.