

RAPID COMMUNICATION

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

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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.^{1,2} 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.^{3–6} 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,^{7–13} but only a few of these acids are suitable catalysts because most are labile in the presence of protic substances, for example, 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)¹⁴ or scandium trifluoromethanesulfonimide (triflylimide) (Sc(NTf₂)₃),^{15,16} affords aliphatic polyesters with number-average molecular weights (M_n) > 10⁴ (room-temperature polycondensation^{17–21}). We also demonstrated that these polycondensation systems can incorporate thermally unstable monomers that contain a carbon–carbon double bond,¹⁶ a bromo group,¹⁶ hydroxyl groups,²² mercapto group²³ and/or a disulfide linkage^{24,25} 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

time (> 100 h). Therefore, we next focused on identifying more active catalysts and found that scandium and thulium bis(nonafluorobutanesulfonyl)imide ((Sc(NNF₂)₃) and (Tm(NNF₂)₃)) were more efficient catalysts and allowed us to obtain high-molecular-weight polyesters ($M_n > 2.0 \times 10^4$) 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.²⁶

Rapid syntheses that depend on microwave irradiation have attracted interest because they are environmentally benign. Since first reported in 1986,^{27,28} microwave irradiation has been used to shorten the reaction time of organic syntheses, to decrease the levels of side products and to improve the yields and/or chemoselectivities of the products.²⁹ The fact that there is an exponentially increasing number of publications dealing with microwave-assisted chain polymerizations, for example, anionic polymerization of acrylamides,³⁰ ring-opening cationic polymerization of 2-oxazolines³¹ and ring-opening polymerization of ϵ -caprolactones,³² indicates the remarkable interest in this technique.^{33,34} In addition to chain polymerizations, microwave-assisted step-growth polymerizations have been successfully attempted in a domestic microwave oven.^{33,34} For example, Scherf *et al.*³⁵ synthesized donor-acceptor pi-conjugated polymers using microwave irradiation at 150 °C for 15 min. Nagahata and colleagues³⁶ obtained poly(butylene succinate) that had a weight-average molecular weight (M_w) of 2.90×10^4 in the incredibly short time of 10 min using microwave irradiation. 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,^{33,34} although there has been a report that non-thermal microwaves have a role in the chain polymerization of a lactone.³² 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.

EXPERIMENTAL PROCEDURE

Materials

AdA, glutaric acid, sebacic acid and succinic acid were purchased from Nacalai Tesque, Inc., (Kyoto, Japan). Methyl succinic acid was purchased from Aldrich Co., Ltd. (Milwaukee, WI, USA). Sc(OTf)₃ was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). MPD and decahydronaphthalene (mixture of *cis* and *trans*) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Scandium bis(nonafluorobutanesulfonyl)imide (Sc(NNF₂)₃) was prepared in our laboratory according to the procedure described in the literature.²⁶

Measurements

¹H-NMR spectra were recorded at 27 °C using a Bruker Analytik DPX200 spectrometer (Bruker BioSpin, Kanagawa, Japan, 200 MHz). The number-average molecular weight (M_n) and the polydispersity index (M_w/M_n) of each polyester were estimated

using a size exclusion chromatography system that included a Tosoh DP8020 pump system, an RI (Tosoh, Tokyo, Japan, Tosoh RI-8020) detector and a Tosoh TSKgel SuperMultipor-eHZ-M column calibrated with polystyrene standards. The eluent was CHCl_3 , the flow rate was 0.35 ml min^{-1} and the temperature was 40°C . Differential scanning calorimetry 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 per 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 differential scanning calorimetry trace. The melting temperature (T_m) was defined as the minimum point of the endothermic trough. Matrix-assisted laser desorption/ionization time-of-flight mass spectra were recorded using a Kratos PCAXima CFRplus V2.4.0 mass spectrometer (Kratos, Manchester, UK) using 1,8,9-anthracenetriol as the matrix reagent. NaI was included to generate sodium cations of the polycondensation products ($[\text{M}+\text{Na}]^+$).

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, MPD (1.65 g, 14.0 mmol), AdA (2.05 g, 14.0 mmol) and catalysts were stirred at 80°C (760 mm Hg) 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), MPD (1.65 g, 14.0 mmol), 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, maximum 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 control and PC software (EYELA, Tokyo, Japan). The temperature and irradiation power profile (Supplementary Figure S1) 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.

RESULTS AND DISCUSSION

Microwave-assisted polycondensation reactions of AdA and MPD catalyzed by Sc compounds

Dehydration polycondensation reactions of AdA with MPD were performed under dif-

ferent conditions to compare the effects of microwave and oil bath heating. The product, poly(3-methylpentamethylene adipate), has a low glass transition point ($T_g=-63^\circ\text{C}$). 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 $\text{Sc}(\text{OTf})_3$ as the catalyst (0.5 mol% relative to the total number of moles of reactants), which yielded a polyester with a M_n of 9.8×10^3 (Table 1, run 3). The M_n of that polyester was larger by $\sim 53\%$ 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 $\text{Sc}(\text{OTf})_3$ concentration was reduced (0.1 mol%, Table 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 ($\text{Sc}(\text{NNf}_2)_3$), was used (Table 1, runs 7–12). When the polymerizations using $\text{Sc}(\text{OTf})_3$ as the catalyst were carried out for 24 h, we obtained polyesters with M_n values of 1.5×10^4 (Table 1, runs 13).

To examine the effects of microwave heating on the polycondensation reaction, $^1\text{H-NMR}$ spectra of poly(3-methylpenta-

Table 1 Direct polycondensations of AdA and MPD under reduced pressure at 80°C^a

Run	Catalyst	Mol%	Heating method	Time (h)	Yield ^b (%)	M_n^c (crude) $\times 10^3$	M_w/M_n^c
1	$\text{Sc}(\text{OTf})_3$	0.5	OB	6	99	6.4	1.87
2	$\text{Sc}(\text{OTf})_3$	0.5	MW ^d	3	—	6.7	1.83
3	$\text{Sc}(\text{OTf})_3$	0.5	MW ^d	6	95	9.8	1.85
4	$\text{Sc}(\text{OTf})_3$	0.1	OB	6	99	3.8	1.91
5	$\text{Sc}(\text{OTf})_3$	0.1	MW ^d	3	—	4.4	1.89
6	$\text{Sc}(\text{OTf})_3$	0.1	MW ^d	6	96	5.6	2.01
7	$\text{Sc}(\text{NNf}_2)_3$	0.1	OB	6	99	7.9	1.84
8	$\text{Sc}(\text{NNf}_2)_3$	0.1	MW ^d	4	—	8.3	1.82
9	$\text{Sc}(\text{NNf}_2)_3$	0.1	MW ^d	6	97	9.6	1.80
10	$\text{Sc}(\text{NNf}_2)_3$	0.05	OB	6	99	5.8	2.06
11	$\text{Sc}(\text{NNf}_2)_3$	0.05	MW ^d	3	—	6.5	2.08
12	$\text{Sc}(\text{NNf}_2)_3$	0.05	MW ^d	6	94	9.3	1.85
13	$\text{Sc}(\text{OTf})_3$	0.5	MW ^d	24	—	15.1	1.96

Abbreviations: AdA, adipic acid; M_n , number-average molecular weights; MPD, 3-methyl-1,5-pentanediol; M_w , weight-average molecular weight; MW, microwave; OB, oil bath.

^aAll runs are performed by bulk condensation at 3.0 kPa and 80°C .

^bWithout reprecipitation.

^cDetermined by size exclusion chromatography with CHCl_3 as the eluent. Values are reported relative to those of poly(styrene) standards.

^dTemperature-controlled irradiation at a maximum power of 200 W.

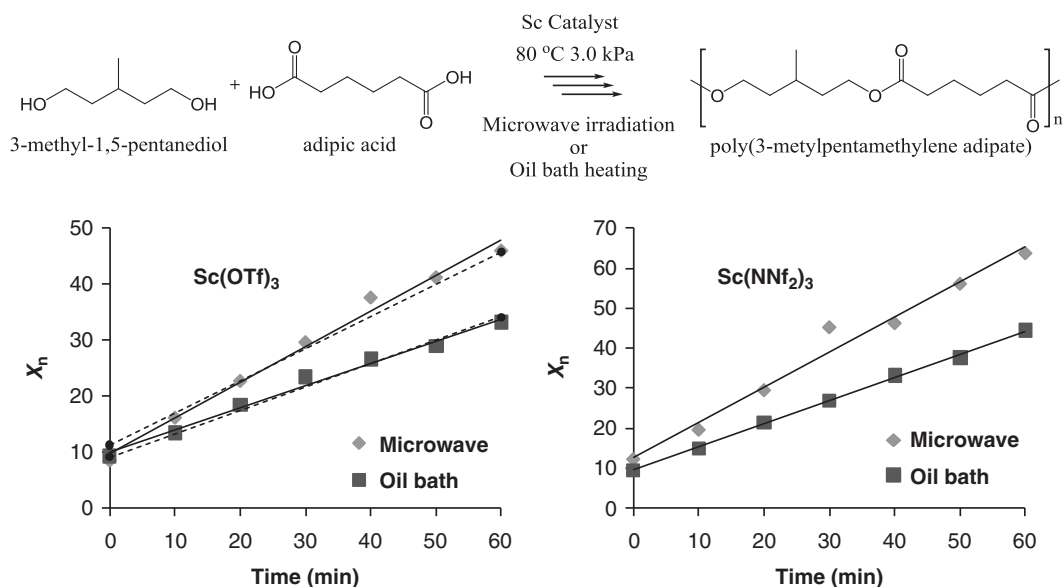


Figure 1 Plots of number-average molecular weights (M_n) vs time for the polycondensation of adipic acid and 3-methyl-1,5-pentanediol. Left panel, 3 kPa, 80 °C, 0.5 mol% $\text{Sc}(\text{OTf})_3$. Samples were removed every 10 min outside of the temperature-controlled environment (solid lines; microwave 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% $\text{Sc}(\text{NNf}_2)_3$ was the catalyst. A full color version of this figure is available at *Polymer Journal* online.

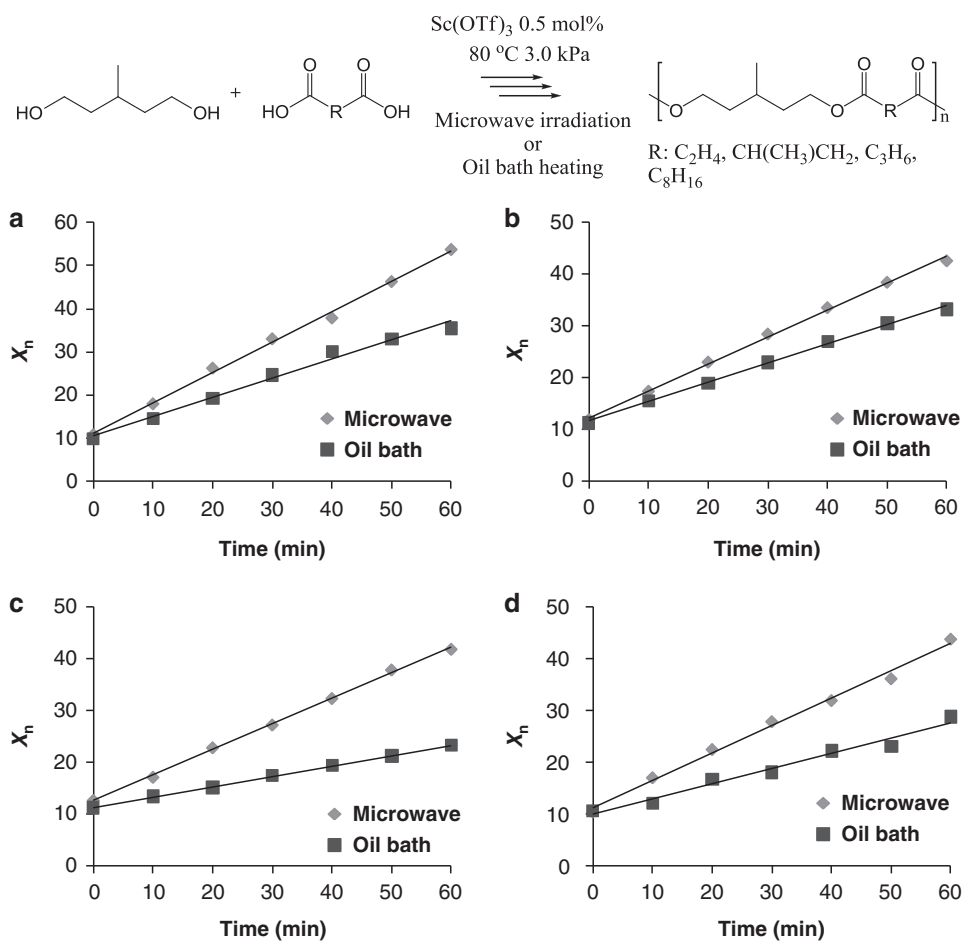


Figure 2 Plots of number-average molecular weights (M_n) vs time for direct polycondensations of 3-methyl-1,5-pentanediol and various dicarboxylic acids ((a) succinic acid, (b) glutaric acid, (c) methyl succinic acid, (d) sebacic acid) under reduced pressure at 80 °C catalyzed by $\text{Sc}(\text{OTf})_3$ (catalyst)=0.5 mol%. A full color version of this figure is available at *Polymer Journal* online.

methylene 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 (Supplementary Figure S2). Matrix-assisted laser desorption/ionization time-of-flight 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 (Supplementary Figure S3). The differences among the m/z values of the three peaks within a group suggest that the polyesters terminated with an α -hydroxyl and an ω -carboxyl, an α - and ω -hydroxyl or an α - and ω -carboxyl. For example, the peaks at 2546, 2647 and 2674 would be derived from polyesters having an α -hydroxyl and an ω -carboxyl, an α - and ω -hydroxyl, and an α - and ω -carboxyl at the termini, respectively. Peaks at 2582, which correspond to cyclic polyesters, were also observed.

Polycondensation kinetics

We also investigated the effect of microwave irradiation on the second-order kinetics of the catalyzed polycondensation reactions.³⁷ 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.³⁷ We removed aliquots from the conventional-heating and microwave-heating reactions every 10 min, which were then used to determine the M_n values (by size exclusion chromatography) and to calculate X_n .

$$R = -\frac{d[\text{COOH}]}{dt} = k[\text{COOH}][\text{OH}]$$

$$\rightarrow -\frac{dc}{dt} = kc^2 \quad (1)$$

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

$$p = \frac{c_0 - c}{c_0} \rightarrow c = c_0(1 - p)$$

$$(p : \text{extent of polymerization}) \quad (3)$$

$$X_n = \frac{c_0}{c} = \frac{1}{1 - p} \rightarrow 1 - p = \frac{1}{X_n} \quad (4)$$

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

Data for the polymerization of AdA with MPD catalyzed by Sc(OTf)₃ or Sc(NNf₂)₃ are shown in Figure 1. The data follow equation 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,^{38,39} where $M_w/M_n = 1 + p$ and p is the extent of reaction. In addition, we found that the proportionality constant ($c_0k = 0.633 \text{ s}^{-1}$) for the microwave-assisted polycondensation was 1.6 times greater than that of the conventional-heating experiment ($c_0k = 0.397 \text{ s}^{-1}$; Figure 1, left panel). Additionally, with Sc(NNf₂)₃ as the catalyst, the polycondensation proportionality constant obtained when microwave irradiation was used ($c_0k = 0.876 \text{ s}^{-1}$) was 1.5 times greater than when conventional heating was used ($c_0k = 0.580 \text{ s}^{-1}$) (Figure 1, 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 (Figure 1, 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.

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-methylpentamethylene succinate), -51 °C; poly(3-methylpentamethylene sebacate), -88 °C; poly(3-methylpentamethylene methylsuccinate), -64 °C; poly(3-methylpentamethylene glutarate), -64 °C). We always obtained linear relationships between X_n and time (Figure 2), 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 polycondensa-

tion.^{38,39} 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-methylpentamethylene succinate), 1.6-fold; poly(3-methylpentamethylene glutarate), 1.4-fold; poly(3-methylpentamethylene methylsuccinate), 2.5-fold; and poly(3-methylpentamethylene 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.

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.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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