Room-Temperature Polycondensation of Dicarboxylic Acids and Diols Catalyzed by Water-Stable Lewis Acids

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ABSTRACT: Room-temperature polycondensations of methylsuccinic acid (MSA) (at 35 °C), bromosuccinic acid (BSA), 2-bromoadipic acid (BAA) (at 40 °C), and citraconic acid (CA) (at 60 °C) with diols containing 1,3-propanediol (1,3-PD) and 1,4-butanediol (1,4-BD) were performed under reduced pressure (0.3–30 mmHg) using scandium trifluoromethanesulfonate [Sc(OTf)$_3$], scandium trifluoromethanesulfonimide [Sc(NTf$_2$)$_3$], and polymer-supported scandium trifluoromethanesulfonate (PS–Sc) to give poly(alkylene alkanoate)s with $M_n = 0.67 \times 10^4 - 1.41 \times 10^4$ ($M_w/M_n = 1.4$–2.1) with quantitative yields. The catalysts are recovered quantitatively and reused. Room-temperature polycondensation made it possible to use thermally unstable monomers containing carbon-carbon double bond and bromo functionality. The atom-transfer radical polymerization (ATRP) of methyl methacrylate (MMA) ([M]$_0$/[I]$_0 = 10$) using poly(butylene succinate-co-butylene bromoadipate) [poly(BS-co-BBA)] ($M_n = 0.75 \times 10^4$, $M_w/M_n = 2.0$) as the macroinitiator and complex of CuBr and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the catalyst was carried out in anisole at 80 °C for 10 h under nitrogen atmosphere to give polyester having PMMA side chains [$M_n = 2.01 \times 10^4$ and $M_w/M_n = 1.9$, 65% yield].   [DOI 10.1295/polymj.37.946]
KEY WORDS   Room-Temperature Polycondensation / Scandium Trifluoromethanesulfonate [Sc(OTf)$_3$] / Scandium Trifluoromethanesulfonimide [Sc(NTf$_2$)$_3$] / Polymer-Supported Scandium Trifluoromethanesulfonate (PS–Sc) / Atom-Transfer Radical Polymerization (ATRP) / Citraconic Acid (CA) / Bromosuccinic Acid (BSA) /

Remarkable attention is paid to polymers that have potentials as biomaterials and environmentally-benign materials. Particularly, aliphatic polyesters including poly(ethylene succinate) (PES) and poly(butylene succinate) (PBS) would replace many conventional plastics in near future because of their biodegradability, acceptable mechanical strength, and comparable softening temperature to low density polyethylene and polystyrene.[1] However, the syntheses require polycondensations of dicarboxylic acids and diols under severe conditions (>250 °C under highly reduced pressure).[2] Although some researchers reported that *in situ* enhancement of monomer (carboxylic acid) reactivity using active reagents made it possible to synthesize polyesters at/near room temperature,[3] recent concern toward environmental problems prompted us to explore "ideal polycondensation system," taking (1) low temperature (2) avoiding organic solvent (3) atomic economy (4) lack of catalyst toxicity after use (5) catalyst recyclability and reuse. While direct polycondensation is considered to be the best way from these viewpoints, a survey of new Lewis acids had been difficult,[4] because most Lewis acids are decomposed or deactivated by protic substances including carboxylic acids, alcohols, and water, which

is not suitable for dehydration polycondensations. Applications of aliphatic polyesters will be further broadened when functional groups are incorporated into the polymer backbones. Room-temperature direct polycondensation promises not only saving heat energy but also extension of the range of monomers having chirality, functionality, and biological activity, because these monomers are labile under severe conditions.

As the catalyst, we focused on scandium catalysts because they are insensitive to protic compounds and they catalyze some reactions even in water because of the low hydrolysis constant[5] and high exchange rate constant for substitution of inner-sphere water ligand,[5b] the catalysts can be quantitatively recovered after reactions and reused. As a preliminary result, we already reported room-temperature direct polycondensation of dicarboxylic acids with diols catalyzed by rare-earth trifluoromethanesulfonate[6a] and trifluoromethanesulfonimide[6d] to afford aliphatic polyesters with M_n of $>1.0 \times 10^4$.

In this paper, we describe one-step syntheses of aliphatic polyesters at/near room temperature, "room-temperature polycondensation[7]" using water-stable catalysts, scandium trifluoromethanesulfonate

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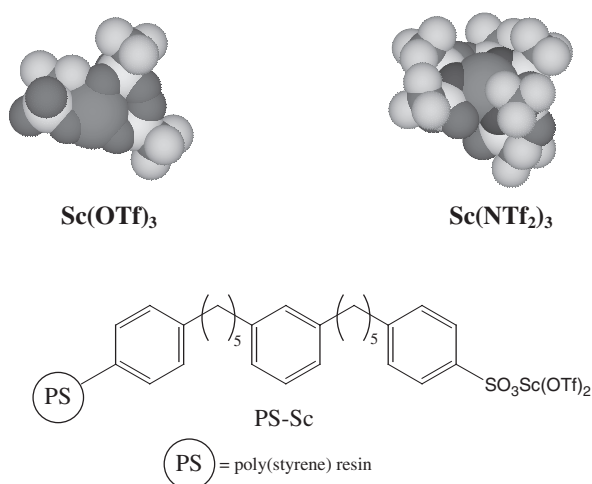
Figure 1. Molecular structure of scandium trifluoromethane-sulfonate [Sc(OTf)$_3$], scandium trifluoromethanesulfonimide [Sc-(NTf$_2$)$_3$], and polymer-supported scandium trifluoromethanesulfonate (PS–Sc).

[Sc(OTf)$_3$], scandium trifluoromethanesulfonimide [Sc(NTf$_2$)$_3$] (Figure 1). The solubility and stability in water realized recovery by extraction with water and subsequent reuse. Moreover procedure for the recovery was simplified by polymer-supported scandium trifluoromethanesulfonate (PS–Sc). Room-temperature polycondensation of dicarboxylic acid containing C=C double bond or bromo functionality produced polyesters having reacting groups. Room-temperature polycondensation combines with atom transfer radical polymerization (ATRP) using poly(butylene bromosuccinate) (PBBS) and poly(butylene succinate-*co*-butylene bromoadipate) [poly(BS-*co*-BBA)] as the macroinitiators to synthesize polyesters having poly-(methyl methacrylate) (PMMA) side chains *via* grafting from techniques (Scheme 3).

EXPERIMENTAL

Materials

Scandium triacetate [Sc(OAc)$_3$] was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Bromosuccinic acid (BSA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), trifluoromethanesulfonimide [HN(CF$_3$SO$_2$)$_2$], polymer-supported scandium trifluoromethanesulfonate (PS–Sc) (scandium content: 0.64 mmol/g), methylsuccinic acid (MSA) were purchased from Sigma Aldrich. Sc(OTf)$_3$ and citraconic acid (CA) were obtained from Tokyo Kasei Co. (Tokyo, Japan) and Wako Pure Chemical Co. (Osaka, Japan), respectively. Succinic acid (SA), methyl methacrylate (MMA), cuprous (I) bromide (CuBr), 1,3-PD, and 1,4-BD were purchased from Nacalai Tesque (Kyoto, Japan). 2-Bromoadipic acid (BAA) was prepared in our laboratory according to Starostin's re-

port.[8] Anisole, chloroform, diethyl ether, methanol, ethanol, hexane, ethyl acetate, acetic acid, and water used were purified by distillation before use.

Preparation of Sc(NTf$_2$)$_3$

The preparation was carried out according to literature.[9] In a flask equipped with reflux condenser, Sc(OAc)$_3$ (1.0 g, 4.5 mmol), HNTf$_2$ (3.3 g, 13.6 mmol), and 24 mL of water were taken. The mixture was stirred at 100 °C for 5 h and evaporated to give white solid. The reaction was monitored by TLC measurement (R$_f$ = 0.06 in methanol) and the structure was confirmed by ^{13}C NMR measurement. ^{13}C NMR (50 MHz, CDCl$_3$, δ, ppm) for Sc(NTf$_2$)·CH$_3$COOH: 21.1 (*C*H$_3$CO), 119.5 (SO$_2$*C*F$_3$, q, J_{CF} = 318 Hz), 178.3 (CH$_3$*C*O).

Model Reaction

In a flask, esterification of acetic acid (1.44 g, 24 mmol) and ethanol (0.55 g, 12 mmol) are catalyzed by PS–Sc (0.38 g, 0.24 mmol) in the absence and presence of methyl acetate (1.79 g, 24 mmol). The reaction condition was at 27 °C for 7 h. The conversion was calculated by ^{1}H NMR intensity ratio.

Room-Temperature Polycondensation of MSA with Diols

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$_2$)$_3$ (0.3 mol %) were mixed and stirred at room temperature for 1 h. 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, yield of the polyester was calculated by subtraction weight of the catalyst from the isolated material (96% yield, run 11 in Table I). After reprecipitation using CHCl$_3$ and diethyl ether, the yield was 85%. ^{1}H NMR (200 MHz, CDCl$_3$, δ, ppm): 1.20–1.24 (CH-C*H*$_3$), 1.69–1.71 (OCH$_2$C*H*$_2$), 2.34–2.45 and 2.67–2.82 (CHC*H*$_2$), 2.85–2.96 (C*H*CH$_2$), 4.11 (COOC*H*$_2$). ^{13}C NMR (50 MHz, CDCl$_3$, δ, ppm): 17.0 (CH*C*H$_3$), 25.2 (OCH$_2$*C*H$_2$), 35.8 (CH*C*H$_2$), 37.5 (*C*HCH$_2$), 64.1 (O*C*H$_2$CH$_2$), 171.8 and 175.2 (*C*OOCH$_2$). 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)].

Catalyst Recovery

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 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%). For recovery of PS–Sc, the reaction mixture was dissolved in ethyl acetate and simply filtered (recovery >99%).

Polycondensation of Bromosuccinic acid with 1,4-BD

Polycondensation of BSA and 1,4-BD was carried out in a similar manner of that for polycondensation of MSA with 1,4-BD. ^{1}H NMR (200 MHz, CDCl$_3$, δ, ppm): 1.71–1.80 (OCH$_2$CH_2), 2.93–3.05 and 3.22–3.35 (CH_2CHBr), 4.16 (CH$_2$COOCH_2), 4.23 (CHBr-COOCH_2). ^{13}C NMR (50 MHz, CDCl$_3$, δ, ppm): 25.0 (OCH$_2$CH$_2$), 38.0 (CH$_2$CHBr), 39.6 (CH$_2$CHBr), 64.5 and 65.5 (OCH$_2$CH$_2$), 169.0 and 169.6 (COOCH$_2$). IR (KBr disk, cm^{-1}): 2960 (ν_{C-H}), 1737 [$\nu_{C=O}$(ester)], 1467 and 1395 (δ_{C-H}), 1334 (δ_{C-Br}), 1260 and 1164 [ν_{C-O}(ester)].

Grafting of MMA from Polyester Containing Pendant Bromo Functionality Using ATRP Technique

A typical ATRP procedure is as follows. Poly(BS-*co*-BBA) (0.2 mmol of bromo content), MMA (2.0 mmol), CuBr (0.2 mmol), 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA) (0.2 mmol) and 6 mL of anisole were weighed into a glass tube equipped with stopcock under nitrogen atmosphere. The solvent was frozen by liquid nitrogen, the stopcock was opened to vacuum and kept for 10 min in order to remove the air completely. The tube was sealed under reduced pressure and placed in an oil bath kept at 80 °C for 10 h. After the reaction, the contents were dropped in excess methanol. The polymeric material was purified by reprecipitation using chloroform and methanol, the yield was 65% (trunk base). ^{1}H NMR (200 MHz, CDCl$_3$, δ, ppm): 0.85, 1.03, 1.26 (CCH_3), 1.32–2.21 [CH_2 in MMA, OCH$_2$CH_2, COCH$_2$CH_2CH_2CH-(PMMA)CO, COCH$_2$CH_2CH_2CHBrCO], 2.21–2.44 [COCH_2CH$_2$CH$_2$CH(PMMA)CO, COCH_2CH$_2$CH$_2$-CHBrCO], 2.63 (COCH_2CH_2CO), 3.61 (COOCH_3), 4.00–4.28 (OCH_2CH$_2$, COCH$_2$CH$_2$CH$_2$CHBrCO). IR (KBr disk, cm^{-1}): 2953 (ν_{C-H}), 1732 [$\nu_{C=O}$(ester)], 1450 and 1392 (δ_{C-H}), 1355 (δ_{C-Br}), 1243 and 1156 [ν_{C-O}(ester)].

Measurements

FT/IR spectra were recorded in KBr disks using a JASCO FT/IR-430 spectrometer. ^{1}H and ^{13}C NMR spectra were measured at 27 °C using a Bruker DPX200 spectrometer (200 MHz for ^{1}H NMR). All chemical shifts were expressed as δ downfield from tetramethylsilane (TMS). Number average molecular weights (M_n) and the polydispersity indexes (M_w/M_n) of polymers were estimated by size exclusion chromatography (SEC) calibrated with polystyrene standards using a pump system of Tosoh DP8020 with a RI (Tosoh RI-8020) detector and Tosoh G2000,

3000, 4000, and 5000-HXL columns (eluent, chloroform; flow rate, 1.0 mL/min; temperature, 40 °C).

RESULTS AND DISCUSSION

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 % of Sc(OTf)$_3$, Sc(NTf$_2$)$_3$ and PS–Sc at 27 °C for 7 h without removing water. The conversions determined by ^{1}H NMR were 89, 72, and 41% 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 ^{1}H NMR measurement. On the basis of the model reaction, we confirmed that these 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 (Scheme 1). Surprisingly, ethanol reacted with acetic acid chemoselectively in the presence of Sc-(OTf)$_3$ (90%), Sc[(NTf$_2$)$_2$]$_3$ (92%) and PS–Sc (97%), respectively, in which PS–Sc showed the highest selectivity. From the results, we could expect the polycondensation proceed minimizing transesterification.

Bulk polycondensations of methylsuccinic acid (MSA) and diols, 1,4-BD (n = 4) and 1,3-PD (n = 3), were carried out under reduced pressure (0.3–30 mmHg) using Sc(OTf)$_3$ at 35 °C (Scheme 2 and Table I). The number-average molecular weights (M_ns) were estimated by size exclusion chromatography (SEC) using CHCl$_3$ as the eluent (polystyrene standards). In all runs, white 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) (PBMS) with M_n of 1.2×10^4 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 Brønsted acid (run 6), the M_n was quite low ($M_n = 0.3 \times 10^4$) compared with that catalyzed by Sc(OTf)$_3$. Surprisingly, the polycondensation using 1.0 mol % Sc(OTf)$_3$ was much superior to that using same amount of HfCl$_4$(THF)$_2$ (runs 3 and 7). As most Lewis acids are sensitive to protic substances, the catalytic activities are lowered during dehydration polycondensation. It seems that the Sc(OTf)$_3$ catalyzed the direct poly-

Room-Temperature Polycondensation Catalyzed by Water-Stable Lewis Acids

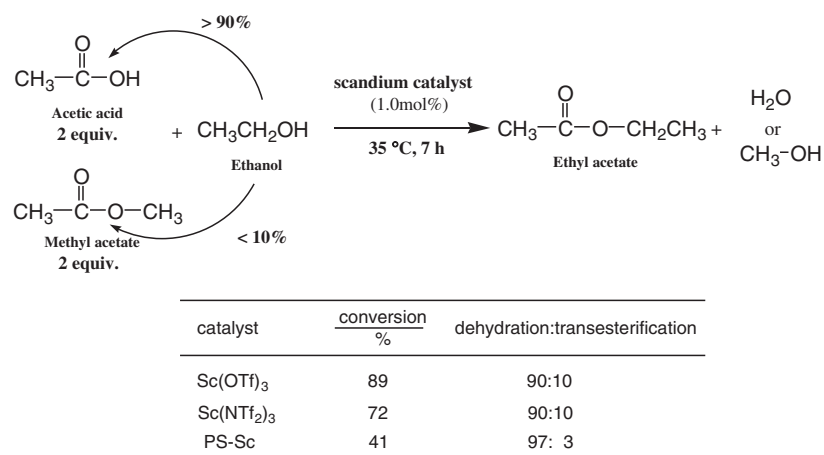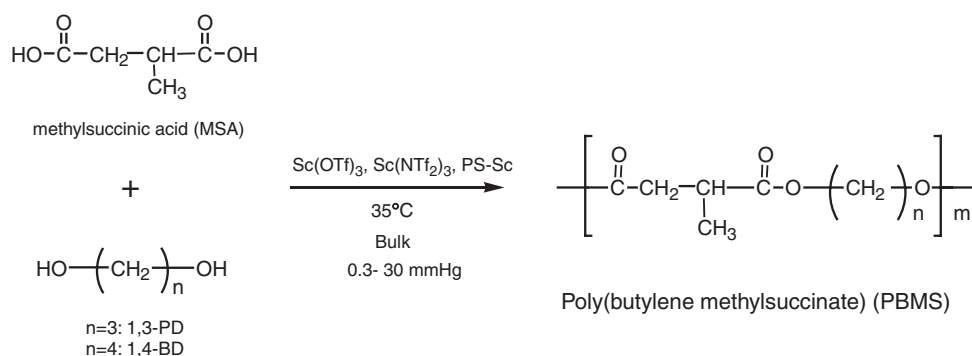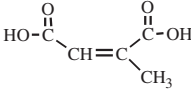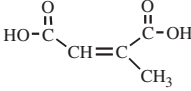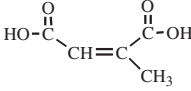| catalyst	conversion %	dehydration:transesterification
Sc(OTf)$_3$	89	90:10
Sc(NTf$_2$)$_3$	72	90:10
PS-Sc	41	97: 3

Scheme 1. Model reaction of carboxylic acid and alcohol in presence of carboxylic acid methyl ester.

Scheme 2. Room-temperature direct polycondensation of dicarboxylic acids with diols.

Table I. 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] $\times 10^{-4}$	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	SA[e]	Sc(OTf)$_3$ (1.0)	120	5	85[f]	1.13	1.7
9	SA[e]	Sc(OTf)$_3$ (0.1)	160	10	83[f]	2.09	1.5
10	SA[e]	Sc(OTf)$_3$ (0.1)	180	10	85[f]	3.07	1.4
11	MSA[c]	Sc(NTf$_2$)$_3$ (0.3)	35	90	96[d](85%[f])	1.22	1.5
12	MSA[c]	Sc(NTf$_2$)$_3$ (0.5)	35	60	97[d]	1.00	1.7
13	MSA[c]	Sc(NTf$_2$)$_3$ (1.0)	35	70	92[d]	0.90	1.5
14	MSA[c]	PS–Sc (1.0)	80	24	90[d]	0.34	1.9
15	MSA[c]	PS–Sc (1.0)	120	72	73[d]	1.04	1.5
16	MSA[c]	Sc(OTf)$_3$[g] (1.4)	35	104	93[d]	0.68	1.4
17	MSA[c]	Sc(NTf$_2$)$_3$[g] (0.3)	35	110	98[d]	0.93	1.5
18	MSA[c]	PS–Sc[g] (1.0)	120	72	70[d]	0.68	1.5

[a]All runs are performed by bulk (melt) polycondensation under reduced pressure (0.3–30 mmHg). [b]Determined by SEC measurement in CHCl$_3$ relative to poly(styrene). [c]Methylsuccinic acid. [d]Without reprecipitation. [e]Succinic acid. [f]After reprecipitation using CHCl$_3$ and hexane. [g]Recovered catalyst.

Table II. Direct Polycondensation of Citraconic Acid (CA) and 1,4-BD[a]

Run	Dicarboxylic Acid	Catalyst (mol %)	Temp. (°C)	Time (h)	Yield (%)	$M_n{}^b \times 10^{-4}$	$M_w/M_n{}^b$	isomerizat ion[c](%)
1	HO-C(=O)-CH=C(CH₃)-C(=O)-OH	none	160	50	gelation	0.38[d]	1.4[d]	12[e]
2	HO-C(=O)-CH=C(CH₃)-C(=O)-OH	Sc(OTf)$_3$ (1.0)	60	50	68	1.41	1.9	0
3	HO-C(=O)-CH=C(CH₃)-C(=O)-OH	TfOH (1.0)	60	50	89	0.26	1.5	0

[a]All runs are performed by bulk (melt) polycondensation under reduced pressure (0.3–30 mmHg). [b]Determined by SEC measurement in CHCl$_3$ relative to poly(styrene). [c]Determined by ^{1}H NMR in CDCl$_3$. [d]Soluble part in THF. [e]Soluble part in CDCl$_3$.

condensation effectively because of high activity, resistance to water, leading to high turnover frequency (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. On the other hand, at 80 °C, etherification (9%) as well as esterification (91%) occurred to give oligo(ester-ether) [69% yield (after reprecipitation), $M_n = 0.65 \times 10^4$, $M_n/M_n = 1.4$].[6a] The improved chemoselectivity was ascribed to the lower condensation temperature.

The Sc(OTf)$_3$ catalyzed-polycondensations of SA and 1,4-BD were also performed to synthesize PBS (runs 8–10). For the polymerization at 120 °C above the T_m, melt polycondensation using 1.0 mol % catalyst could be achieved to give PBS with a M_n of 1.13×10^4 (85% yield, run 8). Sc(OTf)$_3$ catalyzes the polycondensation of succinic acid with 1,4-butanediol at a lower temperature compared with those previously reported.[2,4] The temperature was important for synthesis of higher molecular weight polyester. The polycondensation at 160 and 180 °C for 10 h gave PBS with 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 (runs 9 and 10).

Scandium trifluoromethanesulfonimide [Sc(NTf$_2$)$_3$] is also known to be air stable and powerful Lewis acid,[9] because it has higher fluorine content (Figure 1). In order 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 (run 11–13). 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 higher than that using same amount of Sc(OTf)$_3$ (0.59×10^4, run 1). Using the

SEC data (M_n), calculated TON in this system is 160 (mol/mol), which is superior to that using 0.3 mol % of Sc(OTf)$_3$ (TON: 150). 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.

Sc(OTf)$_3$ and Sc(NTf$_2$)$_3$ used in this study were 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$_2$)$_3$]. 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 16) and M_n of 0.93×10^4 for 110 h ($M_w/M_n = 1.5$, 98% yield, run 17), respectively.

Polymer-supported scandium trifluoromethanesulfonate (PS–Sc) (Figure 1) is known to show high activity in water and can be easily recovered and reused.[10] Polycondensation of MSA and 1,4-BD at 120 °C occurred and afforded PBMS with M_n of 1.04×10^4 ($M_w/M_n = 1.5$) for 72 h (73% yield, run 15 in Table I), while the polycondensation at 80 °C gave the polyester with M_n of 0.34×10^4. PS–Sc was actually recovered after the polycondensation by simple filtration and reused. The recovery was quantitative (>99%) and remarkable loss of activity in the polycondensation was not confirmed. 70% yield was attained using 1.0% of the recovered PS–Sc (run 18), although a slight decrease in the M_n (0.68×10^4) was confirmed.
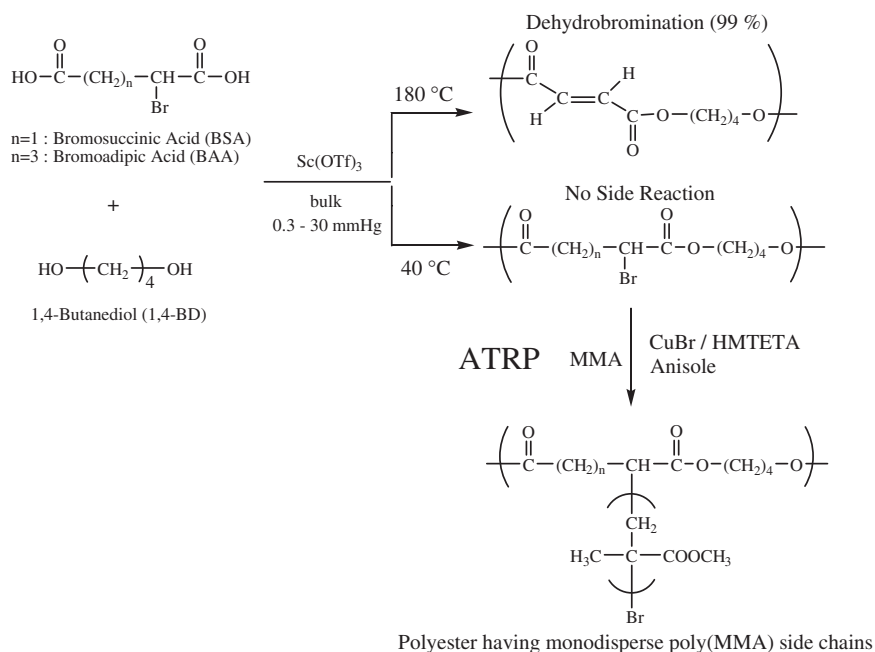
Room-Temperature Polycondensation of Dicarboxylic Acid Having Functionality

As another example to illustrate the mildness of the polycondensation, we present the polycondensation using monomer containing carbon-carbon double bond, citraconic acid (Table II). The structure was

Table III. Direct Polycondensation of Dicarboxylic Acid Having Bromo Functionality and 1,4-BD[a]

Run	Dicarboxylic Acid	Catalyst (mol %)	Temp. (°C)	Time (h)	Yield[b] (%)	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	Dehydro-bromination[d](%)
1	BSA[e]	Sc(OTf)$_3$ (1.4)	180	24	49	1.43	2.9	99
2	BSA[e]	Sc(OTf)$_3$ (1.0)	80	50	66	0.40	1.6	3
3	BSA[e]	Sc(OTf)$_3$ (1.4)	40	70	84	0.67	1.8	0
4	BSA[e]	Sc(OTf)$_3$ (0.7)	40	70	87	0.66	1.7	0
5	BSA[e]	none	40	70	no polymerization	—	—	—
6	BAA[f]	Sc(OTf)$_3$ (0.7)	40	90	78	0.85	2.1	0
7	SA + BAA[g]	Sc(OTf)$_3$ (0.1)	100	50	87	0.75	2.0	0

[a]All runs are performed by bulk (melt) polycondensation under reduced pressure (0.3–30 mmHg). [b]After reprecipitation using CHCl$_3$/diethyl ether. [c]Determined by SEC measurement in CHCl$_3$ relative to poly(styrene). [d]Determined by ^{1}H NMR in CDCl$_3$. [e]Bromosuccinic acid. [f]2-Bromoadipinic acid. [g]Ternary copolycondensation of SA and BBA ([SA]$_0$/[BBA]$_0$ = 4/1) with 1,4-BD.

Scheme 3. Synthesis of polyester having monodisperse poly(methyl methacrylate) side chains by combination of room-temperature polycondensation with ATRP.

confirmed by ^{1}H NMR and the peak assignment was established by comparison with that reported in previous report.[11] The polycondensation with 1,4-BD was carried out at 60 °C for 120 h using 1.0 mol % of Sc(OTf)$_3$. While the polycondensation at 160 °C without catalyst would result in isomerizations (*Z*- to *E*- and citraconic acid to itaconic acid) and gelation,[11] linear polyester ($M_n = 1.41 \times 10^4$) was obtained in this system. In the ^{1}H NMR spectrum, any peaks ascribed to isomerizations (*E*-configuration: 2.29 and 6.81 ppm; itaconic acid unit: 3.37, 5.77, and 6.36 ppm) and gelations (2.5–3.0 ppm) were not observed.

Room-temperature polycondensations of bromosuccinic acid (BSA) (at 40 °C) and 1,4-butanediol (1,4-BD) were performed under reduced pressure (0.3–30 mmHg) using Sc(OTf)$_3$ to give PBBS with $M_n = 0.67 \times 10^4$ ($M_w/M_n = 1.7_7$, 84% yield) (run 3 in Table III). At 180 °C, >99% dehydrobromination oc-

curred and the obtained polyester hardly contains the bromo functionality (run 1). At 80 °C, the dehydrobromination was suppressed within 3% although the M_n is lower (0.4×10^4). As we confirmed no polycondensation in the absence of Sc(OTf)$_3$, this polycondensation system is suitable for polycondensation of dicarboxylic acid having bromo functionality as well as carbon-carbon double bond. Polycondensation of BBA also afforded the expected polyester without dehydrobromination (run 6). Ternary copolycondensation of SA and BAA with 1,4-BD was carried out in order to control bromo content ([SA]$_0$/[BAA]$_0$ = 4/1). The resulting polyester was characterized by IR and NMR measurements. From the ^{1}H NMR relative peak intensity ratio, the molar ratio of [SA]/[BAA] in the copolyester was 4/1, which coincided with the feed the ratio ([SA]$_0$/[BAA]$_0$).
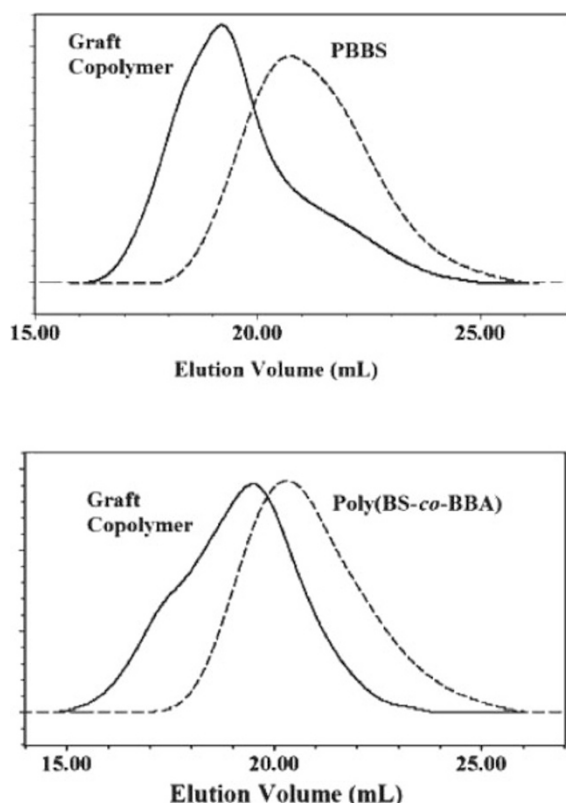
Figure 2. SEC traces of graft copolymers prepared by grafting MMA from PBBS (top) and poly(BS-*co*-BAA) (bottom) as macroinitiators.

Grafting of MMA from Polyester Containing Pendant Bromo Functionality Using ATRP Technique

As shown in Scheme 3, the ATRP of MMA ($[M]_0/[I]_0 = 10$) using PBBS ($M_n = 0.67 \times 10^4$, $M_w/M_n = 1.8$, run 3 in Table III) as the macroinitiator and complex of CuBr and HMTETA[12a] as the catalyst was carried out in anisole at $60\,^\circ C$ for $10\,h$ under nitrogen atmosphere to give polyester having PMMA side chains [$M_n = 1.42 \times 10^4$ and $M_w/M_n = 2.0$, 55% yield (trunk base)]. The structure was confirmed by IR and ^1H NMR measurements. The SEC trace shows an expected shift to higher molecular weight region compared with parent polyester having pendant active bromo groups as shown in Figure 2 (top). These results revealed that PBBS prepared by room-temperature polycondensation acted as a macroinitiator. Using poly(BS-*co*-BAA) as the macroinitiator, ATRP of MMA also occurred (at $80\,^\circ C$ for $10\,h$). The SEC trace shifted to high molecular region after ATRP and the peak corresponding to parent copolyester was not confirmed (Figure 2, bottom). The initiator efficiency and DP of MMA side chain were calculated to be 43% and 16 (68% conversion), respectively, from the ^1H NMR analysis.

In this paper, we demonstrated the room-temperature direct esterification of a carboxylic acid and alcohol catalyzed by Sc(OTf)$_3$, Sc(NTf$_2$)$_3$, and polymer-

supported scandium catalyst (PS–Sc). This breakthrough made it possible to synthesize aliphatic polyesters ($M_n > 1.0 \times 10^4$) by room-temperature polycondensation. All the catalysts could be recycled for the polyester synthesis. The development of polycondensations at lower temperature is extremely effective for not only for environmentally friendly processes but also for advanced material design using monomers having chirality, functionality, and biological activity.

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