New Approach to Investigation of Microwave-Assisted Chemistry Based on Principles of Polymerization

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13903 1949
2014-03-23

URL http://doi.org/10.20602/00003092
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2014

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General Introduction

Currently, because of increasing concerns about the environment extremely, the development of new, eco-friendly chemical reactions and materials is crucial. Microwave-enhanced chemical reactions have attracted much attention in recent years,\(^1\) because, as first reported in 1986,\(^2,3\) microwave irradiation can shorten the reaction time of an organic synthesis, e.g., a polymerization, and decrease the amounts of by-products, which improves product yield and/or product chemoselectivity (reviewed in references 4–6). Methods for step-growth polymerizations, e.g., polycondensation of diols with dicarboxylic acids\(^7\) and polyaddition of dialkynes with diazido via \textit{in situ} azidation of dibromo compounds,\(^8\) as well as chain polymerizations, e.g., radical polymerization of methacrylate,\(^9\) anionic polymerization of acrylamide,\(^10\) ring-opening cationic polymerization of 2-oxazoline derivatives,\(^11\) and ring-opening polymerization (ROP) of cyclic esters,\(^12\) have all incorporated microwave heating. The exponentially increasing number of publications concerning microwave heating of organic reactions indicates the remarkable interest in and effectiveness of this technique.\(^13–15\) However, most of the aforementioned studies focused only on the effect that microwave heating had on the overall polymerization rate; consequently, the accurate non-thermal microwave effect and the underlying kinetics and thermodynamics investigations of microwave-assisted polymerization were hardly reported. Instead, the following hypotheses\(^16\) have been proposed to explain the increased polymerization rates: (a) a more rapid attainment of the final temperature, (b) more uniform heating of the reaction mixture, (c) a change in how the species in the mixture interact, (d) superheating of the mixture, and (e) creation of hot spots. According to Conner and Tompsett, rapid heating and creation of hot spots can be associated with increases in synthesis rates.\(^17\) Zetterlund and Perrier concluded that the observed rate enhancement for the reversible addition-fragmentation chain-transfer polymerization of styrene induced by microwave irradiation, which they investigated \textit{in silico}, was a consequence of microwave-enhanced
propagation and RAFT-moiety addition steps. Stoffer and colleagues proposed that a new dipole partition function existed in the microwave fields and calculated the values of the thermodynamic properties such as internal energy and Gibbs free energy theoretically.

Aliphatic polyesters also have attracted much interest as environmentally benign, biodegradable polymers. Generally, aliphatic polyesters can be synthesized by two fundamental strategies. One approach is the step-growth polymerization (polycondensation) of hydroxy-carboxylic acid or dicarboxylic acid and diol. This approach is generally used for producing many kinds of commercial aliphatic polyesters. However, this method requires heating at high temperature (>250 °C) and extremely reduced pressure. The other approach is the chain-growth polymerization (ring-opening polymerization) of the cyclic ester. Although this technique uses moderate reaction condition and avoids the formation of small molecule by product, the scope of the polymer architecture is generally limited because we have to use ring-strained monomer. Many researchers have been investigated and reported about these fundamental approaches of polymer syntheses; effective catalysts, kinetics, thermodynamics and so on. In my laboratory, room-temperature direct polycondensation of dicarboxylic acids and diols catalyzed by scandium(III) trifluoromethanesulfonate [Sc(OTf)₃] or scandium trifluoromethanesulfonimide [Sc(NTf₂)₃] have been already demonstrated, and revealed that this system afforded aliphatic polyesters with number average molecular weights ($M_n$) greater than 1.0 × 10⁴. Additionally, polycondensation under mild condition can incorporate thermally unstable monomers (chemoselective dehydration polycondensation). Furthermore, ring-opening polymerization of $\varepsilon$-caprolactone catalyzed by Sc(OTf)₃ have been also reported in my laboratory.

In this thesis, I describe the effective catalysts for low-temperature direct polycondensation to evaluate the microwave effect by using various catalysts (chapter 1), the investigations of microwave-assisted chemistry based on kinetics or thermodynamics of the aforementioned polyester syntheses (chapter 2 and 3) and the non-thermal microwave effect of the electric field on polycondensation (chapter 4). Each digest is as follows.
In chapter 1, I describe the synthesis of three scandium compounds—scandium perfluorooctanesulfonate [Sc(OPf)_3], scandium nonafluorobutanesulfonate [Sc(ONf)_3], and scandium bis(nonafluorobutanesulfonfyl)imide [Sc(NNf_2)_3] (Scheme 1)—that have ligands with stronger electron-withdrawing abilities. I have assessed the abilities of these compounds, and hence their Lewis acidities, to catalyze the synthesis of large molecular weight polyesters in short periods of time and under mild conditions. To appraise the strengths of scandium compounds as Lewis acids towards a carboxylic acid moiety, the $^{13}$C-NMR spectra of acetic acid alone and equimolar amounts of acetic acid and each scandium compound in acetone-$d_6$ were recorded. The results of a survey of other rare earth metals—Sm, Gd, Er, Nd, Dy, and Tm—that might be used as catalytic centers for dehydration polycondensations are also reported.

**Scheme 1.** Formulae and Space-Filling Models of the Scandium Catalysts.
In chapter 2, I describe microwave-assisted syntheses of polyesters at a relatively low temperature (80 °C) using a microwave chamber equipped a temperature control catalyzed by Sc compounds shown in chapter 1. To examine the effects of microwave heating on the polycondensation, $^{1}$H-NMR and MALDI-TOF spectra were recorded. I compared the rates of the microwave-assisted polymerizations calculated by the kinetics with those obtained with the use of conventional heating, which allowed us to characterize the contribution of a microwave-induced non-thermal effect.

Although I showed the possibility of the acceleration of polycondensation induced by non-thermal microwave effect in chapter 2, I couldn’t give the further details about microwave-assisted polycondensation using thermodynamic parameters. In chapter 3, I examined the ring-opening polymerization (ROP) of ε-caprolactone in toluene between 50 and 70 °C, and catalyzed by the super Brønsted acids, trifluoromethanesulfonimide (Tf$_2$NH) and nonafluorobutanesulfonimide (Nf$_2$NH), and by the Lewis acids, Sc(NTf$_2$)$_3$ and Sc(NNf$_2$)$_3$ to investigate the effects of microwave versus conventional heating on the kinetics and activation thermodynamics of the reaction. Additionally, we investigated the effect of monomer concentration on the kinetics and thermodynamics of ROP of ε-caprolactone in order to catch clearly the microwave effect.

In chapter 4, I describe microwave-assisted solution polycondensation of L-lactic acid. Because solution polycondensation is performed at constant reaction temperature (boiling point of solvent) by reflux, I investigated the relation between microwave irradiation power and reaction
conditions (e.g. monomer or catalyst concentration and a species of catalyst on the molecular weight of PLLA). Additionally, we investigated the effects of electric/magnetic fields on solution polycondensation of L-LA using singlemode microwave cavity (Scheme 2).

![Scheme 2. Schematic of the singlemode microwave apparatus.](image)

In this thesis, I demonstrated the new approach to investigate microwave-assisted chemistry based on kinetics and thermodynamics of polyester syntheses. These introduced fundamental results provide new insight into the microwave-assisted, energy-saving production of polymeric materials and enable us to the development of microwave chemistry.
Reference


Chapter 1

Polyester Synthesis at Moderate Temperatures via the Direct Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Rare-Earth Perfluoroalkanesulfonates and Bis(perfluoroalkanesulfonyl)imides

Abstract

Recently, we reported that scandium trifluoromethanesulfonate \( [\text{Sc(OTf)}_3] \) and scandium trifluoromethanesulfonimide could catalyze polycondensations of dicarboxylic acids and diols. Although these polycondensations were one-step and occurred at the moderate temperature of 35 °C, they required large amounts of the catalysts (ca. 1 mol%) and long reaction times (>100 h). Therefore, scandium catalysts having stronger electron-withdrawing ligands (scandium perfluorooctanesulfonate, scandium nonafluorobutanesulfonate, and scandium bis(nonafluorobutanesulfonyl)imide \([\text{Sc(NNf}_2]_3\)) were synthesized and their catalytic efficiencies were tested. We have now demonstrated and report herein that scandium catalysts with the stronger electron-withdrawing ligands could catalyze the polycondensation of adipic acid and 3-methyl-1,5-pentanediol under conditions of a moderate temperature, a short time period, and a lesser amount of catalyst. Other rare-earth-metal catalysts containing ligands with strong electron-withdrawing abilities were also synthesized and their catalytic efficiencies were tested using the aforementioned polycondensation. As a result, thulium bis(nonafluorobutanesulfonyl)imide \([\text{Tm(NNf}_2]_3\]) was a more effective catalyst than was \( \text{Sc(OTf)}_3 \), \( \text{Sc(NNf}_2]_3 \). Our work now makes it possible to synthesize aliphatic polyesters of \( M_n > 1.0 \times 10^4 \) at a moderate temperature (60 °C), within a short period of time (6 h), and using a small amount of catalyst (0.05–0.1 mol%).
1-1. Introduction

Recent attention has focused on aliphatic polyesters that have potential as biomaterials, biodegradable polymers, and environmentally benign materials. Aliphatic polyesters are usually produced by polycondensation of dicarboxylic acids and excess amounts of diols (1.1–1.5 eq.), at temperatures greater than 250 °C and under extremely reduced pressures. Polycondensations have been catalyzed by Lewis acids, but not many suitable Lewis acid catalysts exist, because most are labile towards protic substances, including carboxylic acids, alcohols, and water, which are therefore not suitable for dehydration polycondensation. Rare-earth triflates and triflylimides, because they do not react with protic compounds, can catalyze some reactions even in water, because they have small hydrolysis constants and large exchange rate constants for substitution of inner-sphere water ligands. Such catalysts can be quantitatively recovered at the end of a reaction and reused. Recently, we reported that, at or near room temperature, direct polycondensations of diols and dicarboxylic acids, catalyzed by scandium trifluoromethanesulfonate (triflate) \[ \text{Sc(OTf)}_3 \] or scandium trifluoromethanesulfonimide (triflylimide) \[ \text{Sc(NTf}_2)_3 \] afford aliphatic polyesters with number average molecular weights \( M_n \) greater than \( 1.0 \times 10^4 \) (room-temperature polycondensation). We also demonstrated that transesterification does not occur during the polycondensations owing to the mild reaction conditions and the chemoselectivities of the catalysts. This type of polycondensation (chemoselective dehydration polycondensation) proceeds under mild conditions and can incorporate thermally unstable monomers containing a carbon-carbon double bond, a bromo group, and/or hydroxyl groups. Recently, we demonstrated the ring-opening copolymerization of \( \varepsilon \)-caprolactone initiated from the pendent hydroxyl groups of poly(nonamethylene D,L-malate) prepared via chemoselective dehydration polycondensation catalyzed by \( \text{Sc(OTf)}_3 \). This work was a study of a dual-catalytic \[ \text{Sc(OTf)}_3 \] system that combined a chemoselective dehydration polycondensation with a subsequent ring-opening polymerization of \( \varepsilon \)-caprolactone.
Although the polycondensation occurred as a one-step reaction and under mild conditions (35 °C), it required a large amount of the catalyst (ca. 1 mol%) and a long reaction time (>100 h). Therefore, it would be desirable if more efficient rare–earth-metal catalysts could be identified. One way to do so is to incorporate a ligand with a stronger electron-withdrawing ability. Herein, we describe the synthesis of three scandium compounds—scandium perfluorooctanesulfonate [Sc(OPf)₃], scandium nonafluorobutanesulfonate [Sc(ONf)₃] (Figure 1.1), and scandium bis(nonafluorobutanesulfonyl)imide [Sc(NNf₂)₃] (Figure 1.2)—that have ligands with stronger electron-withdrawing abilities. We have assessed the abilities of these compounds, and hence their Lewis acidities, to catalyze the synthesis of large molecular weight polyesters in short periods of time and under mild conditions. The results of a survey of other rare–earth-metals—Sm, Gd, Er, Nd, Dy, and Tm—that might be used as catalytic centers for dehydration polycondensations are also reported.

![Figure 1.1](image1.png)

**Figure 1.1** Molecular structure of scandium trifluoromethanesulfonate [Sc(OTf)₃], scandium nonafluorobutanesulfonate [Sc(ONf)₃], and scandium perfluorooctanesulfonate [Sc(OPf)₃].

![Figure 1.2](image2.png)

**Figure 1.2** Molecular structure of scandium trifluoromethanesulfonimide [Sc(NTF₂)₃] and scandium bis(nonafluorobutanesulfonyl)imide[Sc(NNf₂)₃].
1-2. Results and Discussion

Model Reaction.

As test cases to determine the abilities of the rare-earth-metal compounds to catalyze polyesterifications, the direct and simple esterification of acetic acid by an equimolar amount of ethanol was carried out in bulk in the presence of each rare-earth-metal catalyst (1.0 mol%) at 27 °C for 6 h without attempting to dehydrate the system. The esterification yields, as determined by $^1$H-NMR spectroscopy, using the ratio of the peak intensities at 3.73 ppm (CH$_3$CH$_2$OH, $J = 7.0$ Hz) and 4.12 ppm (CH$_3$CH$_2$OCOCH$_3$, $J = 7.1$ Hz), were between 51 and 67% (Scheme 1.1). Conversely, in the absence of a catalysis, little esterification occurred. Although the possibility existed that esterification could proceed via acid anhydride formation, a $^1$H-NMR signal was not found for acetic anhydride.$^8$ Therefore, given the results of the test runs (Scheme 1.1), rare-earth-metal perfluoroalkylsulfonates and bis(perfluoroalkylsulfonyl)imides can catalyze the direct esterification of carboxylic acids and alcohols at room temperature. Nd, Tm, and Sm imides tended to yield larger amounts of product (62-65%) than did the corresponding triflates (51-56%).

Scheme 1.1 Esterification of Equimolar Ethanol and Acetic Acid.

<table>
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<tr>
<th>Catalyst (0.1 mmol)</th>
<th>Conversion$^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(OTf)$_3$</td>
<td>67</td>
</tr>
<tr>
<td>Sc(ONf)$_3$</td>
<td>68</td>
</tr>
<tr>
<td>Sc(OPf)$_3$</td>
<td>62</td>
</tr>
<tr>
<td>Sc(NNf$_2$)$_3$</td>
<td>63</td>
</tr>
<tr>
<td>Nd(OTf)$_3$</td>
<td>51</td>
</tr>
<tr>
<td>Gd(OTf)$_3$</td>
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</tr>
<tr>
<td>Dy(OTf)$_3$</td>
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</tr>
<tr>
<td>Er(OTf)$_3$</td>
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<td>Tm(OTf)$_3$</td>
<td>56</td>
</tr>
<tr>
<td>Nd(NNf$_2$)$_3$</td>
<td>65</td>
</tr>
<tr>
<td>Tm(NNf$_2$)$_3$</td>
<td>62</td>
</tr>
<tr>
<td>Sm(NNf$_2$)$_3$</td>
<td>62</td>
</tr>
<tr>
<td>no catalyst</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

$^a$ Condition: [Acetic acid]$_0$ = [Ethanol]$_0$ = 5 mmol, Time = 6h, Temp., r.t.; $^b$ Determined by $^1$H-NMR.
Polycondensation Catalyzed by Sc Compounds.

To compare the catalytic efficiencies of Sc(OTf)$_3$\textsuperscript{7,8} (0.1 mol%) and Sc(OPF)$_3$ (0.1 mol%), bulk polycondensations of methylsuccinic acid (MSA) and 1,4-butanediol (1,4-BD) to afford poly(butylene methylsuccinate) ($T_g = -42$ °C) were run at 35 °C for 124 h and at 60 °C for 30 h. Interestingly, at the comparably low temperature of 35 °C, using either of the catalysts, polycondensation occurred; although, the $M_n$, as estimated by SEC, was greater for the Sc(OPF)$_3$-catalyzed reaction ($M_n = 7.3 \times 10^3$; $M_w/M_n = 1.66$; 96% yield) than for the Sc(OTf)$_3$-catalyzed reaction ($M_n = 2.2 \times 10^3$; $M_w/M_n = 1.54$; 97% yield). At 60 °C, $M_n = 9.3 \times 10^3$ ($M_w/M_n = 1.74$) with Sc(OPF)$_3$ as the catalyst and $4.0 \times 10^3$ ($M_w/M_n = 1.86$) when Sc(OTf)$_3$ was the catalyst. Therefore, Sc(OPF)$_3$ was the more effective catalysis, because the extent of the polycondensation was greater and less Sc(OPF)$_3$ could be used (0.1 mol%). At 60 °C, to synthesize a polyester with a $M_n$ of approximately $10.0 \times 10^3$, 1.0 mol% of Sc(OTf)$_3$ was required.\textsuperscript{7,8}

Scheme 1.2 Low Temperature Polycondensation of Adipic Acid and 3-methylpentanediol

The polycondensation of adipic acid (AdA) with 3-methyl-1,5-pentanediol (MPD) served as a model for amorphous polyester production (Scheme 1.2). A variety of rare–earth-metal compounds were used as catalysts and the polymerization conditions were surveyed (Table 1.1–1.4). The product, poly(3-methylpentamethylene adipate), has a low temperature glass point ($T_g = -63$ °C). Therefore, as it is an amorphous solid at the temperature of our experiments, the increased molecular motions of the chain (in comparison with a crystalline solid) should allow the polycondensation to proceed further at lower temperatures. Polycondensation of AdA with MPD proceeded at 80 °C catalyzed by Sc(OTf)$_3$ catalyst (0.1 mol% compared with the total number of moles of reactants) to
give a polyester with a $M_n$ of $10.0 \times 10^3$ even though the reaction was run for only 6 h (Table 1.1, run 2). Unfortunately, the remarkable increase for $M_n$ was not observed when Sc(ONf)$_3$ (runs 9 and 10) and Sc(OPf)$_3$ (runs 6–8) were used as the catalysts. It seems that the increased molecular motion, reflected in the lower $T_g$, more influenced on the polymerization rate than the catalytic activity.

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst</th>
<th>mol%</th>
<th>time</th>
<th>Yield$^d$</th>
<th>$M_n^e$ (crude) $\times 10^3$</th>
<th>$M_w/M_n^e$</th>
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</thead>
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<td>99</td>
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<td>99</td>
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<td>12</td>
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<td>14.7</td>
<td>1.88</td>
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</table>

| a | Adipic acid. | b | 3-Methyl-1,5-pentanediol. | c | All runs are performed by bulk condensation under reduced pressure (0.3-3.0 mmHg) at 80 °C. | d | Without reprecipitation. | e | Determined by SEC measurement in CHCl$_3$ relative to poly(styrene)s. |

Scandium trifluoromethanesulfonimide [Sc(NTf)$_2$] is air stable and a powerful Lewis acid, because of its large fluorine content (Figure 1.2). Koppel and colleagues evaluated various ligands chosen according to their abilities to withdraw electrons. They concluded that bis(nonafluorobutanesulfonyl)imide [NNf$_2$] had even a better electron-withdrawing ability than did trifluoromethanesulfonimide [NTf$_2$]. In an attempt to further decrease the catalyst concentration required for the model polyesterification, Sc(NNf$_2$)$_3$ was prepared according to the literature protocol and the Sc(NNf$_2$)$_3$-catalyzed polyesterification of AdA and MPD was carried out at 60 °C.
(Table 1.2). Both Sc(NTf$_2$)$_3$ (runs 4–6) and Sc(NNf$_2$)$_3$ (runs 7–9) acted as polycondensation catalysts. Even when only 0.05 mol% of Sc(NTf$_2$)$_3$ or Sc(NNf$_2$)$_3$ was used, (runs 6 and 9) poly(3-methyl pentamethylene adipate) with $M_n$s of $12.0 \times 10^3$ and $12.3 \times 10^3$ were synthesized, respectively. Unfortunately, a marked improvement in catalytic efficiency was not observed with Sc(NNf$_2$)$_3$ in comparison with Sc(NTf$_2$)$_3$. These $M_n$s were much larger than that found when using same amount of Sc(OTf)$_3$ ($5.6 \times 10^3$, run 3), indicating that the catalytic activity was increased by using (NTf$_2$)$_3$ or (NNf$_2$)$_3$ as the ligand. For all of the runs reported in Table 1.2 the $M_w/M_n$ values, which are between 1.6 and 2.1, are approximately the theoretical values predicted by Flory’s theory of polycondensation, for which $M_w/M_n = 1 + p$, where $p$ is the extent of reaction.$^{15}$ The results also support the assumption that reaction conditions for polyesterification could be found that did not promote transesterification (data not shown).$^{7,8,10,11}$

<table>
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<tr>
<th>run</th>
<th>catalyst</th>
<th>mol%</th>
<th>time h</th>
<th>Yield$^d$ %</th>
<th>$M_n$ (crude) $\times 10^3$</th>
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</table>

$^a$ Adipic acid. $^b$ 3-Methyl-1,5-pentanediol. $^c$ All runs are performed by bulk condensation under reduced pressure (0.3-3.0 mmHg) at 60 °C. $^d$ Without reprecipitation. $^e$ Determined by SEC measurement in CHCl$_3$ relative to poly(styrene)s.
We consider that a stronger Lewis acid has the possibility to afford the faster reaction rate under kinetic control. To appraise the strengths of Sc(NTf₂)₃ and Sc(NNf₂)₃ as Lewis acids towards a carboxylic acid moiety, the \(^{13}\)C-NMR spectra of acetic acid alone and equimolar amounts of acetic acid and either Sc(NTf₂)₃ or Sc(NNf₂)₃ (in acetone-d₆, at a field strength of 150 MHz, and 27 °C) were recorded. The carbonyl carbon signal of acetic acid (173.0 ppm) shifted downfield to 179.8 ppm when Sc(NTf₂)₃ was present and to 181.1 ppm when Sc(NNf₂)₃ was present. The chemical shift differences [Δν; 6.9 ppm for Sc(NTf₂)₃, and 7.1 ppm for Sc(NNf₂)₃] are larger than those found for Sc(OTf)₃ (4.6 ppm) or for Sc(ONf)₃ (3.2 ppm). The sizes of the Δν values tend to correlate with the sizes of the \(M_n\) values reported in Tables 1.1 and 1.2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Chemical Shift Difference (Δν)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Sc(NNf₂)₃</td>
<td>7.1</td>
</tr>
<tr>
<td>b) Sc(NTf₂)₃</td>
<td>6.9</td>
</tr>
<tr>
<td>c) Sc(OTf)₃</td>
<td>4.6</td>
</tr>
<tr>
<td>d) Sc(ONf)₃</td>
<td>3.2</td>
</tr>
<tr>
<td>e) No catalyst</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 1.3** \(^{13}\)C-NMR spectra of acetic acid in the presence of equivalent scandium catalysts in acetone-\(d_6\) (27 °C).
The relative catalytic strengths of various rare–earth-metals (with triflate ligands) were accessed by performing the polycondensation of AdA and MPD. The rare–earth-metals included Sc, Nd, Sm, Gd, Dy, Er, and Tm \((\text{Table 1.3})\). The polycondensations were run at 60 °C for 24 h with 0.5 mol% equivalent of each catalyst, and the amorphous polyester was synthesized. The \(M_n\) values of the polyesters synthesized with Sm(OTf)\(_3\) \((1.7 \times 10^3)\) and Nd(OTf)\(_3\) \((3.7 \times 10^3)\) as catalysts were much smaller than when Sc(OTf)\(_3\) \((13.3 \times 10^3)\) and Tm(OTf)\(_3\) \((8.3 \times 10^3)\) were the catalysts.

### Table 1.3 Direct polycondensations of AdA\(^a\) and MPD\(^b\) under reduced pressure at 60 °C\(^c\)

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst</th>
<th>time</th>
<th>Yield(^d)</th>
<th>(M_n)(^e) (crude) (\times 10^3)</th>
<th>(M_w/M_n)(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nd(OTf)(_3)</td>
<td>24</td>
<td>&gt;99</td>
<td>3.7</td>
<td>1.76</td>
</tr>
<tr>
<td>2</td>
<td>Sm(OTf)(_3)</td>
<td>24</td>
<td>&gt;99</td>
<td>1.7</td>
<td>1.89</td>
</tr>
<tr>
<td>3</td>
<td>Gd(OTf)(_3)</td>
<td>24</td>
<td>&gt;99</td>
<td>4.1</td>
<td>1.72</td>
</tr>
<tr>
<td>4</td>
<td>Dy(OTf)(_3)</td>
<td>24</td>
<td>&gt;99</td>
<td>4.4</td>
<td>1.81</td>
</tr>
<tr>
<td>5</td>
<td>Er(OTf)(_3)</td>
<td>24</td>
<td>&gt;99</td>
<td>5.9</td>
<td>1.95</td>
</tr>
<tr>
<td>6</td>
<td>Tm(OTf)(_3)</td>
<td>24</td>
<td>&gt;99</td>
<td>8.3</td>
<td>2.05</td>
</tr>
<tr>
<td>7</td>
<td>Sc(OTf)(_3)</td>
<td>24</td>
<td>99</td>
<td>13.3</td>
<td>1.75</td>
</tr>
</tbody>
</table>

\(^a\) Adipic acid. \(^b\) 3-Methyl-1,5-pentanediol. \(^c\) All runs are performed by bulk condensation under reduced pressure (0.3-3.0 mmHg) at 60 °C. \(^d\) Without reprecipitation. \(^e\) Determined by SEC measurement in CHCl\(_3\) relative to poly(styrene)s.

**Polycondensation Catalyzed by rare–earth-metal Compounds.**

To examine the effects of other ligand/metal combinations Sm(NNf\(_2\))\(_3\), Nd(NNf\(_2\))\(_3\), and Tm(NNf\(_2\))\(_3\) were prepared using the same procedure as that used to prepare Sc(NNf\(_2\))\(_3\).\(^{14}\) The polycondensations of AdA and MPD, using Sm(NNf\(_2\))\(_3\), Nd(NNf\(_2\))\(_3\), and Tm(NNf\(_2\))\(_3\), were performed at 60 °C for various lengths of time. The \(M_n\) and \(M_w/M_n\) values and the yields of the polyester are listed in Table 1.4. When the polycondensation was run for 24 h in the presence of 0.5 mol% Sm(NNf\(_2\))\(_3\), the \(M_n\) of the synthesized polyester was much larger \((14.8 \times 10^3, \text{run 2})\) than when Sm(OTf)\(_3\) was used as the catalyst \((2.8 \times 10^3, \text{run 1})\). Nd(NNf\(_2\))\(_3\) \((0.1 \text{ mol%})\) also produced a
polyester with a greater $M_n$ ($14.8 \times 10^3$, run 5) than did the equivalent amount of Nd(OTf)$_3$ ($3.1 \times 10^3$, run 4). The catalytic activity of Tm(NNf$_2$)$_3$ ($M_n = 23.5 \times 10^3$, run 12) was markedly better than that of Tm(OTf)$_3$ ($M_n = 6.3 \times 10^3$, run 8) or Sc(NNf$_2$)$_3$ ($M_n = 17.9 \times 10^3$, run 13 in Table 1.2) (reaction times were 24 h). Compared with Tm(NTF$_2$)$_3$ (0.1 mol%, run 14), an increase of $M_n$ was also observed in the polycondensation at 60 ºC for 12h (run 9), indicating that combination of (NNf$_2$)$_3$ and thulium is a promised candidate for an excellent catalyst for polycondensation.

### Table 1.4 Direct polycondensations of AdA$^a$ and MPD$^b$ under reduced pressure at 60 ºC$^c$

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst</th>
<th>mol%</th>
<th>time h</th>
<th>Yield$^d$</th>
<th>$M_n$ (crude) $\times 10^3$</th>
<th>$M_w$/$M_n$ $^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sm(OTf)$_3$</td>
<td>0.5</td>
<td>24</td>
<td>&gt;99</td>
<td>2.8</td>
<td>2.02</td>
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<tr>
<td>2</td>
<td>Sm(NNf$_2$)$_3$</td>
<td>0.5</td>
<td>24</td>
<td>99</td>
<td>14.8</td>
<td>2.01</td>
</tr>
<tr>
<td>3</td>
<td>Sm(NNf$_2$)$_3$</td>
<td>0.1</td>
<td>24</td>
<td>98</td>
<td>13.6</td>
<td>1.97</td>
</tr>
<tr>
<td>4</td>
<td>Nd(OTf)$_3$</td>
<td>0.1</td>
<td>24</td>
<td>&gt;99</td>
<td>3.1</td>
<td>1.71</td>
</tr>
<tr>
<td>5</td>
<td>Nd(NNf$_2$)$_3$</td>
<td>0.1</td>
<td>24</td>
<td>&gt;99</td>
<td>14.8</td>
<td>2.00</td>
</tr>
<tr>
<td>6</td>
<td>Nd(NNf$_2$)$_3$</td>
<td>0.01</td>
<td>24</td>
<td>&gt;99</td>
<td>3.0</td>
<td>1.74</td>
</tr>
<tr>
<td>7</td>
<td>Tm(OTf)$_3$</td>
<td>0.1</td>
<td>6</td>
<td>&gt;99</td>
<td>2.7</td>
<td>2.09</td>
</tr>
<tr>
<td>8</td>
<td>Tm(OTf)$_3$</td>
<td>0.1</td>
<td>24</td>
<td>&gt;99</td>
<td>6.3</td>
<td>1.97</td>
</tr>
<tr>
<td>9</td>
<td>Tm(NNf$_2$)$_3$</td>
<td>0.1</td>
<td>6</td>
<td>98</td>
<td>13.4</td>
<td>1.83</td>
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<tr>
<td>10</td>
<td>Tm(NNf$_2$)$_3$</td>
<td>0.1</td>
<td>12</td>
<td>97</td>
<td>17.1</td>
<td>1.86</td>
</tr>
<tr>
<td>11</td>
<td>Tm(NNf$_2$)$_3$</td>
<td>0.1</td>
<td>18</td>
<td>97</td>
<td>20.8</td>
<td>1.73</td>
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<tr>
<td>12</td>
<td>Tm(NNf$_2$)$_3$</td>
<td>0.1</td>
<td>24</td>
<td>97</td>
<td>23.5</td>
<td>1.66</td>
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<tr>
<td>13</td>
<td>Tm(NNf$_2$)$_3$</td>
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<td>12</td>
<td>&gt;99</td>
<td>5.0</td>
<td>1.86</td>
</tr>
<tr>
<td>14</td>
<td>Tm(NTf$_2$)$_3$</td>
<td>0.1</td>
<td>6</td>
<td>&gt;99</td>
<td>10.7</td>
<td>1.80</td>
</tr>
</tbody>
</table>

$^a$ Adipic acid. $^b$ 3-Methyl-1,5-pentanediol. $^c$ All runs are performed by bulk condensation under reduced pressure (0.3-3.0 mmHg) at 60 ºC. $^d$ Without reprecipitation. $^e$ Determined by SEC measurement in CHCl$_3$ relative to poly(styrene)s.

MALDI-TOF spectra were recorded to characterize the absolute molecular weights and to identify the composition(s) of the repeating chemical units of the polyesters. In a spectrum of Sc(OTf)$_3$-catalyzed polycondensation, a repeating pattern composed of three peaks was seen, with each peak in the group separated by a $m/z$ of ±229 from the nearest corresponding peaks (Figure
1.4a). The $m/z$ value of 229 corresponds to the molecular weight of the chemical unit formed by AdA and MPD. The differences among the $m/z$ values of the three peaks within a group suggest that the polyesters are terminated with an $\alpha$-hydroxyl and an $\omega$-carboxyl, or an $\alpha$–hydroxyl and an $\omega$-hydroxyl, or an $\alpha$-carboxyl and an $\omega$-carboxyl at the ends. For example, the peaks at 3472, 3572, and 3600 would be derived from polyesters having an $\alpha$-hydroxyl and an $\omega$-carboxyl, an $\alpha$-hydroxyl and an $\omega$-hydroxyl, and an $\alpha$-carboxyl and an $\omega$-carboxyl termini, respectively. There are also smaller peaks found in the mass spectrum of the polyester synthesized in the presence of Sc(OTf)$_3$, e.g., one at 3454 $m/z$ (Figure 1.4a). These peaks have a $m/z$ that is 18 amu smaller than that of the nearest peak associated with a polyester terminated with $\alpha$-hydroxyl and $\omega$-carboxyl groups. The $m/z$ difference of 18 is that expected for the mass difference between a linear and a cyclic polyester (18). Therefore, intermolecular and intramolecular condensation occurred when Sc(OTf)$_3$ was the catalyst. Interestingly, in the spectra of Sc(NNf$_2$)$_3$ (Figure 1.4b) and Tm(NTf$_2$)$_3$-catalyzed polycondensations (Figure 1.4c), signals assigned to the polyesters terminated with an $\alpha$-hydroxyl and an $\omega$-carboxyl and an $\alpha$-carboxyl and an $\omega$-carboxyl at the ends was confirmed, but a signal ascribed to polyester with an $\alpha$–hydroxyl and an $\omega$-hydroxyl termini were not observed. Higher catalytic activities of Sc(NNf$_2$)$_3$ and Tm(NTf$_2$)$_3$ completed the polycondensations until the molar balances of hydroxyl and carboxyl functionalities broke. That may be a reason why the an $\alpha$–hydroxyl and an $\omega$-hydroxyl termini were not observed.
Figure 4. MALDI-TOF mass spectra of poly(3-methypentamethylene adipate) from (a) Sc(OTf)$_3$, (b) Sc(NNf$_2$)$_3$, and (c) Tm(NTf)$_3$-catalyzed polycondensations.
In this chapter, we demonstrated that scandium catalysts with strong electron-withdrawing ligands could catalyze the polycondensation of AdA and MPD under conditions of a moderate temperature, a short time period, and a lesser amount of catalyst. Other rare-earth-metal catalysts containing ligands with strong electron-withdrawing abilities were also synthesized and their catalytic efficiencies tested using the polycondensation of AdA and MPD. Tm(NNf₂)₃ was a more effective catalyst than was Sc(OTf)₃, Sc(NNf₂)₃, Tm(OTf)₃, or Tm(NTf₂)₃. Our work now makes it possible to synthesize aliphatic polyesters of $M_n > 1.0 \times 10^4$ at a moderate temperature (60 °C), within a short period of time (6 h) using a small amount of catalyst (0.05–0.1 mol%). Polycondensations that can be performed at moderate temperatures are environmentally friendly procedures and may find use when designing polymers with specific chiralities, functionalities, and/or biological activities.
1-3. Experimental Section

Materials. 1,4-butanediol (1,4-BD), methylsuccinic acid (MSA), and adipic acid (AdA) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Sc(OTf)₃, 3-methyl-1,5-pentanediol (MPD), Thulium(III) acetate tetrahydrate, thulium trifluoromethanesulfonate [Tm(OTf)₃], 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (PfOH), and samarium(III) acetate tetrahydrate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Bis(nonfluorobutanesulfonyl)imide (HNNf₂) was obtained from JEMCO Co., Ltd. (Tokyo, Japan). Scandium trichloride and neodymium acetate monohydrate were obtained from Mitsuwa Chemical Co. Ltd. (Osaka, Japan). 1,1,2,2,3,3,4,4,4-nonafluoro-1-butanesulfonic acid  (NfOH), Sm(OTf)₃, Gd(OTf)₃, Er(OTf)₃, Nd(OTf)₃, and Dy(OTf)₃ were purchased from Aldrich Co., Ltd. (Milwaukee, WI, U.S.A.) Scandium trifluoromethanesulfonimide [Sc(NTf₂)₃] was prepared in our laboratory according to the procedure described in the literature.⁶

Measurements. ¹H and ¹³C-NMR spectra were recorded at 27 °C using a Bruker DPX200 or a DPX600 spectrometer (200 MHz and 600 MHz, respectively). Chemical shifts were referenced to tetramethylsilane (δ = 0). The number average molecular weight (Mn) and polydispersity index (Mw/Mn) of each polyester was estimated using a size exclusion chromatography (SEC) system that included a Tosoh DP8020 pump system, a RI (Tosoh RI-8020) detector, and a Tosoh TSK-GEL SUPERMULTIPOREHZ-M column calibrated with polystyrene standards. The eluent was CHCl₃; the flow rate was 0.35 mL/min; and the temperature was 40 °C. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Kratos PCAxima CFRplus V2.4.0 mass spectrometer, with 2,5-dihydroxybenzoic acid as the matrix reagent. To generate sodium cations of the polycondensation products ([M+Na]+), NaI was included.

Preparation of Sc(OPf)₃¹² Sc(OPf)₃ was synthesized as previously described. An aqueous solution of ScCl₃•6H₂O (1.0 g, 3.8 mmol, 4 mL) was added to an aqueous solution of PfOH (5.8 g, 11.6 mmol, 35 mL), and the mixture was stirred for 19 h at room temperature. The aqueous layer was
decanted and the residue was washed with H₂O until the pH of the aqueous layer was neutral. The residue, a viscous solid, was dried at 120 °C for 15 h in vacuo to give a white solid (4.7 g, 80%).

**Preparation of Sc(ONf)₃** Sc(ONf)₃ was synthesized as previously described. Sc₂O₃ (0.3 g, 2.2 mmol) was added to an aqueous solution of HONf (3.9 g 13.1 mmol, 10 mL) and the mixture was heated at 100 °C for 1 h. After filtration to remove unreacted Sc₂O₃, water was removed by evaporation under reduced pressure, and a white solid remained (3.9 g, 98%).

**Preparation of Sc(NNF₂)₃,¹⁴ samarium bis(nonafluorobutanesulfonyl)imide [Sm(NNF₂)₃], neodymium bis(nonafluorobutanesulfonyl)imide [Nd(NNF₂)₃], and thulium bis(nonafluorobutanesulfonyl)imide [Tm(NNF₂)₃].** The acetates of Sc, Sm, Nd, and Tm, were each dissolved in H₂O containing HNNF₂. The mixtures were heated and refluxed for 3 h. The products were isolated by drying at 110 °C under high vacuum (<5 mmHg). Anal. Calcd for Sc(NNF₂)₃·4H₂O (76% yield): C, 15.52; H, 0.43; N, 2.26. Found: C, 15.30; H, 0.38; N, 2.63. Anal. Calcd for Sm(NNF₂)₃·4H₂O (98% yield): C, 14.68; H, 0.41; N, 2.14. Found: C, 14.50; H, 0.48; N, 2.49. Anal. Calcd for Nd(NNF₂)₃ (99% yield): C, 15.29; H, 0; N, 2.23. Found: C, 14.48; H, 0; N, 2.72. Anal. Calcd for Tm(NNF₂)₃·4H₂O (98% yield): C, 14.55; H, 0.40; N, 2.12. Found: C, 14.46; H, 0.40; N, 2.61.

**Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Rare-Earth Catalysts.** For poly(3-methylpentamethylene adipate), a typical polycondensation was carried out as follows. In a 10 mL flask, 3-methyl-1,5-pentanediol (MPD; 0.83 g, 7.0 mmol), adipic acid (AdA; 1.02 g, 7.0 mmol), and Sc(OTf)₃ (0.1 mol%) were stirred at 80 °C (760 mmHg) until a homogeneous state was observed. The pressure and temperature were gradually decreased to 0.3-3 mmHg and 60 °C, respectively, at which point polycondensation commenced. When the reaction was finished, the yield of the polyester was calculated by subtracting the known weight of the catalyst from the total weight of the solid present (>99% yield). After precipitating the product from CHCl₃ (5 mL) into diethyl ether (100 mL), the yield was 70%.
1-4. References and Notes


Chapter 2

Microwave-Assisted Low-Temperature Dehydration Polycondensation of
Dicarboxylic Acids and Diols

Abstract

We have demonstrated and report herein that dehydration polycondensations of various
dicarboxylic acids and 3-methyl-1,5-pentanediol catalyzed by Sc(OTf)$_3$ under the condition of a
moderate temperature was accelerated using the multimode microwave heating (2.45 GHz, up to
200W) compared with the conventional heating. We discussed about the acceleration as well as
non-thermal microwave effect from the kinetics. Our work now makes it possible to synthesize
aliphatic polyesters faster than conventional methods and provides the fundamental information
about non-thermal microwave effect on step polymerization.
2-1. Introduction

Currently, because of increasing concerns about damage to the environment, the development of new, eco-friendly (industrially relevant) chemical reactions and materials is crucial. Aliphatic polyesters have attracted much interest as environmentally benign, biodegradable polymers.\(^1\) In general, aliphatic polyesters are commercially produced by polycondensation of a dicarboxylic acid and a 1.1–1.5 mol excess of a diol at a temperature >250 °C and under an extremely reduced pressure.\(^2,3\) These severe reaction conditions preclude the syntheses of aliphatic polyesters with low thermostabilities and the use of thermally unstable monomeric reagents. Polycondensation reactions are catalyzed by Lewis acids,\(^4\) but only a few of these acids are suitable catalysts because most are labile in the presence of protic substances, e.g., carboxylic acids, alcohols, and water, making these reagents unsuitable for dehydration polycondensation reactions. Recently, we reported that at or near room temperature direct polycondensation of diols and dicarboxylic acids, catalyzed by scandium trifluoromethanesulfonate (triflate) [Sc(OTf)\(_3\)]\(^5\) or scandium trifluoromethanesulfonimide (triflylimide) [Sc(NTf\(_2\))\(_3\)]\(^6\), affords aliphatic polyesters with number average molecular weights (\(M_n\)) >10\(^4\) (room-temperature polycondensation\(^7\)). We also demonstrated that these polycondensation systems can incorporate thermally unstable monomers that contain a carbon-carbon double bond,\(^6b\) a bromo group,\(^6b\) hydroxyl groups,\(^8a\) a mercapto group,\(^8b\) and/or a disulfide linkage\(^8c,8d\) and that these reactions are under kinetic control (chemoselective dehydration polycondensation). Although the polycondensation reactions were run as one-step reactions under mild conditions (35 °C), they required large amounts of the catalyst (ca. 1 mol%) and long reaction times (>100 h). Therefore, we next focused on identifying more active catalysts and found that scandium and thulium bis(nonafluorobutanesulfonyl)imide ([Sc(NNf\(_2\))\(_3\)] and [Tm(NNf\(_2\))\(_3\)]) were more efficient catalysts and allowed us to obtain high-molecular-weight polyesters (\(M_n\) > 2.0 × 10\(^4\)) from adipic acid (AdA) and 3-methyl-1,5-pentanediol (MPD) at 60 °C in a short period of time (24 h) and with a smaller amount of catalyst (0.1 mol%) than had previously been possible.\(^9\)
Rapid syntheses that depend on microwave irradiation have attracted interest because they are environmentally benign. Since first reported in 1986,\textsuperscript{10a,10b} microwave irradiation has been used to shorten the reaction times of organic syntheses, to decrease the levels of side products, and to improve the yields and/or chemoselectivities of the products.\textsuperscript{10c} There is an exponentially increasing number of publications dealing with microwave-assisted chain polymerizations, e.g., anionic polymerization of acrylamides,\textsuperscript{11} ring-opening cationic polymerization of 2-oxazolines,\textsuperscript{12} and ring-opening polymerization of \(\varepsilon\)-caprolactones,\textsuperscript{13} indicates the remarkable interest in this technique.\textsuperscript{14} In addition to chain polymerizations, microwave-assisted step-growth polymerizations have been successfully attempted in a domestic microwave oven.\textsuperscript{14} For example, Scherf and colleagues synthesized donor-acceptor pi-conjugated polymers using microwave irradiation at 150 °C for 15 min.\textsuperscript{15} Nagahata and colleagues obtained poly(butylene succinate) that had a weight-average molecular weight (\(M_w\)) of \(2.90 \times 10^4\) in the incredibly short time of 10 min using microwave irradiation.\textsuperscript{16} However, because of the high temperatures that they used (200–260 °C), it is difficult to assess the importance of a non-thermal effect on their polycondensation reactions. To the best of our knowledge, there has been no report concerning a non-thermal effect in microwave-assisted polycondensation reactions,\textsuperscript{14} although there has been a report that non-thermal microwaves play a role in the chain polymerization of a lactone.\textsuperscript{13} Therefore, we studied microwave-assisted syntheses of polyesters at a relatively low temperature (80 °C) using a microwave chamber equipped with a temperature control, and the results are reported herein. We compared the rates of the microwave-assisted polymerizations with those obtained using conventional heating, which allowed us to characterize the contribution of the non-thermal effects of the microwaves. This is the first report of a catalyzed step polymerization for which the second-order rate constant was increased by a non-thermal microwave-induced effect.
2-2. Results and Discussion

Microwave-Assisted Polycondensation of AdA and MPD Catalyzed by Sc Compounds.

Dehydration polycondensation reactions of AdA with MPD were performed under different conditions to compare the effects of microwave and oil bath heating. The product, poly(3-methylpentamethylene adipate), has a low glass transition point ($T_g = -63 ^\circ C$). Because this product was an amorphous solid at the temperature of our experiments, the molecular rotations of the chain should have allowed the polycondensation reactions to proceed as bulk reactions. A microwave-assisted polycondensation of AdA with MPD was performed at 80 °C (temperature-controlled microwave irradiation for 6 h at a maximum power of 200 W) with Sc(OTf)$_3$ as the catalyst (0.5 mol% relative to the total number of moles of reactants), which yielded a polyester with a $M_n$ of $9.8 \times 10^3$ (Table 2.1, run 3). The $M_n$ of that polyester was larger by ~53% than the one obtained by conventional heating ($M_n = 6.4 \times 10^3$, run 1). Additionally, polyesters with similar $M_n$ values were obtained by microwave heating and by conventional heating when using a reaction time for the former was half that of the latter (3 h, run 2 vs. 6 h, run 1). We also observed substantial increases in $M_n$ when the Sc(OTf)$_3$ concentration was reduced (0.1 mol%, Table 2.1, runs 4–6) for the microwave runs in comparison with the conventional heating runs and when the more effective catalyst, scandium bis(nonafluorobutanesulfonyl)imide [Sc(NNf$_2$)$_3$], was used (Table 2.1, runs 7–12). When the polymerizations using Sc(OTf)$_3$ as the catalyst were carried out for 24 h, we obtained polyesters with $M_n$ values of $1.5 \times 10^4$ (Table 2.1, runs 13).
Table 2.1 Direct Polycondensations of AdA\(^{a}\) and MPD\(^{b}\) under Reduced Pressure at 80 °C\(^{c}\)

<table>
<thead>
<tr>
<th>Run</th>
<th>Catalyst</th>
<th>mol%</th>
<th>Heating method</th>
<th>Time (h)</th>
<th>Yield(^{f}) (%)</th>
<th>(M_{n}^{g}) (crude) (\times 10^3)</th>
<th>(M_n/M_w^{h})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sc(OTf)(_3)</td>
<td>0.5</td>
<td>OB(^{d})</td>
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\(^{a}\)Adipic acid. \(^{b}\)3-Methyl-1,5-pentanediol. \(^{c}\)All runs are performed by bulk condensation at 3.0 kPa and 80 °C. \(^{d}\)Oil bath heating. \(^{e}\)Microwave heating. \(^{f}\)Temperature-controlled irradiation at a maximum power of 200 W. \(^{g}\)Without reprecipitation. \(^{h}\)Determined by SEC with CHCl\(_3\) as the eluent. Values are reported relative to those of poly(styrene) standards.

To examine the effects of microwave heating on the polycondensation reaction, \(^{1}\)H-NMR spectra of poly(3-methylpentamethylene adipate) synthesized by Sc(OTf)\(_3\) catalysis under conditions of microwave and conventional heating were recorded. These spectra showed that all polyesters had the expected structures and that peaks that could be ascribed to side-reaction products were absent (Figure 2.1). MALDI-TOF spectra were recorded to characterize the absolute molecular weights and repeat units of the polyesters. In the spectra of the polyesters obtained by each heating method, two peak patterns separated by an \(m/z\) of ±229 were observed. The value of 229 is the expected \(m/z\) for the repeating unit (Figure 2.2). The differences among the \(m/z\) values of the three peaks within a group suggest that the polyesters terminated with an \(\alpha\)-hydroxyl and an \(\omega\)-carboxyl, an \(\alpha\)-hydroxyl and an \(\omega\)-hydroxyl, or an \(\alpha\)-carboxyl and an \(\omega\)-carboxyl. For example, the peaks at 2546, 2647, and 2674 would be derived from polyesters having an \(\alpha\)-hydroxyl and an \(\omega\)-carboxyl, an \(\alpha\)-hydroxyl and
an ω-hydroxyl, and an α-carboxyl and an ω-carboxyl at the termini, respectively. Peaks at 2582, which correspond to cyclic polyesters, were also observed.

<table>
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<th>Split, J (Hz)</th>
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</tr>
<tr>
<td>b</td>
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<td>b</td>
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<tr>
<td>c</td>
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<tr>
<td>d</td>
<td>1.57-1.34</td>
<td>m</td>
</tr>
<tr>
<td>e</td>
<td>0.95</td>
<td>d (5.9)</td>
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</table>

Figure 2.1. 1H-NMR spectra of poly(3-methylpentamethylene adipate) [(a) Microwave heating, (b) Oil bath heating].
Figure 2.2 MALDI-TOF mass spectra of poly(3-methylpentamethylene adipate) [(a) Microwave heating, (b) Oil bath heating].
Polycondensation Kinetics.

We also investigated the effect of microwave irradiation on the second-order kinetics of the catalyzed polycondensation reactions. In general, when equimolar amounts of dicarboxylic acids and diols \( (c = [\text{COOH}] = [\text{OH}]) \) are mixed, polycondensation in the presence of a catalyst is a second-order reaction, and the number-averaged degree of polymerization \( (X_n) \) is expected to increase linearly with time. We removed aliquots from the conventional-heating and microwave-heating reactions every 10 minutes, which were then used to determine the \( M_n \) values (by SEC) and to calculate \( X_n \).

\[
R = -\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}] \quad \Rightarrow \quad \frac{dc}{dt} = kc^2 \quad (1)
\]

\[
\frac{1}{c} = kt + \text{const.} \quad (2)
\]

\[
p = \frac{c_0 - c}{c_0} \quad \Rightarrow \quad c = c_0(1 - p) \quad (p: \text{extent of polymerization}) \quad (3)
\]

\[
X_n = \frac{c_0}{c} = \frac{1}{1 - p} \quad \Rightarrow \quad 1 - p = \frac{1}{X_n} \quad (4)
\]

\[
X_n = c_0kt + \text{const.} \quad (5)
\]

Data for the polymerization of AdA with MPD catalyzed by Sc(OTf)\(_3\) or Sc(NNF\(_2\))\(_3\) are shown in Figure 2.3. The data follow Eq. 5 with values for \( X_n \) that increase linearly as a function of reaction time. The \( M_w/M_n \) values that were obtained from the plots are between 1.8 and 2.1 and are approximately those predicted by Flory’s theory of polycondensation, where \( M_w/M_n = 1 + p \) and \( p \) is the extent of reaction. In addition, we found that the proportionality constant \( (c_0k = 0.633 \text{ sec}^{-1}) \) for the microwave-assisted polycondensation was 1.6 times greater than that of the conventional-heating experiment \( (c_0k = 0.397 \text{ sec}^{-1}; \text{ Figure 2.3, left panel}) \). Additionally, with Sc(NNF\(_2\))\(_3\) as the catalyst, the polycondensation proportionality constant obtained when microwave
irradiation was used \( (c_0k = 0.876 \text{ sec}^{-1}) \) was 1.5 times greater than when conventional heating was used \( (c_0k = 0.580 \text{ sec}^{-1}) \) \( \text{(Figure 2.3, right panel)} \). To conclusively demonstrate that a non-thermal effect was the cause of the increased rate, we had to eliminate the possibility that the rate difference was the result of removing the samples outside of the oil bath and the microwave chamber. Therefore, we also carried out polycondensation reactions for 60 min before sampling \( \text{(Figure 2.3, left panel, dash lines)} \). Given that there was no apparent difference between the sampling methods for both sets of experiments, we concluded that the microwave-assisted polycondensation reactions were accelerated by a non-thermal microwave-induced effect.

![Figure 2.3 Plots of \( M_n \) vs. time for the polycondensation of adipic acid and 3-methyl-1,5-pentanediol. Left panel, 3 kPa, 80 °C, 0.5 mol% Sc(OTf) 3. Samples were removed every 10 min outside of the temperature controlled environment (solid lines; microwave heating, diamonds; oil bath heating, squares), or a sample was removed after 60 min (circle, dashed line). The lines are linear interpolations of the data points. Right panel: Conditions were as for the experiments shown in the left panel except that 0.5 mol% Sc(NNF2) 3 was the catalyst.](image-url)
Microwave-Assisted Polycondensation of MPD with Dicarboxylic Acids Other than AdA.

To determine whether the non-thermal microwave-induced effect was independent of the type of monomer, dicarboxylic acids (succinic acid, glutaric acid, methyl succinic acid, and sebacic acid) were individually polycondensed with MPD at 80 °C and 3.0 kPa with 0.5% mol Sc(OTf)₃. (These conditions were used for a polycondensation of AdA and MPD.) All polycondensation reactions proceeded smoothly as expected because all of the polyester products are amorphous and have a glass transition point lower than room temperature (poly(3-methyl pentamethylene succinate), −51 °C; poly(3-methyl pentamethylene sebacate), −88 °C; poly(3-methyl pentamethylene methylsuccinate), −64 °C; poly(3-methyl pentamethylene glutarate), −64 °C). We always obtained linear relationships between $X_n$ and time ([Figure 2.4](#)), and for $M_w/M_n$, we obtained values between 1.8 and 2.1, which are approximately the values predicted by Flory’s theory of polycondensation.¹⁸ We established that the microwave-assisted polycondensation reactions were at least 1.4-fold more rapid than were the corresponding conventional polycondensation reactions: poly(3-methyl pentamethylene succinate), 1.6-fold; poly(3-methyl pentamethylene glutarate), 1.4-fold; poly(3-methyl pentamethylene methylsuccinate), 2.5-fold; and poly(3-methyl pentamethylene sebacate), 1.8-fold. Interestingly, when MSA was used, the $M_n$ for the polyester produced by microwave-assisted polycondensation with more than two times greater than that for the polyester produced by the conventional heating was attained.
Figure 2.4 Plots of $M_n$ vs time for direct polycondensations of MPD and various dicarboxylic acids [(a) succinic acid, (b) glutaric acid, (c) methyl succinic acid, (d) sebacic acid] under reduced pressure at 80 °C catalyzed by Sc(OTf)$_3$ ([catalyst] = 0.5 mol%).
In summary, for the work reported in this communication, we demonstrated that microwave heating accelerates the rate of AdA/MPD polycondensation catalyzed by Sc(OTf)$_3$ at a moderate temperature and that a smaller amount of catalyst can be used than in a conventional polycondensation. We also investigated how microwave heating affects the kinetics of polycondensation in detail by determining the second-order proportionality constants from plots of $X_n$ as a function of time. Finally, we also found that the non-thermal microwave effect might affect the rates of polycondensation reactions for dicarboxylic acids other than AdA. These fundamental results provide new guidelines for the microwave-assisted, eco-friendly production of materials.
2-3. Experimental Section

Materials. Adipic acid (AdA), glutaric acid (GlA), sebacic acid (SeA), and succinic acid (SuA) were purchased from Nacalai Tesque, Inc., (Kyoto, Japan). Methyl succinic acid (MSA) was purchased from Aldrich Co., Ltd. (Milwaukee, WI). Sc(OTf)₃ was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). 3-Methyl-1,5-pentanediol (MPD) and decahydronaphthalene (mixture of cis and trans) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Scandium bis(nonafluorobutanesulfonylimide [Sc(NNf₂)₃] was prepared in our laboratory according to the procedure described in the literature."9

Measurements. ¹H-NMR spectra were recorded at 27 °C using a Bruker Analytik DPX200 spectrometer (200 MHz). The number-average molecular weight (Mₙ) and the polydispersity index (Mₘ/Mₙ) of each polyester were estimated using a size exclusion chromatography (SEC) system that included a Tosoh DP8020 pump system, an RI (Tosoh RI-8020) detector, and a Tosoh TSKgel SuperMultiporeHZ-M column calibrated with polystyrene standards. The eluent was CHCl₃, the flow rate was 0.35 mL/min, and the temperature was 40 °C. Differential scanning calorimetry (DSC) using a DSC6220S calorimeter (Seiko Instruments Inc., Chiba, Japan) was performed from -130 to 80 °C, with the temperature increased or decreased at a rate of 10 °C/min. The instrument was calibrated using indium and tin samples. For all experimental samples, the heating cycle from -130 to 80 °C and back to -130 °C was reproducible. Each sample weighed between 4 and 6 mg and was placed into 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 corresponding heat capacity jump of the DSC trace. The melting temperature (T_m) was defined as the minimum point of the endothermic trough. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Kratos PCAxima CFRplus V2.4.0 mass spectrometer using 1,8,9-anthracenetriol as the matrix reagent. NaI was included to generate sodium cations of the polycondensation products ([M+Na]⁺).
Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Scandium Catalysts in an Oil Bath. For poly(3-methylpentamethylene adipate), a typical polycondensation was carried out as follows. In a 30 mL three-necked test tube, 3-methyl-1,5-pentanediol (MPD; 1.65 g, 14.0 mmol), adipic acid (AdA; 2.05 g, 14.0 mmol), and catalysts were stirred at 80 °C (760 mmHg) until a homogeneous state was observed. We confirmed that both the temperatures of oil bath and reaction mixture in the flask were 80 °C using thermocouples. The pressure was gradually decreased to 3.0 kPa, at which point polycondensation commenced (t=0), and we confirmed that oligoesters with an $X_n$ of ca. 10 were formed. When the reaction was finished, the yield of the polyester was calculated by subtracting the known weight of the catalyst from the total weight of the solid present.

Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Scandium Catalysts under Microwave Irradiation. For poly(3-methylpentamethylene adipate), 3-methyl-1,5-pentanediol (MPD; 1.65 g, 14.0 mmol), adipic acid (AdA; 2.05 g, 14.0 mmol), and catalysts were mixed in a 30 mL three-necked test tube that was then placed into a multimode microwave reactor (MWO-1000S, EYELA, 2.45 GHz, max. power 500 W). MPD, AdA, and a catalyst were mixed at 80 °C until a homogeneous state was observed. The pressure was then gradually decreased to 3.0 kPa, and we defined this point as t=0, at which we obtained oligoesters with an $X_n$ of ca. 10 without reducing the pressure. A 200 W microwave was used to irradiate the reaction mixture at 80 °C in the temperature control mode using decahydronaphthalene as the cooling medium until a homogeneous state was observed. The internal temperatures of polycondensation reaction mixtures exposed to microwave irradiation were measured using a thermocouple equipped with a microwave reactor (MWO-1000S) and were controlled using a proportional–integral–derivative (PID) control and PC software. The temperature and irradiation power profile (Figure 2.5) of the representative example showed that the temperature was maintained at 80 °C during the polycondensation. The pressure was gradually decreased to 3.0 kPa, at which point the polycondensation commenced. When the reaction was complete, the yield of the polyester was calculated by subtracting the known weight of the catalyst from the total weight of the solid present.

40
Figure 2.5 Temperature and irradiation power profile of the polycondensation of AdA with MPD catalyzed by Sc(OTf)$_3$. 
2-4. References and Notes


Chapter 3

The Effect of Microwave Irradiation on the Kinetics and Activation Thermodynamics of Ring-Opening Polymerization of \( \varepsilon \)-Caprolactone

ABSTRACT

We examined the ring-opening polymerization of \( \varepsilon \)-caprolactone in toluene between 50 and 70 °C, and catalyzed by some Lewis and Brønsted acids to investigate the effects of microwave versus conventional heating on the kinetics and activation thermodynamics of the reaction. The polymerizations proceeded more rapidly when microwave heating, instead of conventional heating, was used to control the temperature. The number-average molecular weight (\( M_n \)) of the polymer could be controlled even when microwave heating was used. To identify which thermodynamic activation constants were responsible for the accelerated polymerizations, we performed the reaction at different temperatures to obtain data for the Arrhenius and Erying equations. Although the values for the activation energies and the activation enthalpies were larger when microwave heating rather than conventional heating was used, the frequency factors and the activation entropies (\( \Delta S^\ddagger \)) over compensated for the less favorable activation energies and enthalpies. The more favorable \( \Delta G^\ddagger \) found for the microwave-assisted polymerizations mainly reflect the larger \( \Delta S^\ddagger \) values, and the rate accelerations appear to be a consequence of differently arranged intermediates and/or transition states.
3-1. Introduction

Recently, microwave has great interest from the viewpoints from environmentally benign heating for organic syntheses. However, the thermodynamic characterization is still far from the scientific fields. Microwave-enhanced chemical reactions have attracted much attention in recent years, because, as first reported in 1986, microwave irradiation can shorten the reaction time of an organic synthesis, e.g., a polymerization, and decrease the amounts of by-products, which improves product yield and/or product chemoselectivity (reviewed in references 4–6). Methods for step-growth polymerizations, e.g., polycondensation of diols with dicarboxylic acids and polyaddition of dialkynes with diazido via in situ azidation of dibromo compounds, as well as chain polymerizations, e.g., radical polymerization of methacrylate, anionic polymerization of acrylamide, ring-opening cationic polymerization of 2-oxazoline derivatives, and ring-opening polymerization (ROP) of cyclic esters, have all incorporated microwave heating. The exponentially increasing number of publications concerning microwave heating of organic reactions indicates the remarkable interest in and effectiveness of this technique.

Most of the aforementioned studies focused only on the effect that microwave heating had on the overall polymerization rate; consequently, the underlying thermodynamic activation constants and mechanisms were not examined. Instead, the following hypotheses have been proposed to explain the increased polymerization rates: (a) a more rapid attainment of the final temperature, (b) more uniform heating of the reaction mixture, (c) a change in how the species in the mixture interact, (d) superheating of the mixture, and (e) creation of hot spots. According to Conner and Tompsett, rapid heating and creation of hot spots can be associated with increases in synthesis rates. Zetterlund and Perrier concluded that the observed rate enhancement for the reversible addition-fragmentation chain-transfer (RAFT) polymerization of styrene induced by microwave irradiation, which they investigated in silico, was a consequence of microwave-enhanced propagation and RAFT-moiety addition steps. Stoffer and colleagues proposed that a new dipole partition function existed in the microwave fields and calculated the values of the thermodynamic
properties such as internal energy and Gibbs free energy theoretically. Liu and colleagues suggested that the acceleration found for the ROP of ε-caprolactone induced by microwave heating would be a non-thermal effect because the rate constants could not be fitted to the Arrhenius equation. However, an accurate assessment of the effects that microwave irradiation had on the rate of ε-caprolactone-ROP acceleration would be difficult to make owing to the high temperatures (165–228 °C) and strong microwave-irradiation power (400–800 W) used by Liu and colleagues. Recently, we reported that the syntheses of polyesters via dehydration-polycondensation of 3-methyl-1,5-pentanediol and various dicarboxylic acids occurred more rapidly at 80 °C (which is a relatively low temperature) in a microwave chamber than did the syntheses, at the same temperatures, using conventional (oil bath) heating.

The aliphatic polyester polycaprolactone (PCL) is a commercially available, biodegradable polymer that has industrial applications in biomedicine, surgical-fiber fabrication, and polyurethane synthesis. Its physico/chemical properties have been thoroughly investigated and improvements to its synthesis have been reported. Various catalysts, i.e., metals, enzymes, or organic catalysts have been tested to obtain PCLs that have narrow polydispersity indexes (Mw/Mn) and to increase the rates of the reactions. We have reported on the ROP of ε-caprolactone catalyzed by Lewis and super Brønsted acids with the temperature of the polymerization controlled by conventional (oil bath) heating. We also determined the Arrhenius- and Eyring-derived thermodynamic activation parameters by assessing the reaction kinetics at various temperatures. To the best of our knowledge, no study has dealt with the activation thermodynamics of microwave-assisted polymerizations, which forms the basis of the study reported herein, in which we characterize the ROP of ε-caprolactone at relatively low temperatures (50–70 °C) controlled by microwave heating and catalyzed by the super Brønsted acids, trifluoromethanesulfonimide (Tf₂NH) and nonafluorobutanesulfonimide (Nf₂NH), and by the Lewis acids, scandium trifluorobutanesulfonimide (Sc(NTf₂)₃) and scandium nonafluorobutanesulfonimide (Sc(NNf₂)₃). These compounds are also effective catalysts of dehydration polycondensations of dicarboxylic acids
and diols.\textsuperscript{27,28} To investigate the ROP kinetics of ε-caprolactone, we performed temperature studies to obtain the Arrhenius and Eyring thermodynamic parameters.
3-2. Results and Discussion

We performed ROPs of ε-caprolactone under microwave- and conventional-heating conditions that were catalyzed by the highly active Lewis acids Sc(NTf₂)₃ and Sc(NNf₂)₃ at 50-70 °C (Table 3.1, runs 1–13). This temperature range was set to eliminate the possibility of thermal degradation and transesterification. These compounds contain perfluoroalkanesulfonimides as the strong electron-withdrawing ligands, (NTf₂)₃ and (NNf₂)₃, respectively. EtOH and toluene were used, respectively, as the initiator and the solvent. At an initial monomer concentration ([M]₀) of 3 M, we found that the ROPs under microwave irradiation proceeded to completion at 50 °C (runs 1 and 7). The ROPs under microwave irradiation proceeded more rapidly at 60 and 70 °C than at 50 °C without increasing the polydispersity index substantially (runs 3, 5, 10, and 12). For both catalysts, it took less time to complete the polymerizations when microwave heating (runs 1, 3, 5, 7, 10, and 12) instead of conventional heating (runs 2, 4, 6, 9, 11, and 13) was used (see also Figures 3.1a and 3.1b).

**Figure 3.1** ln[M]₀/[M] vs. time for ROPs of ε-caprolactone catalyzed by (a) Sc(NTf₂)₃, (b) Sc(NNf₂)₃, (c) Tf₂NH, and (d) Nf₂NH. Solvent, toluene; initiator, EtOH; [M]₀ = 3.0 M; [catalyst] = 0.1 mol %.
Table 3.1 Ring-Opening Polymerizations of ε-Caprolactone Using Microwave or Conventional Heatinga

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<td>70</td>
<td>CH$^c$</td>
<td>2.5</td>
<td>&gt;99</td>
<td>5.1</td>
<td>1.28</td>
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<tr>
<td>14</td>
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<td>MW$^b$</td>
<td>2.5</td>
<td>&gt;99</td>
<td>5.1</td>
<td>1.20</td>
</tr>
<tr>
<td>15</td>
<td>Tf$_2$NH</td>
<td>50</td>
<td>CH$^c$</td>
<td>3</td>
<td>&gt;99</td>
<td>5.6</td>
<td>1.18</td>
</tr>
<tr>
<td>16</td>
<td>Tf$_2$NH</td>
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<td>MW$^b$</td>
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<td>&gt;99</td>
<td>5.2</td>
<td>1.22</td>
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<td>&gt;99</td>
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<td>1.20</td>
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<tr>
<td>18</td>
<td>Tf$_2$NH</td>
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<td>MW$^b$</td>
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<td>&gt;99</td>
<td>5.0</td>
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<td>97</td>
<td>5.5</td>
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<td>20</td>
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<td>50</td>
<td>MW$^b$</td>
<td>2</td>
<td>&gt;99</td>
<td>6.6</td>
<td>1.20</td>
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<tr>
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<td>50</td>
<td>CH$^c$</td>
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<td>&gt;99</td>
<td>6.3</td>
<td>1.21</td>
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<tr>
<td>22</td>
<td>Nf$_2$NH</td>
<td>60</td>
<td>MW$^b$</td>
<td>2</td>
<td>&gt;99</td>
<td>6.6</td>
<td>1.23</td>
</tr>
<tr>
<td>23</td>
<td>Nf$_2$NH</td>
<td>60</td>
<td>CH$^c$</td>
<td>2.5</td>
<td>&gt;99</td>
<td>6.8</td>
<td>1.30</td>
</tr>
<tr>
<td>24</td>
<td>Nf$_2$NH</td>
<td>70</td>
<td>MW$^b$</td>
<td>1.5</td>
<td>&gt;99</td>
<td>5.7</td>
<td>1.32</td>
</tr>
<tr>
<td>25</td>
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<td>CH$^c$</td>
<td>2</td>
<td>&gt;99</td>
<td>6.4</td>
<td>1.33</td>
</tr>
</tbody>
</table>

a Conditions: $[M]_0 = 3$ M (2.0 g); $[M]_0/[I]_0 = 40$; catalyst, 0.1 mol%; initiator (I$_0$), EtOH. Microwave heating. 200 W maximum power. b Conventional heating. c Monomer conversion ([$M]_0 – [M])/[M]$_0$) determined using the intensity ratio of the $^1$H-NMR signals at 4.01–4.11 ppm (t, -CO-O-CH$_2$-, polymer) and 4.17–4.27 ppm (m, -CO-O-CH$_2$-, monomer) with CDCl$_3$ as the solvent. e Determined by SEC with CHCl$_3$ as the eluent. Values are reported relative to those of poly(styrene) standards. $^f$ Second step of a two-step polymerization. At the end of run 7, additional monomer ($[M]_0/[I]_0 = 40$) were, and the sample was allowed to react for an additional 4.5 h.
To demonstrate controlled polymerization under microwave irradiation, we performed a two-addition polymerization with Sc(NNf\(_2\))\(_3\) as the catalyst (runs 7 and 8). A second sample of monomer was added to the reaction mixture 3 h after the start of the reaction, and the mixture was then incubated for an additional 4.5 h. The polymer molecular weight increased (Table 3.1: run 7, \(M_n = 5.1 \times 10^3\); run 8, \(M_n = 9.1 \times 10^3\)) without the molecular weight distribution also increasing substantially (Table 3.1: run 7, \(M_w/M_n = 1.19\); run 8, \(M_w/M_n = 1.23\); Figure 3.2). Additionally, \(M_n\) was plotted as a function of conversion (Figure 3.3). The \(M_n\) increased linearly as a function of conversion without broadening molecular weight distribution. Therefore, polymerization proceeded in a controlled fashion.

**Figure 3.2** Size exclusion chromatograms for the products of runs 7 and 8 produced using microwave heating with Sc(NNf\(_2\))\(_3\) as the catalyst. Before (Table 3.1 run 7, dashed line) and after (Table 3.1 run 8, solid line) the second addition of \(\varepsilon\)-caprolactone. Flow rate, 0.35 mL/min. Eluent, CHCl\(_3\).
Matrix-assisted laser desorption/ionization time-of-flight mass spectra were recorded to confirm the absolute molecular weights and the structures of all PLCs produced using microwave and conventional heating (Figure 3.4). In each spectrum, two sets of peaks were observed. The major set of peaks corresponds to EtOH-initiated ROP of ε-caprolactone [e.g. EtO(COC₅H₁₀O)₂₆H + Na⁺ = 3037 m/z] and the minor set of peaks represents H₂O-initiated one [e.g. HO(COC₅H₁₀O)₂₆H + Na⁺ = 3009 m/z]. Both sets of peaks appeared in each spectrum, of which the set of repeating peaks at 114 m/z correspond to the molecular weight of the repeating ε-caprolactone unit. Because no other mass peaks were observed, cyclic structures were not formed as by-products. The spectral patterns are similar to those found when the polymer was synthesized using conventional heating.²⁵
Figure 3.4 MALDI–TOF mass spectra of PCL produced using (a) microwave heating and (b) conventional heating. ([M]₀ = 3.0 M; catalyst, 0.1 mol % Sc(NTf₂)₃; 50 °C). Insets show expanded portions of the spectra.

Next, in order to check the effect of the metal ion (Sc³⁺), we carried out polymerizations using microwave and conventional heating with the super Brønsted acids Tf₂NH and Nf₂NH, which contain strong electron-withdrawing fluorocarbons, as the catalysts (Table 3.1 runs 14–25). The ROPs under microwave heating at 50 °C using the Brønsted acids (Table 3.1, run 14 and 20) proceeded more rapidly than did those catalyzed by the scandium compounds under microwave heating (Table 3.1, run 1 and 7) or by conventional heating (Table 3.1, runs 15 and 21) as previously reported.²⁶ Plots of the $M_n$ values as a function of the amount of product (conversion) were linear for all runs performed in the presence of Tf₂NH and Nf₂NH, as were those for the
scandium compounds, indicating that transesterification and termination hardly occurred (data not shown).

To determine the polymerization rate constant \( k_p \) for each run, \( \ln[M_0]/[M] \) was plotted as a function of time of minutes (Figure 3.1a, Sc(NTf₂)₃; Figure 3.1b, Sc(NNf₂)₃; Figure 3.1c, Tf₂NH; and Figure 3.1d, Nf₂NH). Using the values of the slopes and eq. (2), in which \([M], [I], [C] \) are concentrations of monomer, initiator, and catalyst, respectively, we calculated the \( k_p \) according to our reported procedure.²⁵ Du and colleagues calculated the \( k_p \) using eq. (2) for ROP of lactide using Sn(Oct)₂ initiate by PEG.²⁹ The correlation coefficient values are >0.99 for all plots. Because we performed sets of ROPs under the same conditions except for the heating method used, (Figure 3.1; solid lines, microwave heating; dashed lines, conventional heating) the \( k_p \) values, calculated using the slopes of the lines, for each type of heating are readily compared, and notably, for each set of polymerizations, the \( k_p \) value for microwave heating is always larger than that for conventional heating.

\[
M + C \xrightleftharpoons{k_c} MC^i \quad 1 + x MC^i \rightarrow P_X
\]

\[
k_{c_i}[M][C] = k_{c_i}[MC]^i
\]

\[
\frac{d[M]}{dt} = \sum_{i=0}^{\infty} k_i [MC]^i [I]
\]

\[
= \sum_{i=0}^{\infty} \frac{k_{c_i} k_i [M][C][I]}{k_{c_i}}
\]

\[
k_{app} = k_i [C][I] = \frac{\ln[M_0]/[M]}{t}
\]

\[
k_p = \frac{k_{app}}{[C][I]} = \frac{\ln[M_0]/[M]}{[C][I]} \frac{t}{t}
\]

\[
k_p = \frac{\ln[M_0]/[M]}{[C][I]} \frac{t}{t}
\]

\[
k_p = k_0 \cdot e^{-E_a/RT}
\]

\[
\log k_p = \frac{-E_a}{RT} + \log A
\]

\[
k_p = \frac{k_0}{h} \cdot e^{-\Delta H^d/RT} \cdot e^{(\Delta S^d/k)}
\]

\[
\log \frac{k_p}{T} = -\frac{\Delta H^d}{RT} + \log \frac{k_0}{h} + \frac{\Delta S^d}{R}
\]

\[
\Delta G^d = \Delta H^d - T \cdot \Delta S^d
\]
Next, the activation energies ($E_a$) were calculated using the values of the slopes of the Arrhenius plots (Figure 3.5a and 3.5b) and the Arrhenius equation (eq. 3). The correlation coefficient values are >0.98 for all plots. The values of the activation parameters are summarized in Table 3.2. The tendency of the relationship of catalysts and $E_a$s for ROPs using microwave heating coincided with that using conventional heating,25,26 in which the faster polymerization system showed not lower but higher $E_a$ values. We expected that microwave heating would cause the value of $E_a$ to be smaller than that for conventional heating, if the microwaves enhanced the catalytic activities. From the results, independent of the catalyst used, the $E_a$ values for the ROPs that used microwave heating were greater than those that used conventional heating. Conversely, all values of frequency factor ($A$) values for ROPs that used microwave heating are greater than those that used conventional heating.

Figure 3.5 Arrhenius plots of the ROPs of $\varepsilon$-caprolactone for (a) microwave heating and (b) conventional heating. Eyring plots of the ROPs of $\varepsilon$-caprolactone for (c) microwave heating, and (d) conventional heating.
Furthermore, to dissect the microwave rate-acceleration effect in greater detail and to compare the $E_a$ and the activation enthalpy ($\Delta H^\ddagger$) values, $\Delta H^\ddagger$ and entropy ($\Delta S^\ddagger$) values were obtained from Eyring plots (Figure 3.4c and 3.4d, eq. 4).\textsuperscript{30,31} The Eyring equation has been used to calculate the activation thermodynamic constants for the ROP of cyclic esters that used conventional heating.\textsuperscript{32-35} The correlation coefficient values are >0.98 for all plots. $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values for the polymerizations performed under the different conditions are also listed in Table 3.2, as are the values for $\Delta G^\ddagger$, obtained using eq. 5.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>heating method</th>
<th>$k_p^a$ (L$^2$ mol$^{-2}$ s$^{-1}$)</th>
<th>$E_a^b$ (kJ mol$^{-1}$)</th>
<th>$A^b$ (L$^2$ mol$^{-2}$ s$^{-1}$)</th>
<th>$\Delta H^{\ddagger c}$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^{\ddagger c}$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta G^{\ddagger d}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(NTf$_2$)$_3$</td>
<td>MW$^e$</td>
<td>0.71</td>
<td>0.99</td>
<td>1.33</td>
<td>29.0</td>
<td>3.4 x 10$^4$</td>
<td>26.2</td>
</tr>
<tr>
<td>Sc(NTf$_2$)$_3$</td>
<td>CH$^f$</td>
<td>0.62</td>
<td>0.76</td>
<td>0.99</td>
<td>21.5</td>
<td>1.8 x 10$^4$</td>
<td>18.7</td>
</tr>
<tr>
<td>Sc(NNf$_2$)$_3$</td>
<td>MW$^e$</td>
<td>0.81</td>
<td>1.30</td>
<td>1.73</td>
<td>34.6</td>
<td>3.3 x 10$^5$</td>
<td>31.9</td>
</tr>
<tr>
<td>Sc(NNf$_2$)$_3$</td>
<td>CH$^f$</td>
<td>0.61</td>
<td>0.81</td>
<td>0.99</td>
<td>21.8</td>
<td>2.1 x 10$^3$</td>
<td>19.0</td>
</tr>
<tr>
<td>Tf$_2$NH</td>
<td>MW$^e$</td>
<td>1.33</td>
<td>1.93</td>
<td>2.81</td>
<td>34.5</td>
<td>5.1 x 10$^5$</td>
<td>31.8</td>
</tr>
<tr>
<td>Tf$_2$NH</td>
<td>CH$^f$</td>
<td>1.16</td>
<td>1.54</td>
<td>2.00</td>
<td>25.0</td>
<td>1.3 x 10$^4$</td>
<td>22.2</td>
</tr>
<tr>
<td>Nf$_2$NH</td>
<td>MW$^e$</td>
<td>1.41</td>
<td>1.94</td>
<td>2.87</td>
<td>32.6</td>
<td>2.6 x 10$^5$</td>
<td>29.8</td>
</tr>
<tr>
<td>Nf$_2$NH</td>
<td>CH$^f$</td>
<td>1.24</td>
<td>1.61</td>
<td>2.09</td>
<td>23.8</td>
<td>8.9 x 10$^3$</td>
<td>21.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $k_p$ values were calculated using the values of the slopes for ln([M]$_0$/[M]) versus time and eq. 2. \textsuperscript{b} $E_a$ and $A$ were calculated using the values of the slopes of Arrhenius plots and eq. 3. \textsuperscript{c} $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated using the values of the slopes and the y intercepts of the Eyring plots, respectively, and eq. 4. \textsuperscript{d} $\Delta G^\ddagger$ were calculated using eq. 5. \textsuperscript{e} Microwave irradiation. \textsuperscript{f} Conventional heating.

Using the well-studied ROP of $\varepsilon$-caprolactone, it was possible to investigate the effect of microwave heating on thermodynamic activation constants of the polymerization. The values of $\Delta H^\ddagger$ for the ROPs that used microwave heating are greater than those that used conventional heating (see Table 3.2). However, the $\Delta S^\ddagger$ values for comparable runs (same catalyst) were larger when microwave heating was used to control the temperature than when conventional heating was used
The results indicated that increases in the $\Delta S^\ddagger$ values over compensated for the unfavorable increase in $\Delta H^\ddagger$ associated with microwave heating. Consequently, the ranked values of the $\Delta G^\ddagger$ inversely parallel the $k_p$ values. The decreased $\Delta G^\ddagger$ values are, therefore, mainly a consequence of the increased $\Delta S^\ddagger$ values irrespective of type of catalysts (Lewis and Brønsted acids). Although similar rate increases and thermodynamic effects were observed for the syntheses of metal-organic frameworks including zeolites and iron benzenedicarboxylate,\textsuperscript{36} this is the first report dealing with polymerizations.

Finally, in order to observe clearly the effect of $\Delta S^\ddagger$ values on the Nf$_2$NH-catalyzed ROPs under microwave irradiation, we decreased the monomer concentrations ([M]$_0$) from 3M to 2M and 1M, and calculated the activation thermodynamic constants, respectively, using aforementioned method (Figure 3.6, 3.7, and Table 3.3). Although we could not find remarkable difference in the thermodynamic parameters using conventional heating (data not shown), increase of $\Delta S^\ddagger$ values was confirmed when microwave heating was used [1M: $-133.1$ (J K$^{-1}$ mol$^{-1}$), 2M: $-149.5$ (J K$^{-1}$ mol$^{-1}$), 3M: $-150.5$ (J K$^{-1}$ mol$^{-1}$), see also Table 3.2 and 3.3]. It is considered that higher microwave irradiation power was necessary to proceed the ROP, when we decrease the [M]$_0$. As the result, this additional experiments made it clear to understand that microwave effects of the ROPs is due to a consequence of the increased $\Delta S^\ddagger$ values. Although the thermodynamic parameters cannot currently be explained in terms of a polymerization mechanism, as suggested by Conner and Tompsett\textsuperscript{16b}, we conclude that the intermediates and/or transition states may differ under the two types of heating conditions.
Figure 3.6 $\ln[M_0]/[M]$ vs. time for ROPs of $\varepsilon$-caprolactone at 50 °C under microwave irradiation catalyzed by $\text{Nf}_2\text{NH}$ at various monomer concentrations.

Figure 3.6 (a) Arrhenius plots of the ROPs of $\varepsilon$-caprolactone using microwave heating at various monomer concentrations. (b) Eyring plots of the ROPs of $\varepsilon$-caprolactone using microwave heating at various monomer concentrations.
Table 3.3 Reaction Rate Constants, Activation Energies, Frequency Factors, and Activation Enthalpies and Entropies for the ROPs of ε-Caprolactone under Microwave Irradiation Catalyzed by Nf$_2$NH at Various Monomer Concentrations.

<table>
<thead>
<tr>
<th>conc. [M]$_0$</th>
<th>$k_p$ $a$ (L$^2$ mol$^{-2}$ s$^{-1}$)</th>
<th>Arrhenius plot</th>
<th>Eyring plot</th>
<th>$\Delta G^{\ddagger}_d$ (kJ mol$^{-1}$)</th>
<th>Microwave power$^e$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$ $b$ (kJ mol$^{-1}$)</td>
<td>$A$ $b$ (L$^2$ mol$^{-2}$ s$^{-1}$)</td>
<td>$\Delta H^{\ddagger}$ $c$ (kJ mol$^{-1}$)</td>
<td>$\Delta S^{\ddagger}$ $c$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>$\Delta G^{\ddagger}_d$ (kJ mol$^{-1}$)</td>
</tr>
<tr>
<td>323 K</td>
<td>333 K</td>
<td>343 K</td>
<td></td>
<td></td>
<td>4.42 × 10$^3$</td>
</tr>
<tr>
<td>1 M</td>
<td>3.53</td>
<td>5.33</td>
<td>7.67</td>
<td>35.7</td>
<td>2.1 × 10$^6$</td>
</tr>
<tr>
<td>2 M</td>
<td>1.52</td>
<td>2.18</td>
<td>3.08</td>
<td>32.7</td>
<td>2.9 × 10$^5$</td>
</tr>
<tr>
<td>3 M</td>
<td>1.41</td>
<td>1.94</td>
<td>2.87</td>
<td>32.6</td>
<td>2.6 × 10$^5$</td>
</tr>
</tbody>
</table>

$^a$ $k_p$ values were calculated using the values of the slopes for ln([M]$_0$/[M]) versus time and eq. 2.

$^b$ $E_a$ and $A$ were calculated using the values of the slopes of Arrhenius plots and eq. 3.

$^c$ $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated using the values of the slopes and the y intercepts of the Eyring plots, respectively, and eq. 4.

$^d$ $\Delta G^{\ddagger}_d$ were calculated using eq. 5.

$^e$ Microwave power = (monitored irradiation power) × (moles of monomer)$^{-1}$ × (irradiation time)$^{-1}$. Polymerization temperature = 50 °C.

In this chapter, we described herein microwave-assisted ROPs of ε-caprolactone catalyzed by Lewis and Brønsted acids (Sc(NTf$_2$)$_3$, and Sc(NNf$_2$)$_3$, and Tf$_2$NH and Nf$_2$NH, respectively). The ROPs that used microwave heating proceeded more rapidly than did those that used conventional heating regardless of the catalyst used and without broadening the polydispersity indexes ($M_w/M_n = 1.17–1.32$). Additionally, for the two-addition polymerization that used microwave heating, $M_n$ increased with the second addition, supporting the possibility that controlled polymerization had occurred. The Arrhenius and the Eyring equations were used to compare the reaction kinetics of the ROPs that used the two types of temperature control but were otherwise run under the same conditions. Although the $E_a$ and $\Delta H^{\ddagger}$ values for the polymerizations were less favorable when microwave heating was used instead of conventional heating, the $A$ and $\Delta S^{\ddagger}$ values over compensated. Consequently, the ranked values of the $\Delta G^{\ddagger}_d$ values inversely paralleled the $k_p$ values, irrespective of the catalyst used. $\Delta G^{\ddagger}_d$ values associated with microwave heating are mainly a consequence of the larger $\Delta S^{\ddagger}$ values, which are possibly associated with differences in the types of intermediates and/or transition states for the two types of temperature control. These fundamental results provide new insight into the microwave-assisted, energy-saving production of polymeric materials.
3-3. Experimental Section

Materials. \( \varepsilon \)-Caprolactone (>99%), ethanol (EtOH, >99.5%), and toluene (>99%) were purchased from Nacalai Tesque (Kyoto, Japan) and were distilled before use. Tf\(_2\)NH (>98%) was purchased from Wako Pure Chemical Industries (Osaka, Japan). Nf\(_2\)NH was obtained from Mitsubishi Materials Electronic Chemicals (Akita, Japan). Sc(NTf\(_2\))\(_3\) and Sc(NNf\(_2\))\(_3\) were prepared according to a literature report.\(^{27}\)

Measurements. \(^1\)H-NMR spectra were recorded at 27 °C using a 200-MHz, DPX200 Bruker Analytik spectrometer. Samples were dissolved in CDCl\(_3\). The number average molecular weights \((M_\text{n})\) and the \(M_\text{w}/M_\text{n}\) of the polymers were measured using a size-exclusion-chromatography (SEC) system that was calibrated with polystyrene standards and included the following components: a Tosoh DP-8020 pump system, a Tosoh RI-8020 detector, and a Tosoh TSKgel SuperMultiporeHZ-M column. The eluent was chloroform. The flow rate was 0.35 mL/min, and the temperature was 40 °C. Matrix-assisted laser desorption/ionization time-of-flight mass spectra were recorded using a mass spectrometer (JMS-S3000 SpiralTOF; JEOL), with dithranol as the matrix reagent. To generate sodium-cationized ions of the PCLs, NaI was used.

Ring-Opening Polymerization of \( \varepsilon \)-Caprolactone in Toluene Using Conventional Heating. A typical polymerization was performed as follows. A catalyst (C) (17.5 \(\mu\)mol; 0.1 mol % relative to monomer (M) mol %), toluene (3.72 mL), the initiator (I) EtOH (25.6 \(\mu\)L, 0.44 mmol; \([M]_0/[I]_0 = 40\)), and \( \varepsilon \)-caprolactone (2.0 g, 17.5 mmol, \([M]_0 = 3\) M) were added into a 50 mL three-necked, round-bottom flask that had been placed in a controlled-temperature water or oil bath under a nitrogen atmosphere. Then the mixture was stirred. We monitored the temperature of the reaction mixture in the flask using a thermocouple, and conversion of the polymerization was evaluated by removing a single drop of the reaction mixture that was immediately diluted (1,000 fold) into CDCl\(_3\) to quench the polymerization at various times and recording the intensities of its \(^1\)H-NMR signals at 4.01–4.11 ppm (t, -CO-O-CH\(_2\)-, polymer) and at 4.17–4.27 ppm (m, -CO-O-CH\(_2\)-, monomer).
Ring-Opening Polymerization of ε-Caprolactone in Toluene Using Microwave Heating. A typical polymerization procedure was performed as follows. A catalyst (17.5 μmol; 0.1 mol % relative to the monomer mol %), toluene (3.72 mL), EtOH (25.6 μL, 0.44 mmol, [M]₀/[I]₀ = 40), and ε-caprolactone (2.0 g, 17.5 mmol, [M]₀ = 3 M) were added into a 50 mL three-necked, round-bottom flask that had been set into an EYELA MWO-100s, multimode microwave reactor (2.45 GHz, maximum power 500 W) under a nitrogen atmosphere. Then the mixture was stirred, and the temperature of the mixture was measured using a thermocouple connected to the microwave and was adjusted using a software-driven proportional-integral-derivative controller. The temperature and irradiation-power profiles indicated that the desired temperatures were maintained during the polymerizations (data not shown). Polymerizations were monitored as described above for those that used conventional heating.
3-4. References and Notes


Chapter 4

Microwave-Assisted Solution Polycondensation of l-Lactic Acid Using a Dean-Stark Apparatus to Take Advantage of a Non-thermal Microwave Polymerization Effect Induced by the Electric Field

ABSTRACT

We examined the solution polycondensation of l-lactic acid (l-LA) in xylene catalyzed by Sc(OTf)_3 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 × 10^3. Using 1.0 mol% SnCl_2 as the catalyst and multi-mode irradiation, the largest PLLA (M_w = 46.7 × 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.
4-1. 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(lactic acid) (PLLA) is biocompatible and exhibits the same excellent mechanical performance as those of petroleum-based aliphatic polyesters.1 Currently, PLLA is produced industrially by the ring-opening polymerization of l-lactide, a cyclic dimer of l-lactic acid (l-LA).2 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 [Sc(OTf)$_3$] and scandium trifluoromethanesulfonimide [Sc(NTf$_2$)$_3$] were effective for a one-step dehydration polycondensation of l-LA$^3$ in the same manner as the syntheses of other aliphatic polyesters.$^4$ 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.$^5$

Recently, microwave-enhanced reactions of organic compounds have attracted much attention$^6$ because, as first reported in 1986,$^7,^8$ 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.$^9$-$^{11}$). Microwave irradiation has been successfully incorporated into chain polymerization procedures—e.g., radical polymerization of methacrylate,$^{12}$ anionic polymerization of acrylamide,$^{13}$ ring-opening cationic polymerization of 2-oxazoline derivatives,$^{14}$ and ring-opening polymerization of cyclic esters,$^{15}$—and into step-growth polymerization procedures—e.g., polycondensation of diols with dicarboxylic acids$^{16}$ and polyaddition of dialkynes with diazido via in situ azidation of dibromo compounds.$^{17}$
exponentially increasing number of publications concerning microwave irradiation for polymer syntheses indicates the remarkable interest in and effectiveness of this technique.\textsuperscript{18-20} 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.\textsuperscript{9-11} For example, Tompsett and coworkers\textsuperscript{21} 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 \textit{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.\textsuperscript{22} We also suggested that a non-thermal microwave effect might affect the rates of polycondensation reactions\textsuperscript{16} and that the more favorable $\Delta G^{\ddagger}$ values associated with the microwave-assisted polymerizations of $\varepsilon$-caprolactone mainly reflect the larger $\Delta S^{\ddagger}$ values.\textsuperscript{23} 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 (\textit{Figure 4.1}).
Figure 4.1 Schematic of the singlemode microwave apparatus.
4-2. Results and Discussion

Multi-mode Microwave-Assisted Solution Polycondensation of l-LA Catalyzed by Sc(OTf)₃.

First, microwave-assisted solution polycondensations of l-LA (85 % aqueous solution) were performed with Sc(OTf)₃ 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. With the power set at 200 or 250 W, we obtained only PLLAs with relatively small $M_w$ values (Table 4.1, 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. From $^1$H-NMR spectra for the sample of run 4 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 CHCl₃, $[\alpha]_D^{25}$ is −149 for the sample of run 4, which coincides with the literature value (−150).²⁶ Although we performed the polycondensation of l-LA under >400-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 4.1, 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 (200 W power), 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 4.1 Microwave-Assisted Solution Polycondensation of l-LA Catalyzed by Sc(OTf)₃.ª

<table>
<thead>
<tr>
<th>run</th>
<th>heating method</th>
<th>[M]₀</th>
<th>yield¹</th>
<th>Mₙ°</th>
<th>Mₘ°</th>
<th>Mₚ°</th>
<th>Mₙ/Mₚ°</th>
<th>T₇°</th>
<th>T₁°</th>
<th>[α]₂⁵°</th>
<th>color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MWb 100 W</td>
<td>3 M</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>MWb 200 W</td>
<td>3 M</td>
<td>&gt;99</td>
<td>1.4</td>
<td>2.7</td>
<td>2.4</td>
<td>1.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>MWb 250 W</td>
<td>3 M</td>
<td>&gt;99</td>
<td>1.5</td>
<td>3.1</td>
<td>2.1</td>
<td>2.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>MWb 300 W</td>
<td>3 M</td>
<td>&gt;99</td>
<td>4.4</td>
<td>11.6</td>
<td>10.6</td>
<td>2.63</td>
<td>40.4</td>
<td>150.4</td>
<td>−149</td>
<td>pale brown</td>
</tr>
<tr>
<td>5</td>
<td>CHb 160 °C</td>
<td>3 M</td>
<td>&gt;99</td>
<td>3.4</td>
<td>8.8</td>
<td>8.8</td>
<td>2.63</td>
<td>33.1</td>
<td>144.0</td>
<td>−145</td>
<td>pale brown</td>
</tr>
<tr>
<td>6</td>
<td>MWb 300 W</td>
<td>5 M</td>
<td>&gt;99</td>
<td>6.3</td>
<td>17.2</td>
<td>10.4</td>
<td>2.75</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>black</td>
</tr>
<tr>
<td>7</td>
<td>MWb 200 W</td>
<td>5 M</td>
<td>&gt;99</td>
<td>3.1</td>
<td>7.8</td>
<td>7.9</td>
<td>2.49</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>white</td>
</tr>
<tr>
<td>8</td>
<td>MWb 200 W</td>
<td>8 M</td>
<td>&gt;99</td>
<td>3.9</td>
<td>16.7</td>
<td>17.6</td>
<td>4.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>white</td>
</tr>
</tbody>
</table>

ªAll runs were performed by a 6 h azeotropic distillation with xylene as the solvent and 0.1 mol% Sc(OTf)₃ as the catalyst. ºMulti-mode microwave heating. ´Conventional heating. "Without reprecipitation. gWithout reprecipitation. Determined by SEC with CHCl₃ as the eluent. Values are reported relative to those of poly(styrene) standards. fTₗ was determined using the first DSC scan, and Tₓ was determined using the second scan (heating rate: 10 °C/min). g1 g/100 mL CHCl₃.


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)₃ concentration. When the Sc(OTf)₃ concentration was increased to 0.3 mol% (relative to l-LA), the PLLA Mₘ was greater than when 0.1 mol% Sc(OTf)₃ was used (Table 4.2, runs 1 and 2). However, when the Sc(OTf)₃ concentration was 0.5 mol%, the Mₘ of the product PLLA decreased (runs 2 and 3). From these results, it seems that the largest Sc(OTf)₃ 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 Sc(NNf₂)₃ and NNf₂NH are effective catalysts for aliphatic polyester syntheses.²⁷,²⁸ However, Sc(NNf₂)₃ was insoluble in the reaction medium, therefore, could not be used, and when NNf₂NH was used, we obtained only a mixture of oligomers and lactides (data not shown). We also tested the SnCl₂/PTSA binary catalyst system that was reported to be an effective catalyst for direct polymerization of l-LA under microwave irradiation.⁵ Although this binary catalyst was effective for microwave-assisted direct polymerization,⁵ we did not obtain...
PLLA with an $M_w$ similar to that found for run 5 in Table 4.2. However, we confirmed the existence of a non-thermal microwave effect (runs 4 and 5) similar to that of the Sc(OTf)$_3$-catalyzed experiments. Next, we used SnCl$_2$ as the catalyst at various concentrations. When the SnCl$_2$ concentration was 0.1 mol%, polymerization hardly occurred (run 6). However, with larger SnCl$_2$ concentrations, PLLAs with larger $M_w$ values were obtained (runs 7 and 9). Particularly, when the 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 SnCl$_2$-catalyzed experiments, a non-thermal microwave effect was also found (runs 8 and 9).

Table 4.2 Microwave-Assisted Solution Polycondensation of L-LA Using Various Catalysts.$^a$

<table>
<thead>
<tr>
<th>run</th>
<th>catalyst (mol%)</th>
<th>heating method</th>
<th>yield$^d$ (%)</th>
<th>$M_n^e \times 10^3$</th>
<th>$M_w^e \times 10^3$</th>
<th>$M_p^e \times 10^3$</th>
<th>$M_w/M_n^e$</th>
<th>$T_g^f$ (°C)</th>
<th>$T_m^f$ (°C)</th>
<th>$[\alpha]_{D}^{25g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sc(OTf)$_3$ (0.1)</td>
<td>MW$^b$</td>
<td>&gt;99</td>
<td>4.4</td>
<td>11.6</td>
<td>10.6</td>
<td>2.63</td>
<td>40.4</td>
<td>148.1</td>
<td>−149</td>
</tr>
<tr>
<td>2</td>
<td>Sc(OTf)$_3$ (0.3)</td>
<td>MW$^b$</td>
<td>&gt;99</td>
<td>7.0</td>
<td>21.2</td>
<td>16.9</td>
<td>3.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Sc(OTf)$_3$ (0.5)</td>
<td>MW$^b$</td>
<td>&gt;99</td>
<td>3.8</td>
<td>13.2</td>
<td>14.6</td>
<td>3.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PTSA (0.6)</td>
<td>CH$^c$</td>
<td>&gt;99</td>
<td>2.0</td>
<td>3.8</td>
<td>3.6</td>
<td>1.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SnCl$_2$ (0.6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>PTSA (0.6)</td>
<td>MW$^b$</td>
<td>&gt;99</td>
<td>3.0</td>
<td>8.3</td>
<td>9.1</td>
<td>2.74</td>
<td>33.2</td>
<td>143.9</td>
<td>−139</td>
</tr>
<tr>
<td>6</td>
<td>SnCl$_2$ (0.1)</td>
<td>MW$^b$</td>
<td>&gt;99</td>
<td>0.8</td>
<td>1.0</td>
<td>0.8</td>
<td>1.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>SnCl$_2$ (0.5)</td>
<td>MW$^b$</td>
<td>&gt;99</td>
<td>3.1</td>
<td>9.6</td>
<td>10.9</td>
<td>3.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>SnCl$_2$ (1.0)</td>
<td>CH$^c$</td>
<td>&gt;99</td>
<td>3.4</td>
<td>19.6</td>
<td>19.6</td>
<td>5.64</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>SnCl$_2$ (1.0)</td>
<td>MW$^b$</td>
<td>&gt;99</td>
<td>9.2</td>
<td>46.7</td>
<td>38.9</td>
<td>5.07</td>
<td>54.9</td>
<td>165.4</td>
<td>−146</td>
</tr>
</tbody>
</table>

$^a$All runs were performed by a 6-h azeotropic distillation with xylene as the solvent ([M]$_0$ = 3 M).
$^b$Microwave heating (300 W). $^c$Conventional heating (160 °C) $^d$Without reprecipitation. $^e$Without reprecipitation. Determined by SEC with CHCl$_3$ as the eluent. Values are reported relative to those of poly(styrene) standards. $^f$ $T_m$ was determined using the first DSC scan, and $T_g$ was determined using the second scan (heating rate: 10 °C/min). $^g$1 g/100 mL CHCl$_3$. 73

We monitored the changes in the temperature of water, xylene, L-LA(aq), and a mixture of L-LA(aq) 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(aq) was the same when subjected to the EF or the MF (Figure 4.2a). L-LA(aq) was heated by the MF more rapidly than by the EF (Figure 4.2b). Conversely, the opposite tendency was found for xylene (Figure 4.2c), 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(aq) and xylene) under EF irradiation was similar to that under MF irradiation (Figure 4.2d).

![Figure 4.2](image)

**Figure 4.2** Temperature (T) profiles for (a) L-LA(aq), (b) water, (c) xylene, and (d) a mixture of L-LA(aq) 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 EF- or MF-Irradiation in a Single-mode Microwave Cavity.

First, we performed polycondensation of L-LA catalyzed with 0.1 mol% Sc(OTf)₃ under EF irradiation (Table 4.3). When the power was 30 W, polycondensation proceeded only to a relatively small extent (Table 4.3, run 1). PLLA with an $M_n > 10,000$ was obtained when the power was increased (runs 2-4). However, when the EF was used with a power of 150 W, the $M_n$ 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 4.1, run 5). In contrast to the effects of the EF, the $M_n$ 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 4.2). 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.

Table 4.3 Solution Polycondensation of L-LA Using a Single Mode Microwave Cavity.a

<table>
<thead>
<tr>
<th>run</th>
<th>heating method</th>
<th>catalyst (mol%)</th>
<th>yieldd (%)</th>
<th>$M_n$ e $ \times 10^{-3}$</th>
<th>$M_w$ e $ \times 10^{-3}$</th>
<th>$M_p$ e $ \times 10^{-3}$</th>
<th>$M_w/M_n$ e</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EFb</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>1.3</td>
<td>2.0</td>
<td>2.0</td>
<td>1.62</td>
</tr>
<tr>
<td>2</td>
<td>EFb</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>4.3</td>
<td>12.6</td>
<td>12.4</td>
<td>2.94</td>
</tr>
<tr>
<td>3</td>
<td>EFb</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>3.8</td>
<td>10.7</td>
<td>11.2</td>
<td>2.84</td>
</tr>
<tr>
<td>4</td>
<td>EFb</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>4.4</td>
<td>11.3</td>
<td>9.2</td>
<td>2.58</td>
</tr>
<tr>
<td>5</td>
<td>EFb</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>3.0</td>
<td>7.2</td>
<td>6.9</td>
<td>2.39</td>
</tr>
<tr>
<td>6</td>
<td>MFc</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>3.1</td>
<td>9.5</td>
<td>10.5</td>
<td>3.03</td>
</tr>
<tr>
<td>7</td>
<td>MFc</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>1.8</td>
<td>4.0</td>
<td>3.8</td>
<td>2.22</td>
</tr>
<tr>
<td>8</td>
<td>MFc</td>
<td>Sc(OTf)₃ (0.1)</td>
<td>&gt;99</td>
<td>1.5</td>
<td>2.9</td>
<td>2.1</td>
<td>1.93</td>
</tr>
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</table>

aAll runs were performed by a 6-h azeotropic distillation with xylene as the solvent ([M]₀ = 3 M). bElectric field. cMagnetic field. dWithout reprecipitation. eWithout reprecipitation. Determined by SEC with CHCl₃ 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)$_3$ (Table 4.4 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 (Table 4.2, runs 1 and 2). We also performed EF-assisted polycondensations catalyzed by SnCl$_2$, 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 4.4 Solution Polycondensation of L-LA under an Electric Field.

<table>
<thead>
<tr>
<th>run</th>
<th>heating method</th>
<th>catalyst (mol%)</th>
<th>yield$^c$ (%)</th>
<th>$M_n^d$ $\times 10^3$</th>
<th>$M_w^d$ $\times 10^3$</th>
<th>$M_p^d$ $\times 10^3$</th>
<th>$M_w/M_n^d$</th>
<th>$T_g^e$ (°C)</th>
<th>$T_m^e$ (°C)</th>
<th>$[\alpha]_{D}^{25f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EF$^b$</td>
<td>50 W Sc(OTf)$_3$ (0.3)</td>
<td>&gt;99</td>
<td>4.9</td>
<td>11.7</td>
<td>11.0</td>
<td>2.37</td>
<td></td>
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</tr>
<tr>
<td>2</td>
<td>EF$^b$</td>
<td>80 W Sc(OTf)$_3$ (0.3)</td>
<td>&gt;99</td>
<td>6.1</td>
<td>19.9</td>
<td>17.0</td>
<td>3.28</td>
<td>37.7</td>
<td>145.0</td>
<td>−135</td>
</tr>
<tr>
<td>3</td>
<td>EF$^b$</td>
<td>100 W Sc(OTf)$_3$ (0.3)</td>
<td>&gt;99</td>
<td>5.3</td>
<td>15.9</td>
<td>15.3</td>
<td>2.99</td>
<td></td>
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</tr>
<tr>
<td>4</td>
<td>EF$^b$</td>
<td>50 W SnCl$_2$ (1.0)</td>
<td>&gt;99</td>
<td>1.9</td>
<td>4.4</td>
<td>4.8</td>
<td>2.36</td>
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</tr>
<tr>
<td>5</td>
<td>EF$^b$</td>
<td>80 W SnCl$_2$ (1.0)</td>
<td>&gt;99</td>
<td>9.3</td>
<td>53.2</td>
<td>45.3</td>
<td>5.73</td>
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<tr>
<td>6</td>
<td>EF$^b$</td>
<td>100 W SnCl$_2$ (1.0)</td>
<td>&gt;99</td>
<td>8.8</td>
<td>60.2</td>
<td>52.8</td>
<td>6.84</td>
<td>50.6</td>
<td>163.8</td>
<td>−147</td>
</tr>
</tbody>
</table>

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

$^b$Electric field.

$^c$Without reprecipitation.

$^d$Without reprecipitation. Determined by SEC with CHCl$_3$ as the eluent. Values are reported relative to those of poly(styrene) standards.

$^e$Values were determined using the first DSC scan, and $T_g$ was determined using the second scan (heating rate: 10 °C/min).

$^f$1 g/100 mL in CHCl$_3$. 

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In this chapter, 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% Sc(OTf)$_3$ as the catalyst than when 100–250 W power was employed. For 1.0 mol% 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$_{(aq)}$ and xylene) under EF and MF irradiations. These fundamental results provide new insight into the microwave-assisted, energy-saving production of polymeric materials.
4-3. Experimental Section

Materials. Aqueous l-LA (85% w/v), anhydrous tin (II) chloride, titanium tetraisopropoxide, 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)₃ was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Nonaoctfluorobutanesulfonimide (Nf₂NH) was purchased from Mitsubishi Materials Electronic Chemicals (Akita, Japan).

Measurements. ¹H-NMR spectra were recorded at 27 °C using a 200 MHz DPX200 spectrometer (Bruker Analytik). The number average molecular weight (Mₙ), the Mₘ, the molecular weight found for the top of the size-exclusion chromatogram peak (Mₚ), and the polydispersity index (Mₘ/Mₙ) 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, [α]_D²⁵, 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 for a 6 h azeotropic dehydration.
Solution Polycondensation of l-Lactic Acid Using a Multi-mode 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 4.1 shows a schematic of the experimental apparatus that incorporated the 2.45 GHz microwave reactor used to produce an EF or an MF. The positions of the microwave EF- and MF-standing waves can be separated in single-mode microwave cavity because their fields are offset by half of a wavelength. The microwave power is the difference between the input power and reflex power. Reduction of titanium oxide and sintering of magnetite (Fe$_3$O$_4$) under a microwave MF using this apparatus have been reported.$^{24,25}$ 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 4.1) for a 6 h azeotropic dehydration under microwave irradiation. The microwave power was manually controlled.
4-4. References and Notes


Conclusions

This thesis focused on the investigation of the microwave-assisted chemistry based on kinetics and thermodynamics of polyester syntheses. These introduced fundamental results provide new insight into the microwave-assisted, energy-saving production of polymeric materials and enable us to the development of microwave chemistry. The experimental results are summarized as follows.

Chapter 1. Polyester Synthesis at Moderate Temperatures via the Direct Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Rare-Earth Perfluoroalkanesulfonates and Bis(perfluoroalkanesulfonylimides)

In chapter 1, I demonstrated that scandium catalysts with strong electron-withdrawing ligands could catalyze the polycondensation of adipic acid (AdA) and 3-methyl-1,5-pentanediol (MPD) under conditions of a moderate temperature, a short time period, and a lesser amount of catalyst. Other rare-earth-metal catalysts containing ligands with strong electron-withdrawing abilities were also synthesized and their catalytic efficiencies tested using the polycondensation of AdA and MPD. Tm(NNf₂)₃ was a more effective catalyst than was Sc(OTf)₃, Sc(NNf₂)₃, Tm(OTf)₃, or Tm(NTf₂)₃. My work now makes it possible to synthesize aliphatic polyesters of $M_n > 1.0 \times 10^4$ at a moderate temperature (60 °C), within a short period of time (6 h) using a small amount of catalyst (0.05–0.1 mol%). Polycondensations that can be performed at moderate temperatures are environmentally friendly procedures and may find use when designing polymers with specific chiralities, functionalities, and/or biological activities.
Chapter 2. Microwave-Assisted Low-Temperature Dehydration Polycondensation of Dicarboxylic Acids and Diols

For the work reported in this chapter, I demonstrated that microwave heating accelerates the rate of AdA/MPD polycondensation catalyzed by Sc(OTf)₃ at a moderate temperature and that a smaller amount of catalyst can be used than in a conventional polycondensation. I also investigated how microwave heating affects the kinetics of polycondensation in detail by determining the second-order proportionality constants from plots of $X_n$ as a function of time. Finally, I also found that the non-thermal microwave effect might affect the rates of polycondensations for dicarboxylic acids other than AdA.

Chapter 3. The Effect of Microwave Irradiation on the Kinetics and Activation Thermodynamics of Ring-Opening Polymerization of ε-Caprolactone

In chapter 3, I described herein microwave-assisted ROPs of ε-caprolactone catalyzed by Lewis and Brønsted acids (Sc(NTf₂)₃, and Sc(NNf₂)₃, and Tf₂NH and Nf₂NH, respectively). The ROPs that used microwave heating proceeded more rapidly than did those that used conventional heating regardless of the catalyst used and without broadening the polydispersity indexes ($M_w/M_n = 1.17–1.32$). Additionally, for the two-addition polymerization that used microwave heating, $M_n$ increased with the second addition, supporting the possibility that controlled polymerization had occurred. The Arrhenius and the Eyring equations were used to compare the reaction kinetics of the ROPs that used the two types of temperature control but were otherwise run under the same conditions. Although the $E_a$ and $\Delta H^\ddagger$ values for the polymerizations were less favorable when microwave heating was used instead of conventional heating, the $A$ and $\Delta S^\ddagger$ values over compensated. Consequently, the ranked values of the $\Delta G^\ddagger$ values inversely paralleled the $k_p$ values, irrespective of the catalyst used. $\Delta G^\ddagger$ values associated with microwave heating are mainly a consequence of the larger $\Delta S^\ddagger$ values, which are possibly associated with differences in the types of intermediates and/or transition states for the two types of temperature control.
Chapter 4. Microwave-Assisted Solution Polycondensation of L-Lactic Acid Using a Dean-Stark Apparatus to Take Advantage of a Non-thermal Microwave Polymerization Effect Induced by the Electric Field

In chapter 4, I 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% Sc(OTf)$_3$ as the catalyst than when 100–250 W power was employed. For 1.0 mol% 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. I 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$_{(aq)}$ and xylene) under EF and MF irradiations. These fundamental results provide new insight into the microwave-assisted, energy-saving production of polymeric materials.
Acknowledgement

The studies dealt in this thesis were carried out under the direction of Associate Professor Akinori Takasu at the Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, during 2008-2014. The author wishes to express his sincere thanks to Associate Professor Akinori Takasu for his valuable guidance, inspiration, assistance, and trenchant advices at times throughout this study.

The author is grateful to Associate Professor Sadatsugu Takayama, National Institute of Fusion Science, to give valuable discussions and advices. The author expresses to thank to Professor Yoshihito Inai, the Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, for many directions of physical chemistry in detail, precious advices, suggestions, and warm encouragement. The author would like to also make the special acknowledgement to Professor Masahito Suzuki, Associate Professor Koji Takagi, and Assistant Professor Shin-ichi Matsuoka the Department of Materials Science and Engineering, Graduate School of Engineering, Nagoya Institute of Technology, for valuable advice and fruitful discussions.

Furthermore, it is pleasure to express the author’s wholehearted appreciates to his all colleagues who spend grateful and precious time with him at Inai-Takasu laboratory, especially to Dr. Miyuki Oshimura, Mr. Tetsuya Makino, Dr. Yu Nagao, Mr. Hiroki Tanaka, Mr. Ken Yamamoto, Ms. Yuka Sato, Mr. Takaya Moyori, Mr. Daiki Yoshimura, Mr. Naoki Nomura, and Mr. Terunari Hayashi for their valuable discussions, advices, information, and technical helps.

Finally, the author would like to express his father and mother, Mr. Katsumi Yamada and Mrs. Mamiko Yamada for their warm encouragement and supports.
1. A. Takasu, T. Makino, S. Yamada

Polyester Synthesis at Moderate Temperatures via the Direct Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Rare-Earth Perfluoroalkanesulfonates and Bis(perfluoroalkanesulfonyl)imides


2. S. Yamada, A. Takasu

Microwave-assisted low-temperature dehydration polycondensation of dicarboxylic acids and diols


3. S. Yamada, A. Takasu, K. Kawamura

The Effect of Microwave Irradiation on the Kinetics and Activation Thermodynamics of Ring-Opening Polymerization of ε-Caprolactone