144 *Macromolecules* **2010**, *43*, 144–149
DOI: 10.1021/ma901945u

Macromolecules
ARTICLE

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

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Received September 2, 2009; Revised Manuscript Received November 1, 2009

ABSTRACT: Recently, we reported that scandium trifluoromethanesulfonate [$Sc(OTf)_3$] 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 [$Sc(NNf_2)_3$]) 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 [$Tm(NNf_2)_3$] was a more effective catalyst than was $Sc(OTf)_3$, $Sc(NNf_2)_3$, thulium trifluoromethanesulfonate [$Tm(OTf)_3$], or thulium trifluoromethanesulfonimide [$Tm(NTf_2)_3$]. 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 %).

Introduction

Recent attention has focused on aliphatic polyesters that have potential as biomaterials, biodegradable polymers, and environmentally benign materials.[1] Aliphatic polyesters are usually produced by polycondensation of dicarboxylic acids and excess amounts of diols (1.1−1.5 equiv), at temperatures greater than 250 °C and under extremely reduced pressures.[2,3] Polycondensations have been catalyzed by Lewis acids,[4] but not many suitable Lewis acid catalysts exist because most are labile toward protic substances, including carboxylic acids, alcohols, and water, which are therefore not suitable for dehydration polycondensation. Rare-earth triflates[5] and triflylimides,[6] because they do not react with protic compounds, can catalyze some reactions even in water because they have small hydrolysis constants[5] and large exchange rate constants for substitution of inner-sphere water ligands.[5b] 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) [$Sc(OTf)_3$][7] or scandium trifluoromethanesulfonimide (triflylimide) [$Sc(NTf_2)_3$],[8] afford aliphatic polyesters with number-average molecular weights (M_n) greater than 1.0×10^4 (room temperature polycondensation[9]). 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,[8b] a bromo group,[8b] and/or hydroxyl groups.[10] Recently, we demonstrated the ring-opening copolymerization of ε-caprolactone initiated from the pendent hydroxyl groups of poly(nonamethylene DL-malate) prepared via chemoselective dehydration polycondensation[10] catalyzed by $Sc(OTf)_3$. This work was a study of a dual-catalytic [$Sc(OTf)_3$] system that combined a chemoselective dehydration polycondensation with a subsequent ring-opening polymerization of ε-caprolactone.[11]

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), and scandium bis(nonafluorobutanesulfonyl)imide [$Sc(NNf_2)_3$] (Figure 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.

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

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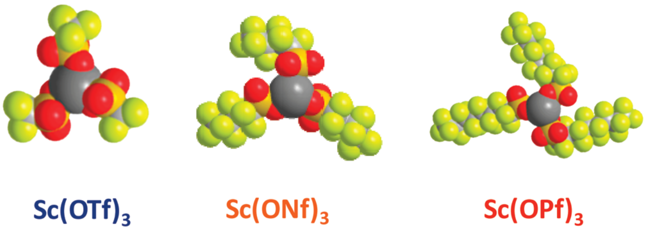


Figure 1. Molecular structure of scandium trifluoromethanesulfonate [$Sc(OTf)_3$], scandium nonafluorobutanesulfonate [$Sc(ONf)_3$], and scandium perfluorooctanesulfonate [$Sc(OPf)_3$].

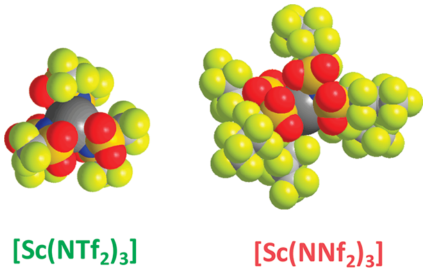


Figure 2. Molecular structure of scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$] and scandium bis(nonafluorobutanesulfonyl)imide [$Sc(NNf_2)_3$].

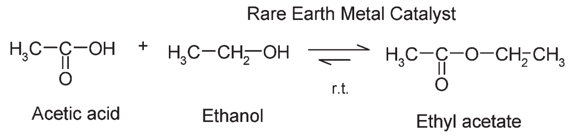
(MPD), thulium(III) acetate tetrahydrate, thulium trifluoromethanesulfonate [$Tm(OTf)_3$], 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluoro-1-octanesulfonic acid (PfOH), and samarium(III) acetate tetrahydrate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Bis(nonafluorobutanesulfonyl)imide ($HNNf_2$) 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). Scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$] was prepared in our laboratory according to the procedure described in the literature.[6]

Preparation of $Sc(OPf)_3$.[13] $Sc(OPf)_3$ was synthesized as previously described. An aqueous solution of $ScCl_3 \cdot 6H_2O$ (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 H_2O 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 $Sc(ONf)_3$.[13] $Sc(ONf)_3$ was synthesized as previously described. Sc_2O_3 (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 Sc_2O_3, water was removed by evaporation under reduced pressure, and a white solid remained (3.9 g, 98%).

Preparation of $Sc(NNf_2)_3$,[14] Samarium Bis(nonafluorobutanesulfonyl)imide [$Sm(NNf_2)_3$], Neodymium Bis(nonafluorobutanesulfonyl)imide [$Nd(NNf_2)_3$], and Thulium Bis(nonafluorobutanesulfonyl)imide [$Tm(NNf_2)_3$]. The acetates of Sc, Sm, Nd, and Tm, were each dissolved in H_2O containing $HNNf_2$. 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 $Sc(NNf_2)_3 \cdot 4H_2O$ (76% yield): C, 15.52; H, 0.43; N, 2.26. Found: C, 15.30; H, 0.38; N, 2.63. Anal. Calcd for $Sm(NNf_2)_3 \cdot 4H_2O$ (98% yield): C, 14.68; H, 0.41; N, 2.14. Found: C, 14.50; H, 0.48; N, 2.49. Anal. Calcd for $Nd(NNf_2)_3$ (99% yield): C, 15.29; H, 0; N, 2.23. Found: C, 14.48; H, 0; N, 2.72. Anal. Calcd for $Tm(NNf_2)_3 \cdot 4H_2O$ (98% yield): C, 14.55; H, 0.40; N, 2.12. Found: C, 14.46; H, 0.40; N, 2.61.

Scheme 1. Esterification of Equimolar Acetic Acid and Ethanol



Catalyst (0.1 mmol)	Conversion[b] %
$Sc(OTf)_3$	67
$Sc(ONf)_3$	68
$Sc(OPf)_3$	62
$Sc(NNf_2)_3$	63
$Nd(OTf)_3$	51
$Gd(OTf)_3$	52
$Dy(OTf)_3$	52
$Er(OTf)_3$	53
$Tm(OTf)_3$	56
$Nd(NNf_2)_3$	65
$Tm(NNf_2)_3$	62
$Sm(NNf_2)_3$	62
no catalyst	no reaction

[a] Condition; acetic acid=ehanol: 5 mmol, temp., r,t., time, 6h. [b] Determined by ^{1}H NMR.

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 $CHCl_3$ (5 mL) into diethyl ether (100 mL), the yield was 70%.

Measurements. ^{1}H NMR spectra were recorded at 27 °C using a Bruker DPX200 or a DPX600 spectrometer (200 and 600 MHz, respectively). Chemical shifts were referenced to tetramethylsilane ($\delta = 0$). The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) 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 $CHCl_3$, 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.

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

Scheme 2. Low-Temperature Polycondensation of Adipic Acid and 3-Methylpentanediol

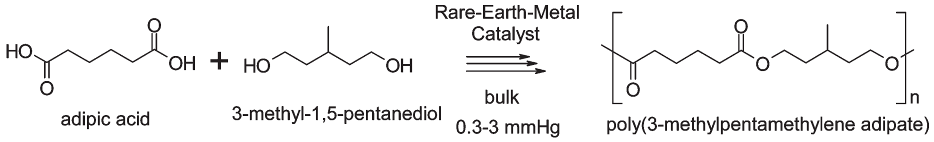


Table 1. Direct Polycondensations of AdA[a] and MPD[b] under Reduced Pressure at 80 °C[c]

run	catalyst	mol %	time (h)	yield[d] (%)	M_n[e](crude) × 10^3	M_w/M_n[e]
1	$Sc(OTf)_3$	0.05	6	99	6.4	2.2_2
2	$Sc(OTf)_3$	0.1	6	99	10.0	1.7_5
3	$Sc(OTf)_3$	0.2	6	99	10.5	1.8_9
4	$Sc(OTf)_3$	0.5	6	99	10.1	1.9_3
5	$Sc(OTf)_3$	0.5	12	99	13.7	2.0_5
6	$Sc(OPf)_3$	0.05	6	99	7.0	2.0_5
7	$Sc(OPf)_3$	0.1	6	99	9.5	1.8_6
8	$Sc(OPf)_3$	0.2	6	99	10.8	1.9_3
9	$Sc(ONf)_3$	0.5	6	99	10.8	1.8_3
10	$Sc(ONf)_3$	0.5	12	99	14.7	1.8_8

[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.

Table 2. Direct Polycondensations of AdA[a] and MPD[b] under Reduced Pressure at 60 °C[c]

run	catalyst	mol %	time (h)	yield[d] (%)	M_n[e] (crude) × 10^3	M_w/M_n[e]
1	$Sc(OTf)_3$	0.05	6	>99	1.6	1.6_4
2	$Sc(OTf)_3$	0.05	12	>99	2.8	1.6_4
3	$Sc(OTf)_3$	0.05	24	>99	5.6	2.0_1
4	$Sc(NTf_2)_3$	0.05	6	>99	2.7	2.1_3
5	$Sc(NTf_2)_3$	0.05	12	99	5.5	1.8_6
6	$Sc(NTf_2)_3$	0.05	24	99	12.0	1.7_9
7	$Sc(NNf_2)_3$	0.05	6	99	3.3	2.2_5
8	$Sc(NNf_2)_3$	0.05	12	99	5.6	2.0_1
9	$Sc(NNf_2)_3$	0.05	24	99	12.3	1.8_6
10	$Sc(OTf)_3$	0.1	6	>99	6.4	1.9_3
11	$Sc(OTf)_3$	0.1	12	>99	12.3	1.9_3
12	$Sc(NNf_2)_3$	0.1	6	98	8.8	2.1_6
13	$Sc(NNf_2)_3$	0.1	24	98	17.9	2.0_7

[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.

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_3CH_2OH, $J = 7.0$ Hz) and 4.12 ppm ($CH_3CH_2OCOCH_3$, $J = 7.1$ Hz), were between 51% and 67% (Scheme 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), 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%).

To compare the catalytic efficiencies of $Sc(OTf)_3$[7,8] (0.1 mol %) and $Sc(OPf)_3$ (0.1 mol %), bulk polycondensations of MSA and 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 ($M_n = 7.3 \times 10^3$; $M_w/M_n = 1.6_6$; 96% yield) than for the $Sc(OTf)_3$-catalyzed reaction ($M_n = 2.2 \times 10^3$; $M_w/M_n = 1.5_4$; 97% yield). At 60 °C, $M_n = 9.3 \times 10^3$ ($M_w/M_n = 1.7_4$) with $Sc(OPf)_3$ as the catalysis and 4.0×10^3 ($M_w/M_n = 1.8_6$) 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 80 °C, to synthesize a polyester with a M_n of approximately 10.0×10^3, 1.0 mol % of $Sc(OTf)_3$ was required.[7,8]

The polycondensation of adipic acid (AdA) with 3-methyl-1,5-pentanediol (MPD) served as a model for amorphous polyester production (Scheme 2). A variety of rare-earth-metal compounds were used as catalysts, and the polymerization conditions were surveyed (Tables 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 10.0×10^3 even though the reaction was run for only 6 h (Table 1, run 2). Unfortunately, the remarkable increase for M_n was not observed when $Sc(ONf)_3$ (Table 1, runs 9 and 10) and $Sc(OPf)_3$ (Table 1, 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.

Scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$] is air-stable and a powerful Lewis acid[12] because of its large fluorine content (Figure 2). Koppel and colleagues evaluated various ligands chosen according to their abilities to withdraw electrons.[15] They concluded that bis(nonafluorobutanesulfonyl)imide [$(NNf_2)_3$] had even a better election-withdrawing ability than did trifluoromethanesulfonimide [$(NTf_2)_3$]. 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,[14] and the $Sc(NNf_2)_3$-catalyzed polyesterification of AdA and MPD was carried out at 60 °C (Table 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, Table 2) poly(3-methylpentamethylene adipate) with M_ns of 12.0×10^3 and 12.3×10^3 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_ns were much larger than that found when using same amount of $Sc(OTf)_3$ (5.6×10^3, run 3, Table 2), 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 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.[16] 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]

We consider that a stronger Lewis acid has the possibility to afford the faster reaction rate under kinetic control. To appraise the strengths of $Sc(NTf_2)_3$ and $Sc(NNf_2)_3$ as Lewis acids toward a carboxylic acid moiety, the ^{13}C NMR spectra of acetic acid alone and equimolar amounts of acetic acid and either $Sc(NTf_2)_3$ or $Sc(NNf_2)_3$ (in acetone-d_6, at a field strength of 150 MHz, and 27 °C) were recorded (Figure 3). The carbonyl carbon signal of acetic acid (173.0 ppm) shifted downfield to 179.8 ppm when $Sc(NTf_2)_3$ was present and to 181.1 ppm when $Sc(NNf_2)_3$ was present. The chemical shift differences [$\Delta\nu$; 6.9 ppm for $Sc(NTf_2)_3$ and 7.1 ppm for $Sc(NNf_2)_3$] are larger than those found for $Sc(OTf)_3$ (4.6 ppm) or for $Sc(ONf)_3$ (3.2 ppm). The sizes of the $\Delta\nu$ values tend to correlate with the sizes of the M_n values reported in Tables 1 and 2.

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 (Table 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

Table 3. Direct Polycondensations of AdA[a] and MPD[b] under Reduced Pressure at 60 °C[c]

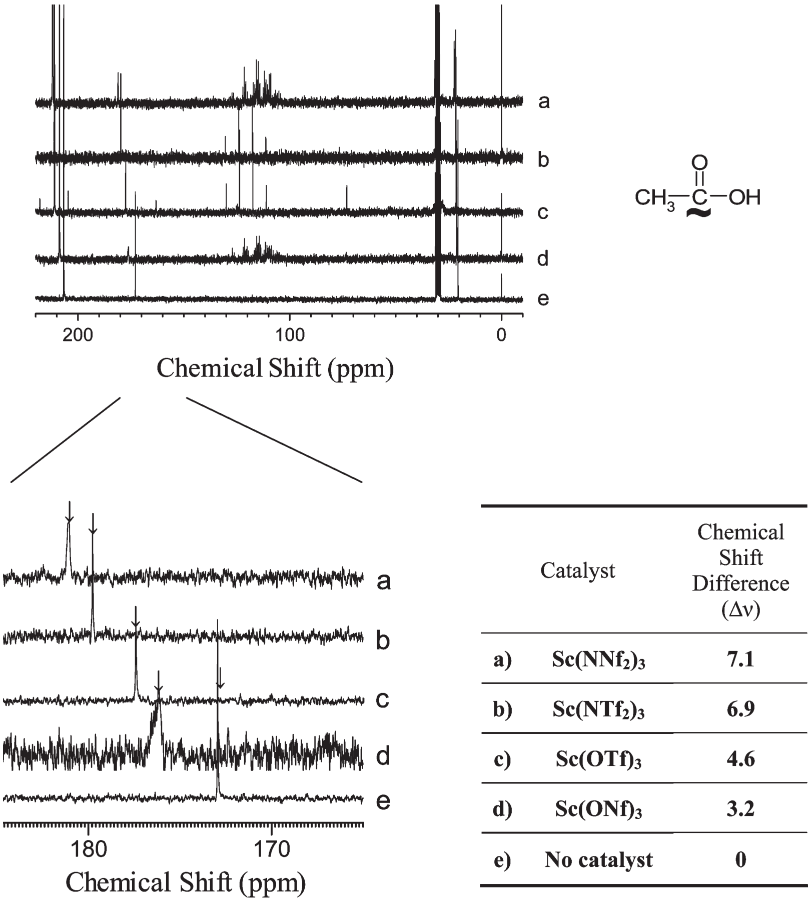
run	catalyst (0.5 mol %)	time (h)	yield[d] (%)	M_n^e(crude) $\times 10^3$	M_w/M_n^e
1	$Nd(OTf)_3$	24	>99	3.7	1.7_6
2	$Sm(OTf)_3$	24	>99	1.7	1.8_9
3	$Gd(OTf)_3$	24	>99	4.1	1.7_2
4	$Dy(OTf)_3$	24	>99	4.4	1.8_1
5	$Er(OTf)_3$	24	>99	5.9	1.9_5
6	$Tm(OTf)_3$	24	>99	8.3	2.0_5
7	$Sc(OTf)_3$	24	99	13.3	1.7_5

[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.

Table 4. Direct Polycondensations of AdA[a] and MPD[b] under Reduced Pressure at 60 °C[c]

run	catalyst	mol %	time (h)	yield[d] (%)	M_n^e(crude) $\times 10^3$	M_w/M_n^e
1	$Sm(OTf)_3$	0.5	24	>99	2.8	2.0_2
2	$Sm(NNf_2)_3$	0.5	24	99	14.8	2.0_1
3	$Sm(NNf_2)_3$	0.1	24	98	13.6	1.9_7
4	$Nd(OTf)_3$	0.1	24	>99	3.1	1.7_1
5	$Nd(NNf_2)_3$	0.1	24	>99	14.8	2.0_0
6	$Nd(NNf_2)_3$	0.01	24	>99	3.0	1.7_4
7	$Tm(OTf)_3$	0.1	6	>99	2.7	2.0_9
8	$Tm(OTf)_3$	0.1	24	>99	6.3	1.9_7
9	$Tm(NNf_2)_3$	0.1	6	98	13.4	1.8_3
10	$Tm(NNf_2)_3$	0.1	12	97	17.1	1.8_6
11	$Tm(NNf_2)_3$	0.1	18	97	20.8	1.7_3
12	$Tm(NNf_2)_3$	0.1	24	97	23.5	1.6_6
13	$Tm(NNf_2)_3$	0.01	12	>99	5.0	1.8_6
14	$Tm(NTf_2)_3$	0.1	6	>99	10.7	1.8_0

[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.



	Catalyst	Chemical Shift Difference (Δv)
a)	**$Sc(NNf_2)_3$**	**7.1**
b)	**$Sc(NTf_2)_3$**	**6.9**
c)	**$Sc(OTf)_3$**	**4.6**
d)	**$Sc(ONf)_3$**	**3.2**
e)	**No catalyst**	**0**

Figure 3. ^{13}C NMR spectra of acetic acid in the presence of equivalent scandium catalyst in acetone-d_6 (27 °C).

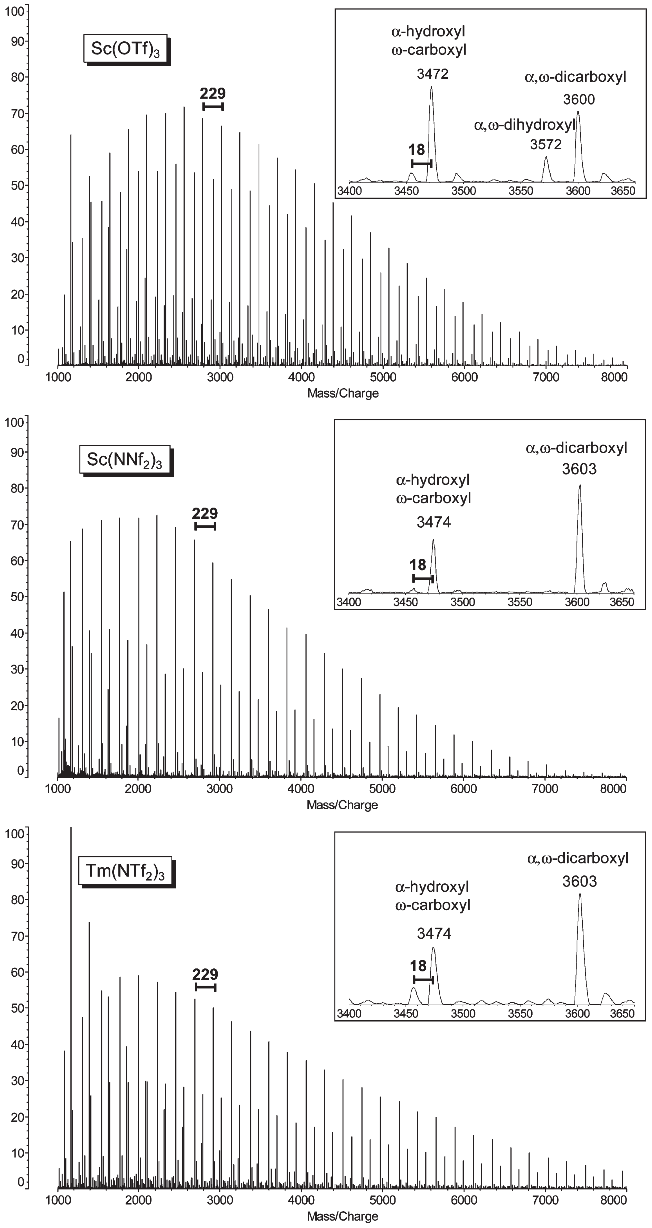


Figure 4. MALDI-TOF mass spectra of poly(3-methypentamethylene adipate) from Sc(OTf)$_3$ (top), Sc(NNf$_2$)$_3$ (middle), and Tm(NTf$_2$)$_3$ (bottom)-catalyzed polycondensations.

synthesized with Sm(OTf)$_3$ (1.7×10^3) and Nd(OTf)$_3$ (3.7×10^3) as catalysts were much smaller than when Sc(OTf)$_3$ (13.3×10^3) and Tm(OTf)$_3$ (8.3×10^3) were the catalysts.

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 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 (14.8×10^3, run 2) than when Sm(OTf)$_3$ was used as the catalyst (2.8×10^3, run 1). Nd(NNf$_2$)$_3$ (0.1 mol %) also produced a polyester with a greater M_n (14.8×10^3, run 5) than did the equivalent amount of Nd(OTf)$_3$ (3.1×10^3, 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 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 °C for 12 h (run 9), indicating that combination of (NNf$_2$)$_3$ and thulium is a promised candidate for an excellent catalyst for polycondensation.

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 4, top). 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 α-hydroxyl and an ω-carboxyl, or an α-hydroxyl and an ω-hydroxyl, or an α-carboxyl and an ω-carboxyl at the ends. For example, the peaks at 3472, 3572, and 3600 would be derived from polyesters having an α-hydroxyl and an ω-carboxyl, an α-hydroxyl and an ω-hydroxyl, and an α-carboxyl and an ω-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 4, top spectrum). These peaks have a m/z that is 18 amu smaller than that of the nearest peak associated with a polyester terminated with α-hydroxyl and ω-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 4, middle) and Tm(NTf$_2$)$_3$-catalyzed polycondensations (Figure 4, bottom), signals assigned to the polyesters terminated with an α-hydroxyl and an ω-carboxyl and an α-carboxyl and an ω-carboxyl at the ends were confirmed, but a signal ascribed to polyester with an α-hydroxyl and an ω-hydroxyl temini 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 α-hydroxyl and an ω-hydroxyl temini were not observed.

For the work reported herein, 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 were tested using the polycondensation of AdA and MPD. Tm(NNf$_2$)$_3$ was a more effective catalyst than was Sc(OTf)$_3$, Sc(NNf$_2$)$_3$, Tm(OTf)$_3$, or Tm(NTf$_2$)$_3$. 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) 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.

Acknowledgment. Financial support came from the Japan Science and Technology Agency (JST) for potentially verification stage (to A.T.).

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