Environmentally Benign Polyester Synthesis by Room Temperature Direct Polycondensation of Dicarboxylic Acid and Diol

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Nowadays, polyesters are essential materials for our life. Particularly, aliphatic polyesters including poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS) would replace many conventional plastics in the near future because of their biodegradability, acceptable mechanical strength, and comparable softening temperature to low-density polyethylene and polystyrene.[1] In general, the synthesis is commercially produced by the polycondensation of aliphatic dicarboxylic acid and diol compounds at >250 °C under highly reduced pressure.[2] Therefore, room temperature polycondensation of dicarboxylic acids and diols is still a revolutionary subject in polymer science field. Although some researchers reported that in situ enhancement of monomer (carboxylic acid) reactivity using active reagents made it possible to synthesize polyesters under mild condition,[3] recent concern toward environmental problems prompted us to explore an “ideal polycondensation system”, taking (1) low temperature, (2) avoiding organic solvent, (3) atomic economy, (4) lack of catalyst toxicity after use, and (5) catalyst recyclability and reuse. In principle, a survey of new Lewis acids had been difficult[4] because most Lewis acid catalysts are liable toward protic substances, including carboxylic acids, alcohols, and water, which is not suitable for the dehydration polycondensation. Recently, Ishihara et al.[4c] reported that the $HfCl_4(THF)_2$ complex efficiently catalyzed the direct polycondensation of diols and dicarboxylic acid compounds, in which the procedure was a solution polycondensation in *o*-xylene with reflux (ca. 144 °C). In this communication, we describe polyesters synthesis in order to achieve the one-step synthesis of aliphatic polyesters at/near room temperature, “room temperature polycondensation”[5] using reusable catalysts, scandium trifluoromethanesulfonate [$Sc(OTf)_3$] and scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$] (Figure 1).

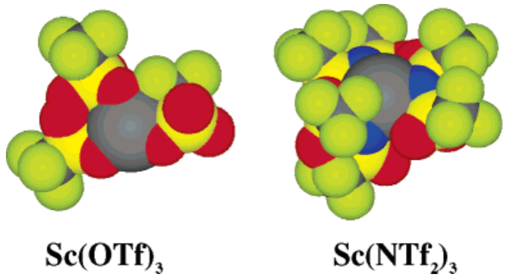
Sc(OTf)$_3$ Sc(NTf$_2$)$_3$

Figure 1. Molecular structure of scandium trifluoromethanesulfonate [$Sc(OTf)_3$] and scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$].

As the catalyst, we focused on rare-earth catalysts because they are insensitive to protic compounds and they catalyze some reactions even in water because of the low hydrolysis constant[6] and high exchange rate constant for substitution of inner-sphere water ligand;[6b] the catalysts can be quantitatively recovered after the reactions and reused. Although it was reported that $Sc(OTf)_3$ catalyzed the reaction of alcohols with carboxylic anhydride[7] and activated esters[7,8] at low temperature, we found that $Sc(OTf)_3$ catalyzed direct esterification of aliphatic alcohol with carboxylic acid at room temperature.[9] We also reported the direct polycondensation (at 80−180 °C) of a dicarboxylic acid (succinic acids) with diols [ethylene glycol (EG), 1,3-propanediol (1,3-PD), and 1,4-butanediol (1,4-BD)] catalyzed by rare earth triflate to synthesize poly(alkylene succinate)s, in which $Sc(OTf)_3$ catalyzed not only the esterification but also etherification for EG and 1,3-PD unfortunately. Room temperature direct polycondensation would lead to not only saving heat energy but also high chemoselectivity (suppression of etherification) and a widespread range of dicarboxylic acid and diol monomers having chirality, functionality, and biological activity. As a model reaction of the polyesterification, the direct esterification of ethanol using 2 equimolar amounts of acetic acid was carried out in bulk using 1.0 mol % $Sc(OTf)_3$ and $Sc(NTf_2)_3$ at 27 °C for 7 h without removing water. The conversions determined by ^1H NMR were 89% and 72%, respectively. On the other hand, the esterification scarcely occurs without the catalysts. Although one may envision that esterification proceeds through the acid anhydride, we could not observe any peaks ascribed to acetic anhydride in the ^1H NMR measurement. On the basis of the model reaction, we confirmed that $Sc[(NTf)_2]_3$ as well as $Sc(OTf)_3$ catalyzed the direct esterification of carboxylic acids and alcohols at room temperature. To clarify which reacts with ethanol faster in the presence of the scandium catalysts, we examined chemoselective esterification for a 1:1 mixture of acetic acid or methyl acetate. Surprisingly, ethanol reacted with acetic acid chemoselectively in the presence of $Sc(OTf)_3$(90%) or $Sc[(NTf)_2]_3$ (92%), and we could expect this polycondensation system to proceed, minimizing transesterification. Bulk polycondensations of methylsuccinic acid (MSA) and diols, 1,4-BD ($n = 4$), were carried out under reduced pressure (0.3−30 mmHg) using $Sc(OTf)_3$ at 35 °C.[10] The number-average molecular weights (M_ns) were estimated by size exclusion chromatography (SEC) using THF as the eluent (polystyrene standards). In all runs, polymeric solids were obtained which were soluble in chloroform, tetrahydrofuran (THF), and acetonitrile. Interestingly, the direct polycondensation proceeded even at room temperature (35 °C) to afford poly(butylene methylsuccinate) with $M_n = 1.2 \times 10^4$ for 96 h in the presence of 1.4 mol % catalyst (94% yield, run 4); i.e., room temperature direct polyesterification was established to give the polyester ($M_n = 1.0 \times 10^4$) by a one-step procedure. In the absence of catalyst, the polyester was not obtained ($M_n = 400$, run 5). Using trifluoromethanesulfonic acid (TfOH) as the Brϕnsted acid (run 6), the M_n was quite low ($M_n = 0.3 \times 10^4$)

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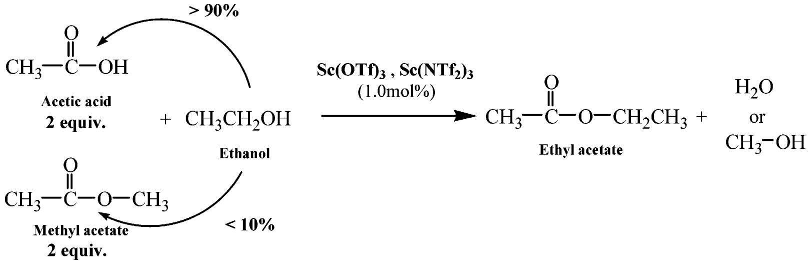
Scheme 1. Model Reaction of Carboxylic Acid and Alcohol in the Presence of Carboxylic Acid Methyl Ester



Scheme 2. Room Temperature Direct Polycondensation of Dicarboxylic Acids with Diols

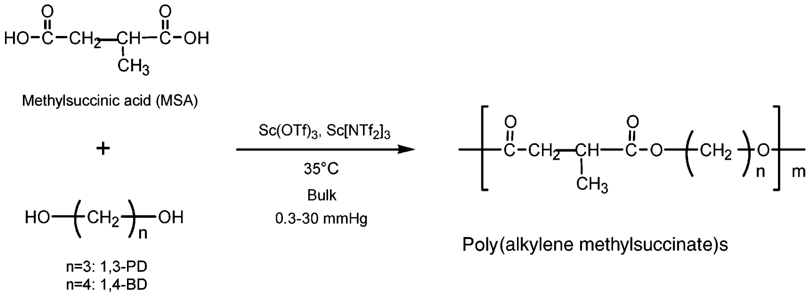
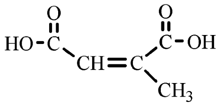
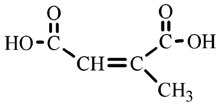


Table 1. Room Temperature Direct Polycondensation of Dicarboxylic Acids and 1,4-BD[a]

run	dicarboxylic acids	catalyst (mol%)	temp. (°C)	time (h)	yield (%)	M_n[b] x 10^{-4}	M_w/M_n[b]
1	MSA[c]	$Sc(OTf)_3$ (0.3)	35	110	95[d]	0.59	1.6
2	MSA[c]	$Sc(OTf)_3$ (0.5)	35	110	88[d]	0.54	1.6
3	MSA[c]	$Sc(OTf)_3$ (1.0)	35	110	99[d]	0.97	1.5
4	MSA[c]	$Sc(OTf)_3$ (1.4)	35	96	94[d]	1.24	1.4
5	MSA[c]	blank	35	99	97[d]	0.04	1.3
6	MSA[c]	TfOH (1.0)	35	99	91[d]	0.30	1.7
7	MSA[c]	$HfCl_4(THF)_2$ (1.0)	35	70	92[d]	0.11	1.3
8		$Sc(OTf)_3$ (1.0)	60	50	68[d]	1.41	1.9
9		TfOH (1.0)	60	50	89[d]	0.26	1.5
10	MSA[c]	$Sc(NTf_2)_3$ (0.3)	35	90	96[d](85%[f])	1.22	1.5
11	MSA[c]	$Sc(NTf_2)_3$ (0.5)	35	60	97[d]	1.00	1.7
12	MSA[c]	$Sc(NTf_2)_3$ (1.0)	35	70	92[d]	0.90	1.5
13	MSA[c]	$Sc(OTf)_3$[e] (1.4)	35	104	93[d]	0.68	1.4
14	MSA[c]	$Sc(NTf_2)_3$[e] (0.3)	35	110	98[d]	0.93	1.5

[a] All runs are performed by bulk (melt) polycondensation under reduced pressure (0.3–3.0 mmHg). [b] Determined by SEC measurement in THF relative to poly(styrene). [c] Methylsuccinic acid. [d] Without reprecipitation. [e] Recovered catalyst. [f] After reprecipitation using $CHCl_3$ and diethyl ether.

compared with that catalyzed by $Sc(OTf)_3$. Surprisingly, the polycondensation behavior using 1.0 mol % $Sc(OTf)_3$ was much superior to that using the same amount of $HfCl_4(THF)_2$ (runs 3 and 7). The results revealed that the $Sc(OTf)_3$ catalyzed the direct polycondensation effectively because of high activity, resistance to water, and turnover number (TON). In the polycondensation of MSA with 1,3-PD, the polyesterification proceeded chemoselectively (without etherification) to give the corresponding polyester with $M_n = 0.7 \times 10^4$ for 110 h. The improved chemoselectivity was ascribed to the lower condensation temperature. As another example to illustrate the mildness of the polycondensation, we present the polycondensation using monomer containing carbon−carbon double bond, citraconic acid. The polycondensation with 1,4-BD was carried out at 60 °C for 50 h using 1 mol % of $Sc(OTf)_3$ (run 8). While the polycondensation at 160 °C without catalyst would result in both *Z*- to *E*- and citraconic acid to itaconic acid isomerizations, and gelatin as usual,[11] linear polyester ($M_n = 1.41 \times 10^4$) was obtained in this system. In the ^1H NMR spectrum, any peaks ascribed to isomerization and gelation were not observed expectedly (Supporting Information).

Scandium trifluoromethanesulfonimide [$Sc(NTf_2)_3$] is also known to be air stable and a powerful Lewis acid[12] because it has a higher fluorine content (Figure 1). To decrease the catalyst amount required for the polyesterification, $Sc(NTf_2)_3$-catalyzed direct polyesterification of MSA and 1,4-BD was carried out at 35 °C (runs 10−12). The catalytic activity was higher than that of $Sc(OTf)_3$ in this polyesterification. Using 0.3 mol % of $Sc(NTf_2)_3$, we could synthesize poly(butylene methylsuccinate) with M_n of 1.2×10^4. The molecular weight was much higher than that using the same amount of $Sc(OTf)_3$ (0.59×10^4). Using the SEC data (M_n), calculated TON in this system is 314 (mol/mol), which is superior to that using 0.3 mol % of $Sc(OTf)_3$ (TON: 294). As to molecular weight distribution (M_w/M_n), the distributions are relatively narrow (1.4−1.7). The results supported that the polyesterification proceeded suppressing transesterification expectedly.

The catalysts used in this study was easily recovered by solubilization in $CHCl_3$ or $CHCl_3$/hexane (1/1, v/v) and successive extraction with water [95% for $Sc(OTf)_3$, 90% for $Sc(NTf_2)_3$].[13] Direct polycondensation of MSA and 1,4-BD using the recovered catalysts gave polyesters with M_n of 0.68×10^4 for 104 h ($M_w/M_n = 1.4$, 93% yield, run 13) and M_n of 0.93×10^4 for 110 h ($M_w/M_n = 1.5$, 98% yield, run 14), respectively.

In this paper, we demonstrated the room temperature direct esterification of a carboxylic acid and alcohol catalyzed by $Sc(OTf)_3$ and $Sc(NTf_2)_3$ and reported that this breakthrough made it possible to synthesize aliphatic polyesters ($M_n > 1.0 \times 10^4$) by room temperature polycondensation. The catalyst could be recycled for the polyester synthesis. The development of polycondensations at lower temperature is extremely effective not only for environmentally friendly processes but also for advanced material design using monomers having chirality, functionality, and biological activity.

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Supporting Information Available: ^1H NMR spectrum of poly(butylene citraconate). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Takasu, A.; Oishi, Y.; Iio, Y.; Inai, Y.; Hirabayashi, T. *Macromolecules* **2003**, *36*, 1772−1774. Although Ishihara et al. tried $Sc(OTf)_3$-catalyzed direct esterification of 4-phenylbutyric acid and benzyl alcohol in ref 3c, dehydration (not esterification) proceeded predominantly to give α-tetralone as a major product.

(10) For poly(butylene methylsuccinate): A typical polycondensation procedure is as follows. In a three-necked tube, MSA (7.0 mmol), 1,4-BD (7.0 mmol), and $Sc(NTf_2)_3$ were dissolved in acetonitrile (1.0 mL) and stirred at room temperature for 1 h. After removing the acetonitrile under reduced pressure, the polycondensation started at 35 °C under 30 mmHg. After 10 h, the reduced pressure gradually increased to 0.3−3 mmHg and kept for 80 h to complete the condensation. After the reaction, the yield of polyester was calculated by subtraction weight of catalyst from the isolated material (96% yield, run 10 in Table 1). After reprecipitation using $CHCl_3$ and diethyl ether, the yield was 85%. ^1H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.20−1.24 ($CHCH_3$), 1.69−1.71 (OCH_2CH_2), 2.34−2.45 and 2.67−2.82 ($CHCH_2$), 2.85−2.96 ($CHCH_2$), 4.11 ($COOCH_2$). ^{13}C NMR (50 MHz, $CDCl_3$, δ, ppm): 17.0 ($CHCH_3$), 25.2 (OCH_2CH_2), 35.8 ($CHCH_2$), 37.5 ($CHCH_2$), 64.1 (OCH_2CH_2), 171.8 and 175.2 ($COOCH_2$). IR (KBr disk, cm^{-1}): 2965 (ν_{C-H}), 1734 [$\nu_{C=O}$(ester)], 1464 (δ_{C-H}), 1277 and 1169 [ν_{C-O}(ester)].

(11) As an example, see: Takenouchi, S.; Takasu, A.; Inai, Y.; Hirabayashi, T. *Polym. J.* **2001**, *33*, 746−753.

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(13) Procedure of recovery of the catalyst is as follows. The reaction mixture was resolved in $CHCl_3$ (3 mL) and washed with water (5 mL). The aqueous layer was evaporated, and the residue was washed with $CHCl_3$ to give recovered $Sc(OTf)_3$ (95% yield). $Sc(NTf_2)_3$ could be also recovered by similar procedure using $CHCl_3$/*n*-hexane (1:1, v/v) instead of $CHCl_3$ (recovery 90%).

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