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Dual Catalytic System for Combination of Chain and Step Polymerizations: Ring-Opening Polymerization of ϵ-Caprolactone and Successive Dehydration Polycondensation with Dicarboxylic Acid Using the Same Catalyst

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ABSTRACT: We demonstrate a new system for the combination of chain and step polymerizations in which scandium trifluoromethanesulfonate [Sc(OTf)$_3$] catalyzes both polymerization modes. Ring-opening polymerization of ϵ-caprolactone initiated from a diol was carried out in acetonitrile at 45 °C (M_n =1.2 × 10^3−3.6 × 10^3, M_w/M_n = 1.3). After removing acetonitrile under reduced pressure, bulk polycondensation with methylsuccinic acid was performed at 100 °C for 15 h to give the polyester in an excellent yield (92−94%): M_n and M_w/M_n were respectively 1.4 × 10^4 and 1.9. To check whether transesterification occurred or not during the two polymerizations, ^{13}C NMR measurement was carried out in CDCl$_3$. Suppressed transesterification was also supported from reductive cleavage of polyester containing disulfide linkage synthesized using ring-opening copolymerization of ϵ-caprolactone and successive polycondensation with 3,3′-dithiopropionic acid. Reversibly, chemoselective polycondensation of dicarboxylic acid containing a hydroxyl group and a diol and subsequent ring-opening copolymerization initiated from the pendent hydroxyl groups were also demonstrated using Sc(OTf)$_3$ as the dual catalyst.

Introduction

The control of polymer properties through the synthesis of block copolymers and complex macromolecular architectures is central to many areas of research and advanced technological application.[1,2] As a synthetic strategy, the utility of the double-headed initiator is effective for combination for chain polymerizations of two kinds. It was used for cationic/radical,[3] anionic/radical,[4] and radical/ring-opening[5] polymerizations to synthesize block copolymers. The combination of chain and step polymerization is expected to expand the range of polymer combinations including polyester, polyamide, and poly(phenylenevinylene) that are generally produced using step polymerization. Nevertheless, to date, few reports have described such a combination.[6] Such approaches are actually limited by the lack of a versatile catalyst that catalyzes both chain and step polymerizations: two catalysts must be used for each polymerization.[6] Kobayashi et al. used lipases, *Candida antarctica* and *Pseudomonas cepacia*, as catalysts for concurrent ring-opening polymerization of macrolides (12-, 13-, and 16-membered lactones) and ternary polycondensation with glycols and dicarboxylic acid divinyl esters.[7] The impetus for research of aliphatic polyesters over the past 20 years has centered on the need for efficient synthesis of functional polyesters because they are of interest to polymer science and biomedical fields because they are known as the most promising category of biodegradable polymers and environmentally benign materials.[8] However, polycondensation of diols and dicarboxylic acids has generally been performed at >250 °C to obtain the polyesters,[9] which makes their combination with chain polymerizations more difficult. Recently, we reported room temperature direct polycondensation of diols and dicarboxylic acids that had been catalyzed using scandium trifluoromethanesulfonate [Sc(OTf)$_3$] to afford aliphatic polyesters with M_n of >1.0 × 10^4.[10a,b] We also demonstrated that polycondensation proceeds with suppression of transesterification because of the mild reaction condition[10a] and chemoselectivity of the catalyst.[10b] This polycondensation system, under mild conditions, has enabled the use of thermally unstable monomers containing a carbon−carbon double bond[10c] as well as bromo[10c] and hydroxyl[10d] functionalities (chemoselective dehydration polycondensation[10d]). These results prompted us to explore a new system for the combination of dehydration polycondensation and ring-opening polymerization to synthesize a new polyester-based material, in which, after Sc(OTf)$_3$-catalyzed ring-opening polymerization of ϵ-caprolactone (CL), polycondensation was performed using the same catalyst (Scheme 1).

Scheme 1. Dual Catalytic System for Combination of Ring-Opening Polymerization of Caprolactone and Subsequent Dehydration Polycondensation with Dicarboxylic Acid

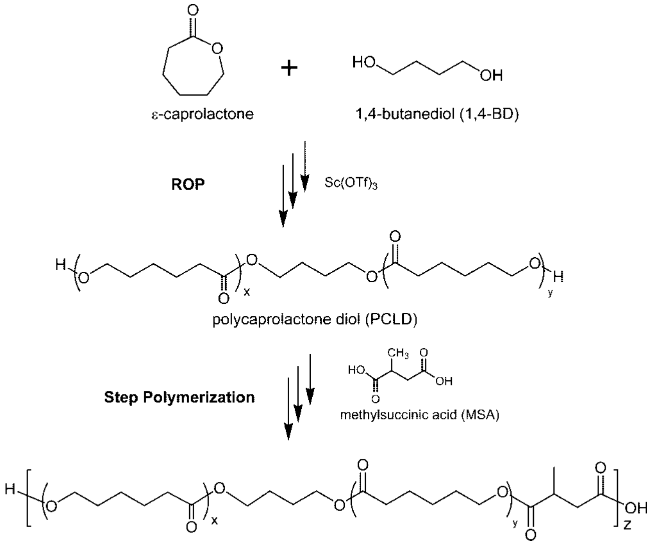

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Table 1. Dehydration Polycondensation of Commercially Available PCLD with MSA[a]

sample	yield,[b] g (%)	M_n[c] $\times 10^{-3}$	$M_\mathrm{w}/M_\mathrm{n}$[c]	T_g[d] (°C)	T_m[e] (°C)	ΔH[e] (mJ/mg)
poly(MSA-*co*-Placcel 205)	1.73 (92)	6.4	2.4	−61	11	
Placcel 205		0.9	1.6	−80	13	
poly(MSA-*co*-Placcel 208)	2.50 (90)	5.8	2.2	−61	42	47
Placcel 208		1.6	1.8	−66	48	81
poly(MSA-*co*-Placcel 220)	5.79 (92)	16.4	2.1	−59	55	97
Placcel 220		3.4	1.8	−60	58	94

[a] Placcel: 3.0 mmol; MSA: 3.0 mmol; $Sc(OTf)_3$: 1.0 mol %; at 80 °C for 110 h under 0.3 mmHg. [b] Without reprecipitation. [c] Determined by SEC measurements (polystyrene standards). [d] Determined by DSC (heating rate: 10 °C/min, second run). [e] Determined by DSC (heating rate: 10 °C/min, first run).

Table 2. Ring-Opening Polymerization and Successive Dehydration Polycondensation

		ring-opening polymerization[a]				polycondensation with MSA[b]					
run	catalyst	DP(calc): $[M]_0/[I]_0$	conv[c] (%)	M_n[d] $\times 10^{-3}$	$M_\mathrm{w}/M_\mathrm{n}$[d]	yield,[e] g (%)	M_n[d] $\times 10^{-3}$	$M_\mathrm{w}/M_\mathrm{n}$[d]	T_g[f] (°C)	T_m[g] (°C)	ΔH[g] J/g
1	$Sc(OTf)_3$	4	>99	1.2	1.3	1.37 (94)	13.9	1.9	−72	9	34
2	$Sc(OTf)_3$	8	>99	1.5	1.3	(93, 44[h])	7.7	2.2	−59	40	43
3	$Sc(OTf)_3$	16	>99	3.5	1.3	(94, 57[h])	6.0	2.2	−59	48	55
4	$Sc(OTf)_3$	64	>99	3.6	1.3	0.97 (92, 65[h])	10.7	2.3	−65	47	63
5	$Sc(NTf_2)_3$	4	>99	0.9	1.6	1.44 (99)	2.1	2.9	−59		
6	$Y(OTf)_3$	4	>99	1.2	1.4	1.41 (97)	9.3	2.2	−62	8	5
7	$Sm(OTf)_3$	4	>99	1.2	1.4	1.40 (96, 83[h])	6.7	1.9	−62	6	5
8	*p*-TSA	4	>99	1.2	1.4	1.40 (96)	3.3	2.7	−68	−1	trace

[a] Initiator: 1,4BD; monomer: ϵ-caprolactone (1.03 g, 9 mmol, $[M]_0 = 4.5$ M); catalyst: $[\text{catalyst}]_0/[1{,}4\text{BD}]_0 = 0.02$; in acetonitrile, at 45 °C, for 10 h. [b] At 100 °C, for 15 h, under 0.3 mmHg. [c] Determined by ^1H NMR measurement in $CDCl_3$. [d] Determined by SEC measurements (polystyrene standards). [e] Without reprecipitation. [f] Determined by DSC (heating rate: 10 °C/min, second run). [g] Determined by DSC (heating rate: 10 °C/min, first run). [h] After reprecipitation.

Experimental Section

Materials. CL, 1,4-butanediol (1,4BD), 1,9-nonanediol, methylsuccinic acid (MSA), *p*-toluenesulfonic acid (*p*-TSA), succinic acid (SA), sebacic acid (Seb), and acetonitrile were purchased from Nacalai Tesque Inc. (Kyoto, Japan). The $Sc(OTf)_3$, 3,3′-dithiodipropionic acid, and tributylphosphine were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). For this study, 1,8-octanediol (1,8OD) was obtained from Kishida Chemical Co. Ltd. Samarium trifluoromethanesulfonate $[Sm(OTf)_3]$ and yitterbium trifluoromethanesulfonate $[Yb(OTf)_3]$ were purchased from Aldrich Co., Ltd. Scandium trifluoromethanesulfonimide $[Sc(NTf_2)_3]$ was prepared in our laboratory according to procedures described in the literature.[11] Three commercially available α,*ω*-dihydroxyl poly(ϵ-caprolactone)s [polycaprolactone diol (PCLD): Placcel 205, Placcel 208, Placcel 220] were obtained from Daicel Chemical Industries Ltd., and the number-average molecular weights (M_ns) were estimated using size exclusion chromatography (SEC) to be 0.9×10^3 (molecular weight distributions: $M_\mathrm{w}/M_\mathrm{n} = 1.6$), 1.6×10^3 ($M_\mathrm{w}/M_\mathrm{n} = 1.8$), and 3.4×10^3 ($M_\mathrm{w}/M_\mathrm{n} = 1.8$).

Measurements. SEC measurement was used to determine M_ns and molecular weight distributions $M_\mathrm{w}/M_\mathrm{n}$s of polymer samples calibrated with polystyrene standards (Polysciences Inc.). The ^1H and ^{13}C NMR spectra were measured at 27 °C using spectrometers (200 MHz for ^1H, DPX200; Bruker Analytik and 600 MHz for ^1H, DRX600; Bruker Analytik). Differential scanning calorimetry (DSC) was performed from −100 to 100 °C at a heating rate of 10 °C/min (DSC-6220s; Seiko Instruments Inc.). The instrument was calibrated with indium and tin. To provide the same thermal history for all samples, thermal data were obtained after one heating cycle to 100 °C followed by quenching to −100 °C. A sample of 4−6 mg was used in an aluminum pan with a lid. The glass transition temperature (T_g) was determined at the inflection point of the corresponding heat capacity jump of the DSC trace. The melting temperature was defined as the endothermic peak top. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed (Voyager DEPRO; Applied Biosystems) using dithranol as a matrix reagent. To generate sodium cationized ions ($[M + Na]^+$), NaI was used as a cationization salt.

Ring-Opening Polymerization of ϵ-Caprolactone Using Diol as Initiator and Successive Polycondensation. A typical polymerization procedure is as follows. In the flask, acetonitrile (1 mL), CL (1.03 g, 9.04 mmol), 1,4BD (0.013 g, 0.14 mmol), and $Sc(OTf)_3$ (1.39 mg, 0.003 mmol) were added to a nitrogen atmosphere and stirred at 45 °C for 10 h. Polymerization was traced using ^1H NMR analysis. For PCLD (conversion > 99%, run 4 in Table 2). ^1H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.33−1.45 $(-CH_2-CH_2-CH_2-COO-)$, 1.52−1.73 $(-CH_2-CH_2-OCO-$, $-CH_2-CH_2-COO-)$, 2.27−2.46 $(-CH_2-COO-)$, 3.66 (t, 6.5 Hz, terminal $-CH_2-OH$), 4.03−4.22 $(-CH_2-OCO-)$.

Then, MSA (18.5 mg, 0.14 mmol) was added to the reaction mixture. The reaction was run at 100 °C for 16 h under reduced pressure to afford poly(MSA-*co*-PCLD) (0.97 g: 92% yield, run 4 in Table 2). Yield of the polyester was calculated by subtraction weight of the catalyst from the isolated material. ^1H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.19−1.23 $(-OOC-CH(CH_3)-CH_2-)$, 1.33−1.45 $(-CH_2-CH_2-CH_2-COO-)$, 1.58−1.73 $(-CH_2-CH_2-OCO-)$ $(-CH_2-CH_2-COO-)$, 2.27−2.34 $(-CH_2-COO-)$, 2.33−2.79 $(-OOC-CH_2-CH(CH_3)-COO-)$, 2.85−3.00 $(-OOC-CH(CH_3)-CH_2-)$, 3.67−3.71 (terminal $-CH_2-OH$), 4.03−4.09 $(-CH_2-OCO-)$. ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 17.1 $(-OOC-CH(CH_3)-CH_2-)$, 24.6 $(-CH_2-CH_2-CH_2-COO-)$, 25.5 $(-OOC-CH_2-CH_2-)$, 28.4 $(-OCO-CH_2-CH_2-)$, 34.1 $(-OOC-CH_2-)$, 35.9 $(-OOC-CH(CH_3)-CH_2-COO-)$, 37.6 $(-OOC-CH(CH_3)-CH_2-)$, 63.8 $[-OCO-CH_2-$ (1,4BD-CL)], 64.2 $[-OCO-CH_2-$ (CL-CL)], 64.4−64.5 $[-OCO-CH_2-$, (MSA-CL)], 172.2 and 175.6 $[-OCO-$ (SA)], 173.6 $[-OCO-$ (PCLD)].

Using same procedure, poly(SA-*co*-PCLD) was also synthesized (93% yield, entry 2 in Table 3). ^1H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.34−1.45 $(-CH_2-CH_2-CH_2-COO-)$, 1.58−1.69 $(-CH_2-CH_2-OCO-)$ $(-CH_2-CH_2-COO-)$, 2.27−2.35 $(-CH_2-COO-)$, 2.58−2.70 $(-OOC-CH_2-CH_2-COO-)$, 3.62−3.68 (terminal $-CH_2-OH$), 4.03−4.10 $(-CH_2-OCO-)$. ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 24.6 $(-CH_2-CH_2-CH_2-COO-)$, 25.5 $(-OOC-CH_2-CH_2-)$, 28.4 $(-OCO-CH_2-CH_2-)$, 34.1 $(-OOC-CH_2-)$, 63.8 $[-OCO-CH_2-$ (1,4BD-CL)], 64.2 $[-OCO-CH_2-$ (CL-CL)], 64.6 $[-OCO-CH_2-$, (SA-CL)], 171.7 $[-OCO-$ (SA)], 173.5 $[-OCO-$ (PCLD)].

Cleavage of S−S linkage in Stimuli Cleavable Polyester. A typical process was performed as follows: 50 mg of the produced stimuli-cleavable polymer, poly(MSA-*co*-3,3′-dithiodipropionic acid), was added to a 10 mL vial containing 1.6 mL of solution of tributylphosphine (0.1 M) in $CHCl_3$; the reaction mixtures were kept at 25 °C for 12 h. The reaction mixture was then evaporated; the remaining solution was filtered and washed with hexane to remove the unreacted reagent.

Table 3. Ring-Opening Polymerization and Successive Polycondensation with Several Dicarboxylic Acids

run	ring-opening polymerization[a]		polycondensation with dicarboxylic acids[b]						
	DP(calc): $[M]_0/[I]_0$	conv (%)[c]	dicarboxylic acid	yield,[d] g (%)	M_n[e]	M_w/M_n[e]	T_g[f] (°C)	T_m[g] (°C)	ΔH[g] (J/g)
1	4	>99	MSA	1.37 (94)	9.4	1.5	−61	8	32
2	4	>99	SA	1.33 (93)	8.3	1.5	−58	26	57
3	4	>99	Seb	1.44 (89)	19.7	1.6	−50	45	98

[a] Initiator: 1,4BD (2.3 mmol); monomer: ϵ-caprolactone (1.03 g, 9 mmol, $[M]_0 = 4.5$ M); catalyst: $[Sc(OTf)_3]_0/[1,4BD]_0 = 0.02$; in acetonitrile, at 30 °C, for 3−5 h. [b] MSA: 0.3 g (2.3 mmol), at 70 °C, for 22 h, under 0.3 mmHg. [c] Determined by ^{1}H NMR measurement in $CDCl_3$. [d] Without reprecipitation. [e] Determined by SEC measurements (polystyrene standards). [f] Determined by DSC (heating rate: 10 °C/min, second run). [g] Determined by DSC (heating rate: 10 °C/min, first run).

Table 4. Characterization of Poly(MSA-*co*-PCLD-*co*-1,8OD) Segment Block Copolyesters Prepared by Ring-Opening Polymerization[a] and Successive Ternary Polycondensation with MSA[b]

run	1,8OD/PCLD (mol/mol)	yield[c] (%)	M_n[d] × 10^{-3}	M_w/M_n[d]	T_g[e] (°C)	T_m[f] (°C)	ΔH[f] (mJ/mg)
1	100/0	93[c] (84[g])	22.0	2.6	−54		
2	80/20	90[c]	14.0	2.1	−58		
3	70/30	91[c]	13.0	2.1	−60		
4	60/40	93[c]	13.0	2.0	−61		
5	50/50	94[c] (23[g])	9.0	2.5	−63	−2	16
6	40/60	90[c] (54[g])	17.0	2.6	−61	4	45
7	30/70	92[c] (70[g])	15.0	2.8	−62	18	30
8	20/80	90[c] (62[g])	17.0	2.5	−63	21	26
9	PCLD		11.0	2.0	−61	52	26

[a] In acetonitrile. $[M]_0/[I]_0 = 8$, conversion (^{1}H NMR), >99%, M_n(SEC): 1.7 × 10^3. [b] Bulk polycondensation at 90 °C for 30 h. [c] Without reprecipitation. [d] Determined by SEC measurements (polystyrene standards). [e] Determined by DSC (heating rate: 10 °C/min, second run). [f] Determined by DSC (heating rate: 10 °C/min, first run). [g] After reprecipitaion using chloroform/diethyl ether.

Biodegradation Test. Using a BOD tester (Model 200F; Taitec Co., Koshigaya-shi, Japan) fundamentally according to ISO standard guidelines (ISO 14851), BOD was determined by oxygen consumption at 25 °C. The BOD-based biodegradability was estimated by the percentage of the consumed amount of oxygen, correlated for a blank test to the theoretical amount of oxygen required for complete oxidation of the sample. All BOD values are means of three samples. Activated sludge was obtained from a sewage plant in Naka-ku, Nagoya. The supernatants (15 mL) were added to the incubation medium (150 mL), which contained the following (mg/L): K_2HPO_4, 217; KH_2PO_4, 85; Na_2HPO_4, 447; NH_4Cl, 5; $CaCl_2$, 27; $MgSO_4 \cdot 7H_2O$, 23; and $FeCl_3 \cdot 6H_2O$, 0.25. The sample 10 mg/L was coated onto the bottle, and $NaOH_{(aq)}$ (11 mol/L) was placed to absorb the produced CO_2.

Results and Discussion

First, polycondensation of commercially available PCLD (Placcel 205, $M_n = 0.9 \times 10^3$) with MSA was carried out at 80 °C for 110 h (Table 1). Before reprecipitation, M_n was determined by SEC measurement to be 6.4 × 10^3 (M_w/M_n was 2.4). Assuming that the prepolymers have a molecular weight distribution M_w/M_n of 1.6, it is considered that the polycondensation proceeded without transesterification because the possibility of removal of the oligomeric part by the reprecipitation procedure was eliminated. Using the DSC measurement, T_g and T_m were −61 and 11 °C (run 1 in Table 1). The T_g was 20 °C higher than that of the corresponding prepolymer (Placcel 205: T_g was −80 °C). Increased T_g was explained by restricted molecular motion of the PCL terminal segment by polycondensation with MSA. The value of T_m (11 °C) was the same as that of the prepolymers (T_m = 13 °C). Polycondensations of Placcel 208 (PCLD, $M_n = 1.6 \times 10^3$) and Placcel 220 (PCLD, $M_n = 3.4 \times 10^3$) with MSA also proceeded without broadening of the M_w/M_n values (M_w/M_n = 2.2 and 2.1; Table 1). The results also indicated dependence of the T_m and ΔH of the obtained segment block copolyesters on the chain length of the parent PCLD prepolymers. The T_g and T_m of the authentic PCL sample ($M_n = 10.8 \times 10^3$, $M_w/M_n = 1.1_5$) obtained by $Sc(OTf)_3$-catalyzed ring-opening polymerization of CL[12] were −67 and 60 °C with ΔH of 121 J/g,[12d] which coincides with reported values.[13]

Actually, ring-opening polymerization of CL was carried out in acetonitrile at 45 °C for 10 h, in which ring-opening polymerization proceed in a living manner[12] and the α,ω-dihydroxyl termini were confirmed using NMR and MALDI-TOF mass spectra ($M_n = 1.2 \times 10^3 - 3.6 \times 10^3$, $M_w/M_n = 1.3$). After removing acetonitrile under reduced pressure, bulk polycondensation with MSA was subsequently performed at 100 °C for 15 h to give polyester in an excellent yield (92−94%, runs 1−4 in Table 2).[14] They agree with the formation of polymer according to the mechanism of chain polymerization and successive step polymerization. When the feed monomer/initiator ratio ($[M]_0/[I]_0$) was 4, M_n and M_w/M_n of obtained polyester were respectively 13.9 × 10^3 and 1.9 after polycondensation (run 1). As a control, direct esterification of dimethyl methylsuccinate [$CH_3OCOCH(CH_3)CH_2COOCH_3$] with PCLD did not occur. The results supported that $Sc(OTf)_3$ catalyzes, chemoselectively, not transesterification but dehydration condensation in this condition.

To optimize experimental conditions, we surveyed other catalysts including $Y(OTf)_3$, $Sm(OTf)_3$, and *p*-TSA in ring-opening polymerization and successive polycondensation of the PCLD and MSA (runs 6−8).[14] However, the M_ns (6.7 × 10^3 −9.4 × 10^3) were lower than that of the polyester synthesized with $Sc(OTf)_3$ (run 1) as the catalyst. Using *p*-TSA as the catalyst, both ring-opening polymerization and polycondensation proceeded; however, broadening of the molecular weight distribution (M_w/M_n = 2.7) was observed, indicating that the transesterification occurred during the polycondensation. Transesterification was also indicated by the lower T_m (−1 °C) with lower ΔH (trace) than other samples (6−9 °C) because T_m of the segment block copolyester was sensitive to the PCL chain length, as shown in Table 1. In addition, $Sc(NTf_2)_3$ as well as $Sc(OTf)_3$ is known as a powerful Lewis acid;[11] the catalytic activity is unfortunately not so high in this polymerization system (run 5).

Using other dicarboxylic acids containing SA and Seb, similar ring-opening polymerization of CL and successive polycondensation with dicarboxylic acids were carried out (Table 3). After monitoring that the ring-opening polymerization of CL was completed, successive polycondensation with SA (run 2) and Seb (run 3) occurred at 70 °C for 22 h under reduced pressure to afford the corresponding segment block copolyester with 8.3 × 10^3 (M_w/M_n = 1.5) and 19.7 × 10^3 (M_w/M_n = 1.6). Their T_gs and T_ms were T_g = −58 °C, T_m = 26 °C for poly(SA-

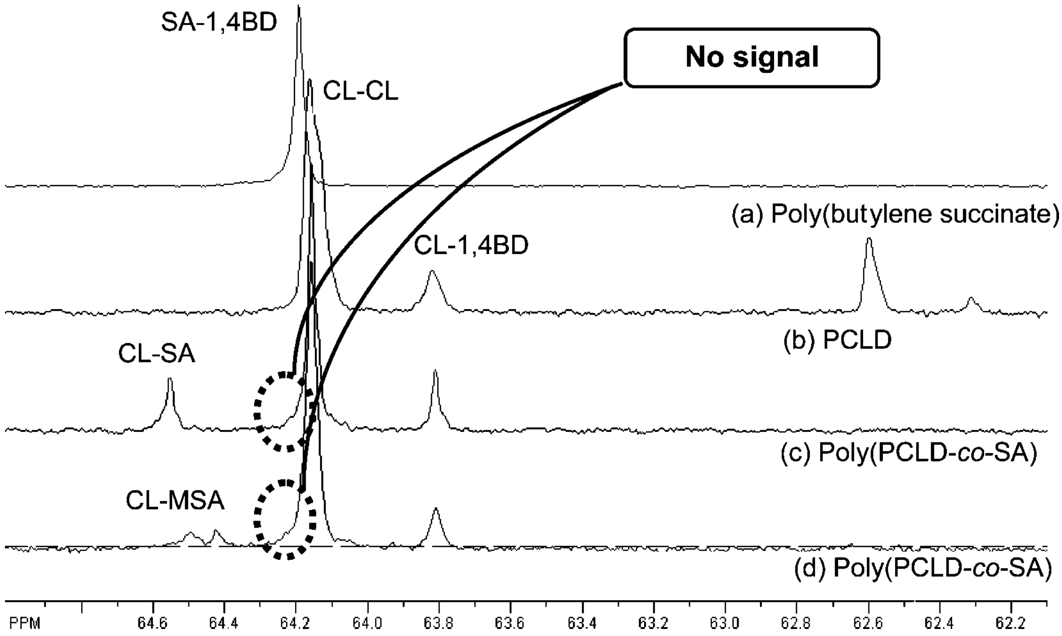


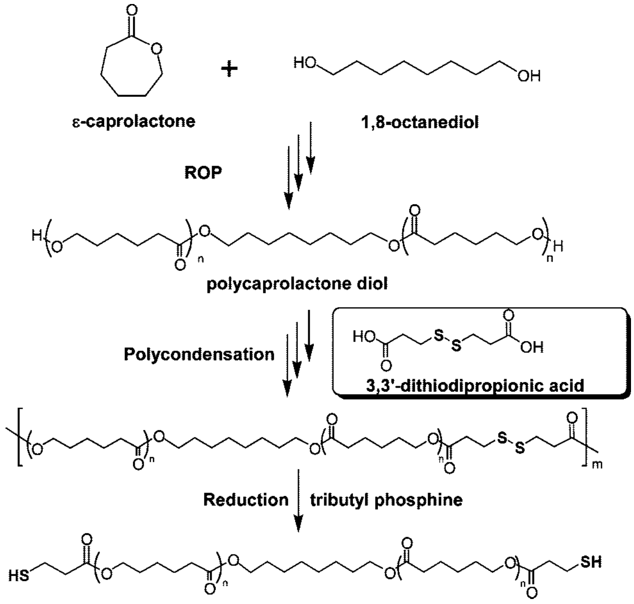
Figure 1. Expanded ^{13}C NMR spectra of (a) poly(SA-*co*-1,4BD), (b) PCLD (M_n = 1.2 × 10^3), (c) poly(MSA-*co*-PCLD), and (d) poly(SA-*co*-PCLD) in CDCl$_3$ (27 °C, TMS, 200 MHz).

co-PCLD) and T_g = −50 °C, T_m = 45 °C for poly(Seb-*co*-PCLD). Results revealed that the T_g and T_m depend on the structure of dicarboxylic acid.

To confirm that transesterification did not occur in the Sc(OTf)$_3$-catalyzed chain and step polymerizations, ^{13}C NMR spectra of poly(MSA-*co*-PCLD) (run 1, Table 1) and poly(SA-*co*-PCLD) (run 2, Table 3) were measured in CDCl$_3$ (Figure 1) and compared to poly(SA-*co*-1,4BD), i.e., poly(butylene succinate) (Figure 1a) or PCLD (Figure 1b). The peak at 64.3 ppm [$-OCO-CH_2-$ (1,4BD-SA)] ascribed to the transesterification was not observed within the NMR detection level. However, the detection is not so sensitive because the peak at 64.3 ppm appeared only when the initiator unit (1,4BD) for ring-opening polymerization participates in transesterification. Therefore, we prepared polymers with a cleavable backbone and tunable structure to investigate whether the transesterification of the PCL block occurs or not (Scheme 2). Synthesis of a polymer with a stimuli-cleavable backbone is an active research area for polymer chemists.[15] Disulfide/thiol chemistry is well-known to protein chemists and is becoming increasingly popular in conventional polymer syntheses because the disulfide bond is very sensitive to biological stimuli [such as glutathione and chemical stimuli (such as dithiothreitol (DTT) and tributylphosphine)] at room temperature.[16] Hong et al. reported complete scission S−S linkage in poly(amino ester).[16g]

Scheme 2 shows polycondensation of dicarboxylic acid containing disulfide linkage (3,3′-dithiodipropionic acid) with PCLD initiated by 1,8-OD [M_n of 3.6 × 10^3 (M_w/M_n = 1.4), M_n(peak top) = 4.3 × 10^3, Figure 2a]. The Sc(OTf)$_3$-catalyzed polycondensation proceeded at 25 °C for 12 h to afford the corresponding segment block polyester with M_n of 10.7 × 10^3 [M_w/M_n = 2.3, M_n(peak top) = 17.0 × 10^3, Figure 2b]. Cleavage of the disulfide linkage was carried out using tributylphosphine in CHCl$_3$ at 25 °C for 12 h to give oligomer with M_n of 4.7 × 10^3 [M_w/M_n = 1.4, M_n(top) = 5.8 × 10^3] (Figure 2c). Although the M_n was ca. 1.0 × 10^3 higher than the parent prepolymer (PCLD) by the change of the hydrodynamic volume ascribed to terminal transformation from −OH to $-OCOCH_2CH_2SH$, the M_w/M_n (1.4) was identified with that of the prepolymer (M_w/M_n = 1.4). These results indicate that transesterification of the PCL segment was suppressed during the polycondensation.

Scheme 2. Ring-Opening Polymerization of Caprolactone and Successive Polycondensation with Dicarboxylic Acid Containing S−S Linkage



Next, to control thermal properties, ternary polycondensation of MSA, PCLD, and 1,8OD was carried out at 90 °C for 30 h (M_n = 0.9 × 10^3−2.2 × 10^3, M_w/M_n = 2.0−2.8). The obtained polyester, poly(MSA-*co*-PCLD-*co*-1,8OD) had the same molar ratio as the feed ([1,8OD]$_0$/[PCLD]$_0$) and showed a single T_g, which increases with 1,8OD molar ratio. Figure 3 also displays the melting thermograms on the obtained segment block copolyester. As the content of 1,8OD is increased to 50 mol %, the endothermic peak tends to lose its prominence with an accompanying depression of the T_m values. The results also support that microphase separation did not take place.

Biodegradability of the Segment Block Copolyester

Biodegradation of the segment block copolyesters, poly(MSA-*co*-PCLD-*co*-1,8OD)s, in activated sludge (pH 7.4, 25 °C) was

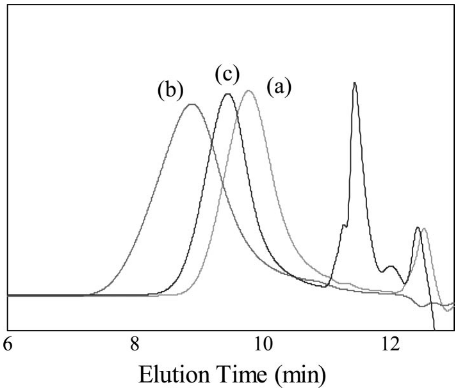


Figure 2. SEC traces of (a) PCLD ($M_n = 3.6 \times 10^3$, prepolyester), (b) poly(3,3′-dithiodipropionic acid-*co*-PCLD), and (c) after reduction at 25 °C for 12 h (eluent, $CHCl_3$, 40 °C, 0.35 mL/min).

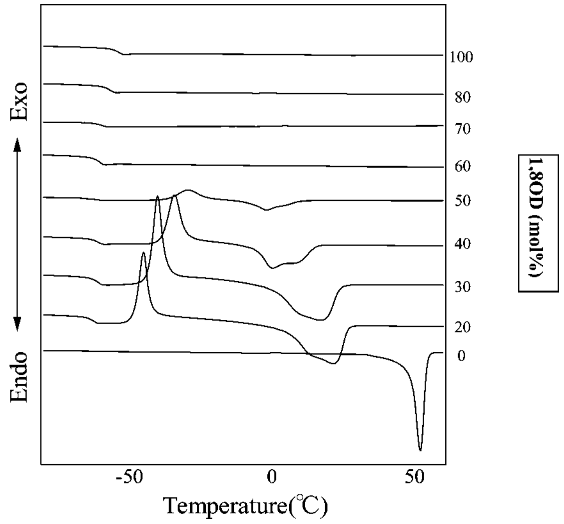


Figure 3. DSC charts of (top) poly(MSA-*co*-1,8OD)(100/0), poly(MSA-*co*-1,8OD-*co*-PCLD)(80/20), poly(MSA-*co*-1,8OD-*co*-PCLD)(70/30), poly(MSA-*co*-1,8OD-*co*-PCLD)(60/40), poly(MSA-*co*-1,8OD-*co*-PCLD)-(50/50), poly(MSA-*co*-1,8OD-*co*-PCLD)(40/60), poly(MSA-*co*-1,8OD-*co*-PCLD)(30/70), poly(MSA-*co*-1,8OD-*co*-PCLD)(20/80), and PCLD ($M_n = 1.1 \times 10^4$) (bottom); heating rate, 10 °C/min.

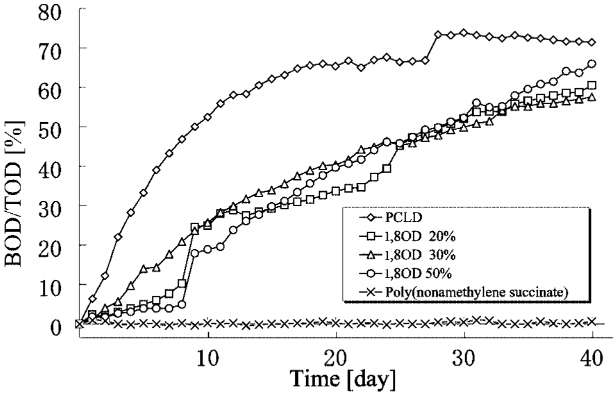
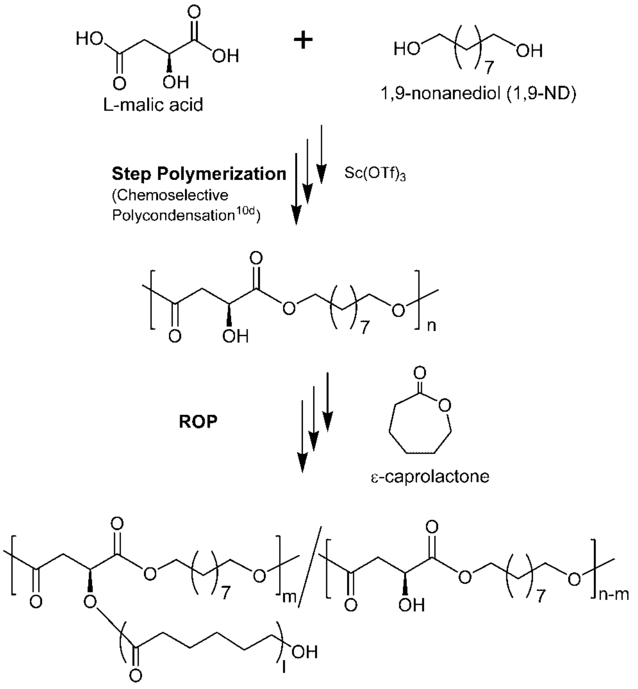


Figure 4. BOD curves of poly(nonamethylene succinate), poly(MSA-*co*-1,8OD-*co*-PCLD)(80/20), poly(MSA-*co*-1,8OD-*co*-PCLD)(70/30), and poly(MSA-*co*-1,8OD-*co*-PCLD)(50/50) in an activated sludge (pH, 7.5, 25 °C).

Scheme 3. Dual Catalytic System for Combination of Dehydration Polycondensation and Subsequent Ring-Opening Copolymerization of CL



monitored using BOD. The degradation percentages were calculated from the BOD value and the theoretical oxygen demand (TOD) value (Figure 4). The BOD-based biodegradability is defined in the Experimental Section. All three BOD values showed good reproducibility. In the BOD measurement, PCLD was degraded by ca. 70% of BOD/TOD within 20 days, indicating high biodegradability. The dependence of biodegradability of the copolyesters on the variety of their structures is shown in Figure 4. The degradations of the obtained segment block copolyesters [poly(MSA-*co*-PCLD-*co*-1,8OD), PCLD/1,8OD = 80/20, 70/30, 50/50] were comparable to that of PCLD, while poly(nonamethylene succinate) showed no biodegradability (BOD/TOD = 2% after 40 days).

Furthermore, according to our previously described procedures,[10d] chemoselective polycondensation of hydroxyl group containing monomers, L-malic acid, and 1,9-nonanediol was performed in bulk at 60 °C for 30 h. To diminish the terminal primary hydroxyl group, the feed $[\text{L-malic acid}]_0/[\text{1,9-nonanediol}]_0$ ratio was 1.3. Polycondensation proceeds chemoselectively to afford polyester having pendent hydroxyl groups in a good yield (80%, $M_n = 3.0 \times 10^3$, $M_w/M_n = 1.93$). After ^1H NMR analysis indicated the disappearance of the terminal primary alcohols, ring-opening copolymerization from the pendent hydroxyl groups occurred, adding dichloromethane as the solvent and CL to give polyester having PCL side chains (95% yield, $M_n = 5.0 \times 10^3$, $M_w/M_n = 1.80$, Scheme 3).

Conclusions

In this paper, we described a new system for combination of chain (ring-opening polymerization of CL) and step (dehydration polycondensation) polymerizations for polyester-based new material, in which $Sc(OTf)_3$ catalyzes both types of polymerizations. The combination of chain polymerization and step polymerization is expected to expand the range of material design. These fundamental results are anticipated to be useful for new material design using both step and chain polymerizations.

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