Synthesis of Aliphatic Polyesters by Direct Polyesterification of Dicarboxylic Acids with Diols under Mild Conditions Catalyzed by Reusable Rare-Earth Triflate

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Received September 10, 2002
Revised Manuscript Received January 22, 2003

Introduction. Poly(alkylene succinate)s including poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS) are some of the most important biodegradable polyesters which may replace many conventional plastics in the near future because of their 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 200−250 °C under highly reduced pressure.[2] However, it was very difficult to prepare aliphatic polyesters with a high molecular weight by direct polycondensation because of the thermal degradation at high temperature and low hydrolytic stability in one step.[2a,b] Therefore, a tedious chain extension is needed using diisocyanates and diphenyl carbonates as the chain extenders at high temperature.[2b,c] Although a survey of new Lewis acids is urgently required,[3] 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.[3c] reported that the $HfCl_4(THF)_2$ complex more 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) for 24 h. We believed that it is still a challenging subject to seek other excellent catalysts for the aliphatic polyesters in order to achieve the one-step synthesis of aliphatic polyesters under milder conditions (lower temperature and short time). Polycondensations under mild conditions are very important from an environmental technology viewpoint. We were interested in lanthanide triflates for the following reasons: (1) they are insensitive to protic compounds, and it is well-known that rare-earth triflates catalyze some reactions even in water because of the high exchange constant with water and low hydrolysis constant;[4] (2) one advantage of the catalyst is that the catalyst can be quantitatively recovered after the reactions are completed and reused, which are suitable for the molecular design in "Green Polymer Chemistry".[5]Although it was reported that scandium trifluoromethanesulfonate [$Sc(OTf)_3$] catalyzed the reaction of alcohols with carboxylic anhydride[6] and activated esters[6,7] (mixed anhydride,[6] acylurea,[7] and *N*-hydroxysuccinimide[7]) at low temperature, we surprisingly found that $Sc(OTf)_3$ catalyzed direct esterification of aliphatic alcohol with carboxylic acid at room temperature.[8] In this communication, the direct polycondensation 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 was carried out at 35−180 °C to synthesize poly(alkylene succinate)s.

Results and Discussion. As a model reaction of the polyesterification, the direct esterification of equimolar amounts of acetic acid and ethanol was carried out in bulk using 1.0 mol % $Sc(OTf)_3$ at 27 °C for 5 h. The conversion determined by ^1H NMR was ca. 50% and leveled off for 48 h. In the same reaction at 50 °C for 2 h, the conversion was increased to 72% temporarily, but the conversion was decreased to ca. 50% by leaving the reaction mixture at 27 °C for 24 h. Using 2.0 equiv of acetic acid, the conversion was increased to 95% at 27 °C for 5 h and the conversion did not change, while the esterification scarcely occurs without $Sc(OTf)_3$ (Scheme 2). On the basis of the model reaction, we found that $Sc(OTf)_3$ catalyzed the direct esterification of carboxylic acids and alcohols at room temperature as a new finding.[8] Furthermore, it was revealed that the reaction includes the equilibrium state as the rate-determining step; i.e., reverse reaction hydrolysis also occurs so that the removal of the formed water is necessary for the polyesterification.

The melt (bulk) polycondensations of methylsuccinic acid (MSA) and EG ($n = 2$) were carried out under reduced pressure (3 mmHg) using various lanthanide triflates (runs 1−4 in Table 1). As PES and PBS have poor solubilities in organic solvents, we used methylsuccinic acid in order to investigate the number-averaged molecular weight (M_n) by SEC using THF as the eluent. In all runs except for yttrium triflate [$Y(OTf)_3$], white polymeric solids were obtained which were soluble in chloroform, tetrahydrofuran, and acetonitrile. Based on the size exclusion chromatography (SEC) measurements, the M_n's of the polymers calibrated with polystyrene standards were $(0.35-0.40) \times 10^4$, indicating that the polymerization system produced oligomers. These results coincided with those reported by Carothers et al.[2a] Their structures were determined by IR, ^1H NMR, and ^{13}C NMR spectra.[9] In the ^1H NMR spectra of the oligomers, a peak at 3.68, which could not be assigned to the corresponding polyester, i.e., poly(ethylene methylsuccinate), was unexpectedly observed (Supporting Information). These results revealed that not only esterification but also etherification as a side reaction (10−20%) occurred during the polycondensation of MSA and EG. Using 1,3-PD ($n = 3$), a similar etherification was observed under same conditions (9%, run 5), which was lower than that for EG (17%). The etherification breaks the stoichiometric control, being essential for the polycondensation, so that resulting polymers were cooligo(ester−ether)s. In the case of the polycondensation of MSA and 1,4-BD ($n = 4$), the 100% esterification proceeded to give poly(butylene methylsuccinate) with a M_n of 1.0×10^4 even at 80 °C for 24 h (run 6).[10] The results indicated that the ratio of esterification and etherification depends on the methylene chain length of the diol. Using dimethyl methylsuccinate (DMMS) as a monomer, the polycondensation hardly occurred, confirming that the polyesterification proceeds

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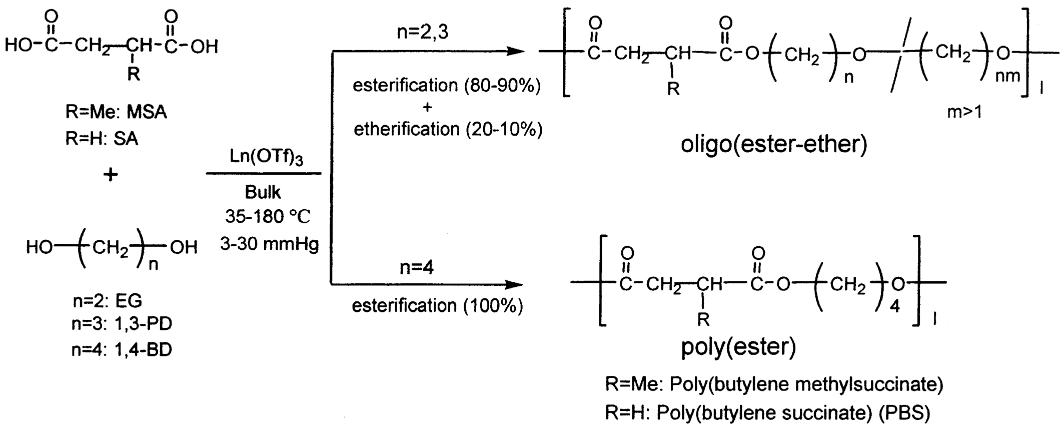
10.1021/ma021462v CCC: $25.00

Scheme 1. Direct Polyesterification of Dicarboxylic Acids with Diols



Scheme 2. Direct Esterification of Carboxylic Acids with Alcohols

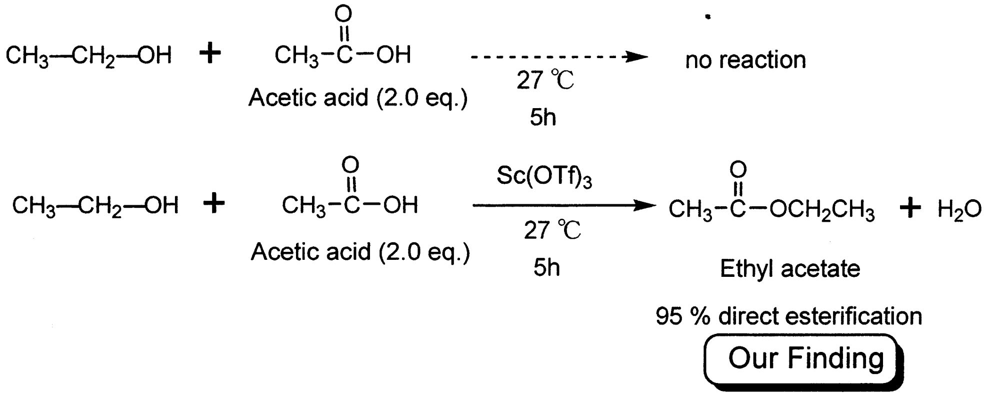


Table 1. Direct Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Lanthanide Triflates[a]

run	dicarboxylic acids	diols	catalyst (mol %)	temp (°C)	time (h)	yield (%)	M_n[b] × 10^{-4}	M_w/M_n[b]	[esterification]/[etherification][c]
1	MSA[d]	EG ($n = 2$)[e]	$Sc(OTf)_3$ (1.0)	80	24	43	0.40	1.3_9	83/17
2	MSA[d]	EG ($n = 2$)[e]	$Y(OTf)_3$ (1.0)	80	24	trace			
3	MSA[d]	EG ($n = 2$)[e]	$Sm(OTf)_3$ (1.0)	80	24	17	0.35	1.1_9	80/20
4	MSA[d]	EG ($n = 2$)[e]	$Yb(OTf)_3$ (1.0)	80	24	6	0.36	1.1_4	82/18
5	MSA[d]	1,3-PD ($n = 3$)[f]	$Sc(OTf)_3$ (1.0)	80	24	69	0.65	1.3_8	91/ 9
6	MSA[d]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (1.0)	80	24	57	1.00	1.2_8	100/0
7	DMMS[h]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (1.0)	80	24	0			
8	MSA[d]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (1.0)	35	75	94[i]	1.24	1.4_1	100/0
9	MSA[d]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (1.0)	80[j]	24	60	0.91	1.2_5	100/0
10	MSA[d]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (1.0)	120	5	61	1.13	1.4_0	100/0
11	SA[k]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (1.0)	120	5	85	1.13	1.7_2	100/0
12	SA[k]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (0.1)	160	10	83	2.09	1.4_9	100/0
13	SA[k]	1,4-BD ($n = 4$)[g]	blank	160	10	73	0.16	2.0_9	100/0
14	SA[k]	1,4-BD ($n = 4$)[g]	$Sc(OTf)_3$ (0.1)	180	10	85	3.07	1.4_3	100/0

[a] All runs are performed by bulk (melt) polycondensation ($[\text{catalyst}]_0$ = 1.0 or 0.1 mol %) under reduced pressure (3.0 mmHg). [b] Determined by SEC measurement in THF (runs 1−10) or $CHCl_3$ (runs 11−14) relative to poly(styrene). [c] Determined by ^1H NMR (in $CDCl_3$) intensity ratio. [d] Methylsuccinic acid. [e] Ethylene glycol. [f] 1,3-Propanediol. [g] 1,4-Butanediol. [h] Dimethyl methylsuccinate. [i] Without reprecipitation. [j] Reduced pressure, 30 mmHg. [k] Succinic acid.

via direct esterification predominantly. Interestingly, the direct polycondensation proceeded even at room temperature (35 °C) to afford poly(butylene methylsuccinate) with $M_n = 1.2 \times 10^4$ (94% yield, run 8). Moreover, the polycondensation was established under 30 mmHg ($M_n = 0.9 \times 10^4$, run 9). Polycondensation at the 120 °C could shorten the reaction time in which the polyester with a M_n of 1.13×10^4 and polydispersity index (M_w/M_n) of 1.4_0 was obtained for 5 h (run 10).

The $Sc(OTf)_3$-catalyzed polycondensations of SA and 1,4-BD were also performed to synthesize PBS, and we investigated influence of temperature, time, and concentration of the catalyst on the M_n's. For the polymerization at 120 °C above the T_m, melt polycondensation using the 1.0 mol % catalyst could be achieved to give PBS with a M_n of 1.13×10^4 (85% yield, run 11). $Sc(OTf)_3$ catalyzes the polycondensation of succinic acid with 1,4-butanediol at a lower temperature compared with those previously reported.[2,3] The temperature mainly affected the M_n for the higher molecular weight polyester. The polycondensation at 160 and 180 °C for 10 h gave PBS with an M_n of 2.09×10^4 ($M_w/M_n = 1.4_9$) and 3.07×10^4 ($M_w/M_n = 1.4_3$), respectively, even in the presence of 0.1 mol % catalyst. The catalyst was easily recovered by reprecipitation and successive extraction with water (95% recovery)[11] and could be reused for the polyester synthesis. Direct polycondensation of SA and 1,4-BD using the recovered catalyst gave PBS with a M_n of 1.43×10^4 ($M_w/M_n = 1.4_9$, 86% yield).

In the present communication, we describe the direct esterification of a carboxylic acid and alcohol catalyzed by Sc(OTf)$_3$ and reported that this breakthrough made it possible to synthesize aliphatic polyesters without transesterification under milder conditions compared to conventional methods. Owing to the polycondensation, it was revealed that Sc(OTf)$_3$ catalyzes not only the esterification but also etherification as a side reaction, which depends on the chain length (methylene number) of the diols. The catalyst make it possible to prepare biodegradable polyesters, PBS having an M_n of $>1.0 \times 10^4$ even at 35 °C. The development of polycondensations at lower temperature is strongly desired for environmentally friendly processes. The catalyst could be recycled for the polyester synthesis. This procedure would be suitable for molecular and material design taking the "Green Polymer Chemistry" concept[5] into consideration.

Acknowledgment. Financial support from Nagoya Institute of Technology, research promotion program (to A.T.), and Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Development Scientific Research, No. 13750816) (to A.T.) is gratefully acknowledged. The authors also acknowledge Dr. Keigo Aoi and Dr. Nobuyoshi Nomura (Nagoya University) for their permit to use the SEC system using CHCl$_3$ solvent.

Supporting Information Available: ^{1}H NMR spectra of oligo(ester−ether) and poly(butylene methylsuccinate). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) 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.

(9) For poly(ethylene methylsuccinate) (43% yield, run 1 in Table 1). ^{1}H NMR (200 MHz, CDCl$_3$, δ, ppm): 1.21−1.25 ($\mathrm{CHC}H_3$), 2.41−2.50 and 2.70−2.83 ($\mathrm{CHC}H_2$), 2.92−2.95 ($\mathrm{C}H\mathrm{CH}_2$), 3.68 ($\mathrm{CH_2C}H_2\mathrm{OC}H_2\mathrm{CH}_2$), 4.29 ($\mathrm{COOC}H_2$). ^{13}C NMR (50 MHz, CDCl$_3$, δ, ppm): 16.9 ($\mathrm{CH}C\mathrm{H}_3$), 35.6 ($\mathrm{CH}C\mathrm{H}_2$), 37.2 ($C\mathrm{HCH}_2$), 62.2 and 62.3 (COOCH_2), 68.9 ($\mathrm{CH_2}C\mathrm{H_2O}C\mathrm{H_2CH_2}$), 171.4 and 174.8 ($\mathrm{COO}C\mathrm{H}_2$). IR (KBr disk, cm^{-1}): 2975 ($\nu_{\mathrm{C-H}}$), 1738 [$\nu_{\mathrm{C=O}}$(ester)], 1458 ($\delta_{\mathrm{C-H}}$), 1279 and 1164 [$\nu_{\mathrm{C-O}}$(ester)].

(10) For poly(butylene methylsuccinate): A typical polycondensation procedure is as follows. In a three-necked tube, SA (7.0 mmol), 1,4-BD (7.0 mmol), and Sc(OTf)$_3$ were dissolved in acetonitrile (1.0 mL) and stirred at 40 °C for 2 h. After removing the acetonitrile at 40 °C by vacuum pump, the reaction temperature was gradually increased to 180 °C and kept for 10 h. The produced water was removed by evaporation under reduced pressure (3.0 mmHg). After the reaction, the polymeric material was purified by repeated reprecipitation from CHCl$_3$ into diethyl ether to afford a white powder (85% yield, run 11 in Table 1). ^{1}H NMR (200 MHz, CDCl$_3$, δ, ppm): 1.20−1.24 ($\mathrm{CHC}H_3$), 1.69−1.71 ($\mathrm{OCH_2C}H_2$), 2.34−2.45 and 2.67−2.82 ($\mathrm{CHC}H_2$), 2.85−2.96 ($\mathrm{C}H\mathrm{CH}_2$), 4.11 ($\mathrm{COOC}H_2$). ^{13}C NMR (50 MHz, CDCl$_3$, δ, ppm): 17.0 ($\mathrm{CH}C\mathrm{H}_3$), 25.2 ($\mathrm{OCH_2}C\mathrm{H_2}$), 35.8 ($\mathrm{CH}C\mathrm{H}_2$), 37.5 ($C\mathrm{HCH}_2$), 171.8 and 175.2 ($\mathrm{COO}C\mathrm{H}_2$). IR (KBr disk, cm^{-1}): 2965 ($\nu_{\mathrm{C-H}}$), 1734 [$\nu_{\mathrm{C=O}}$(ester)], 1464 ($\delta_{\mathrm{C-H}}$), 1277 and 1169 [$\nu_{\mathrm{C-O}}$(ester)].

(11) Procedure of recovery of the catalyst is as follows. The supernatant was dried and resolved in CHCl$_3$ (3 mL) and washed with water (5 mL). The aqueous layer was evaporated to give recovered Sc(OTf)$_3$ (95% yield). Sm(OTf)$_3$ could be also recovered by reprecipitation and successive extraction with water (recovery 78%).

MA021462V