Controlled Ring-Opening Polymerization of ϵ-Caprolactone Using Polymer-Supported Scandium Trifluoromethanesulfonate in Organic Solvent and Ionic Liquids

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ABSTRACT: In this article, we described the ring-opening polymerization (ROP) of ϵ-caprolactone using a polymer-supported scandium(III) trifluoromethanesulfonate [$Sc(OTf)_3$] catalyst (PS−Sc) under mild conditions. In this system, it is possible to synthesize poly(ϵ-caprolactone) PCL ($M_n = 4.1-10.8 \times 10^3$) with low polydispersity ($M_w/M_n = 1.12-1.16$). The Arrhenius equation was used to investigate the reaction kinetics. Furthermore, in two-step polymerization, the molecular weight increased without broadening of the molecular weight distributions. A plot of M_w/M_n versus conversion and the reaction time showed that M_w/M_n was constant during polymerization and had no relation to the increase of molecular weight. A plot of M_n versus conversion showed that M_n increased linearly as a function of conversion. These results indicate that PS−Sc catalyzed living polymerizations of ϵ-caprolactone as well as did $Sc(OTf)_3$. After polymerization, the catalyst was easily recovered quantitatively, and no loss of Sc was observed after use. Next, we used ionic liquids instead of toluene, and found that [bmim][PF_6] and [emim][PF_6] accelerated the ROP of ϵ-caprolactone in this system. The ROP in some ionic liquids also made it possible to chemically modify cellulose using grafting from technique.

Introduction

Polycaprolactone (PCL) is a well-known, commercially available biodegradable polymer. Polycaprolactone with a narrow molecular weight distribution is of great interest especially for use in medical applications and polyurethane synthesis.[1] The most commonly explored catalysts for PCL synthesis are metal complexes, including tin,[2,3] aluminum,[4−7] iron,[8,9] yittrium,[10,11] zinc,[12,13] bismuth,[14] ruthenium,[15] and zirconocene.[16] Ring-opening polymerization (ROP) of ϵ-caprolactone catalyzed by enzymes has also been investigated.[17,18] The most popular polymerization system for PCL is ROP of ϵ-caprolactone catalyzed by an organotin compound.[2,3] These homogeneous systems have drawbacks, namely (1) the toxicity of the heavy metal catalysts, (2) the use of organic solvents, and (3) contamination of the resulting polyesters by residual metal catalyst.

Recently, it was found that PCL may be synthesized by ROP of ϵ-caprolactone catalyzed by scandium(III) trifluoromethanesulfonate [$Sc(OTf)_3$], and that the ROP proceeds in a quasi-living manner.[19−22] In fact, $Sc(OTf)_3$ is attractive as a water-stable Lewis acid because of its low hydrolysis constant and high exchange rate constant,[23] and has other advantages such as recyclibility, suppressed transesterification during room temperature polycondensation,[24−30] and lower toxicity.[29,31] The stability of $Sc(OTf)_3$ in highly protic environments enables its use even in ionic liquids.[20] However, the procedure for catalyst recovery is time-consuming and requires tedious washing and extraction with water, thereby producing aqueous waste containing organic solvent.

The use of a solid catalyst would simplify and hasten catalyst recovery, although retardation of the polymerization rate would be expected. Although some metal complexes might be grafted onto a silica or alumina support,[10,32−35] the regeneration and recycling of such material has to this point been unsuccessful.[32] From the perspective of green chemistry, further development of a recoverable polymer-supported catalyst is desired.

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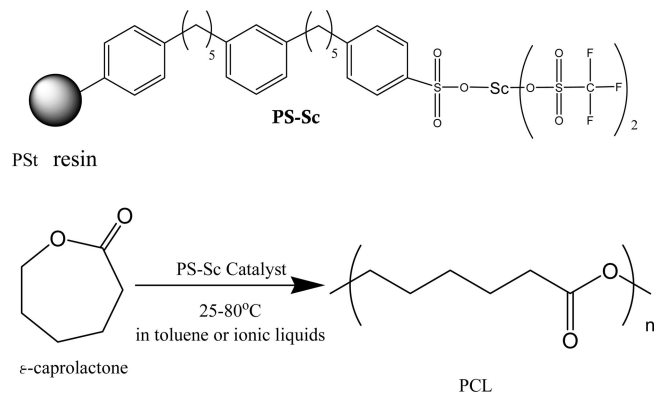
Scheme 1. ROP of ϵ-Caprolactone Using Polymer-Supported Catalyst



For this study, we specifically examine a polymer-supported catalyst containing Sc (PS−Sc) (Scheme 1), which consists of a polystyrene bead and $Sc(OTf)_3$ and is easily recovered after reaction by simple filtration. Kobayashi and co-workers have first used this PS−Sc catalyst in an Aldol reaction.[36] We have already demonstrated room-temperature direct polycondensation of methyl succinic acid and 1, 4-butanediol catalyzed by $Sc(OTf)_3$[24−30] and PS−Sc ($M_n > 1.0 \times 10^4$),[26] and revealed that polycondensation using recovered PS−Sc catalyst also proceeded.[26] But we believe that this catalyst can also be applied to other polymerization reactions.

In this paper, we found the living ROP of ϵ-caprolactone catalyzed by PS−Sc in an organic solvent under mild conditions.[37] The molecular weight and polydispersity of the products, and the activation energy and polymerization rate of the process, are compared with those of reactions catalyzed by $Sc(OTf)_3$. We emphasize that quantitative analysis using electron probe microanalysis (EPMA) and experiments using recovered catalyst for ROP of ϵ-caprolactone have demonstrated that this polymer-supported catalyst is recyclable easily. Ionic liquids are presently recognized as green solvents because of their recyclability and low volatility. Some ionic liquids have proved to be not only

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Table 1. ROP of ϵ-Caprolactone Catalyzed by Sc(OTf)$_3$ and PS−Sc in Toluene[a]

							$M_n \times 10^{-3}$				
run	catalyst	initiator	$[M]_0/[I]_0$	temp (°C)	time (h)	convn[b] (%)	calcd[c]	SEC[d]	NMR[e]	MS[f]	M_w/M_n[d]
1	Sc(OTf)$_3$	EtOH	40	25	24	95	4.4	5.1	2.0		1.15
2	Sc(OTf)$_3$	EtOH	40	35	21	98	4.5	6.1	2.4		1.16
3	Sc(OTf)$_3$	EtOH	40	45	8	96	4.4		2.1		
4	Sc(OTf)$_3$	EtOH	40	50	8	98	4.5				1.19
5	Sc(OTf)$_3$	EtOH	40	60	2	95	4.4				
6	PS−Sc	EtOH	40	25	72	89	4.1	5.5	2.7		1.14
7	PS−Sc	EtOH	40	35	72	86	4.0	6.2	3.0		1.12
8	PS−Sc	EtOH	40	50	26	86	4.0	5.3	2.4		1.16
9	PS−Sc	EtOH	40	60	12	93	4.3				
10	PS−Sc	2-PrOH	40	50	30	89	4.1	4.7	1.8		1.13
11	PS−Sc	H_2O	40	50	8	81	3.7	2.8			1.26
12	PS−Sc	BnOH	40	50	18	91	4.3	4.1	2.3	2.9	1.11
13	PS−Sc	BnOH	40	80	10	93	4.4	4.9			1.27
14	PS−Sc	BnOH	240	50	76	74	20.4	10.8			1.15
15	recovered PS−Sc	EtOH	40	35	72	84	3.9	5.8			1.10
16	PS−Sc	BnOH	20	50	10	83	2.0	3.0			1.15
17	1st recovered PS−Sc	BnOH	20	50	10	57	1.4	2.7			1.12
18	2nd recovered PS−Sc	BnOH	20	50	10	38	1.0	1.8			1.18

[a] Conditions: monomer, 1.0 g; $[M]_0 = 3$ mol/L; catalyst, 1.0 mol %. [b] Monomer conversion determined by ^{1}H NMR spectroscopy (in $CDCl_3$) intensity ratio. [c] Calculated from the molecular weight of ϵ-caprolactone × $[M]_0/[I]_0$ × conversion + F_w(initiator). [d] Determined by SEC in chloroform, calibrated using standard poly(styrene)s. [e] Determined by ^{1}H NMR spectroscopy (in $CDCl_3$) intensity ratio. [f] Determined by MALDI−TOF mass using dithranol as a matrix reagent and NaI as a cationization salt.

solvents but also effective catalysts for various reactions.[38] Polymer synthesis without organic solvents is a requirement for environmentally friendly polymer design. Therefore, we used ionic liquids and found that some ionic liquids accelerated the ROP of ϵ-caprolactone. Furthermore, we demonstrated PS−Sc-catalyzed ring-opening copolymerization of ϵ-caprolactone using cellulose as the macroinitiator (grafting from technique), because it has been recently reported that some ionic liquids dissolve cellulose at or near room temperature[39] although cellulose has poor solubility in organic solvents because of its highly rigid crystalline structure. Most Lewis acids are unstable in protic or polar solvents; however, the use of rare-earth triflates in an ionic liquid presents a new fascinating possibility of application to chemical modification of cellulose.

Experimental Section

Materials. ϵ-Caprolactone, ethanol (EtOH), 2-propanol (2-PrOH), benzyl alcohol (BnOH), petroleum ether, ethyl acetate, methanol, benzene, chloroform, and toluene were purchased from Nacalai Tesque (Kyoto, Japan) and were purified by distillation before use. The Sc(OTf)$_3$ was purchased from Wako Pure Chemical (Osaka, Japan), and polymer-bound scandium trifluoromethanesulfonate (PS−Sc) was obtained from Aldrich Co.; both materials were used after freeze-drying with benzene. Cellulose powder was used as purchased from Aldrich Co; 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]), 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), and 1-butyl-3-methylimidazolium chloride ([bmim]Cl) were used as purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan); 1-Ethyl-3-methylimidazolium hexafluorophosphate ([emim][PF_6]) was used as purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), and 1,3-dimethylimidazolium methylphosphonate [dmim][(MeO)HPO_2] and 1,3-dimethylimidazolium dimethylphosphate [dmim][$(MeO)_2PO_2$] were prepared according to a previously reported procedure.[39]

Measurements. The ^{1}H NMR spectra were measured at 27 °C using a Bruker DPX200 (200 MHz) spectrometer. The number average molecular weights (M_n) and the polydispersity index (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) calibrated with polystyrene standards using a Tosoh DP8020 pump system with an RI detector (Tosoh RI-8020) and Tosoh G2000, 3000, 4000, and 5000-HXL columns (eluent, chloroform; flow rate, 1.0 mL/min; temperature, 40 °C) or a TSKgel SuperMultiporeHZ-M column (eluent, chloroform; flow rate, 0.35 mL/min; temperature, 40 °C). Matrix-assisted laser desorption/ionization time-of-flight (MALDI−TOF) mass spectra were measured on a Voyager RN using dithranol as a matrix reagent. To generate sodium-cationized ions ($[M + Na]^+$), NaI was used as a cationization salt. Differential scanning calorimetry (DSC) measurements were carried out on a DSC 210 unit with a Seiko SSC/5200H TA Station unit from −100 to 120 °C at a heating rate of 10 °C/min. 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. Electron probe microanalysis was performed using a JEOL JXA-8800 at an accelerating voltage of 10 kV.

Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by PS−Sc in Toluene. Following previously reported procedures,[19,20,37] the PS−Sc was freeze-dried to remove water adsorbed on the scandium catalyst. Benzene and PS−Sc were added in a 10 mL round-bottom flask. The flask was dried via freeze-drying. A typical polymerization procedure consisted of the following. In the flask, toluene, ϵ-caprolactone, and an initiator (ethanol, 2-propanol, benzyl alcohol, or water) were added in a nitrogen atmosphere and stirred. The polymerization was tracked by ^{1}H NMR analysis. When the monomer was consumed, ethyl acetate was added in order to dissolve the polymer. The PS−Sc was filtered off, and the filtrate was added dropwise to petroleum ether. After centrifugal separation, the precipitate was dried under vacuum, and the PCL was obtained as a white powder.

FT IR (KBr): 3439 (ν_{O-H}), 2947 (ν_{C-H}), 1727 [$\nu_{C=O}$(ester)], 1471 (δ_{C-H}), 1295, 1243 and 1189 [ν_{C-O}(ester)], and 1092 (ν_{C-O}) cm^{-1}. ^{1}H NMR ($CDCl_3$), $\delta = 1.28-1.48$ (2H, $COOCH_2CH_2CH_2CH_2CH_2$), 1.54−1.76 (4H, $COOCH_2CH_2CH_2CH_2CH_2$), 2.24−2.38 (2H, $COO(CH_2)_4CH_2$), 3.65 [t, $-CH_2OH$ (terminus), $J = 6.6$ Hz], 4.00−4.12 (4H, $COOCH_2$), 5.11 [$BnCH_2OCO$ (terminus)], 7.32−7.38 [aromatic (terminus)] (initiated by BnOH).

Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by PS−Sc in Ionic Liquids. The typical polymerization procedure was the same as that used for the ROP in toluene. When the monomer was consumed, ethyl acetate was added in order to dissolve the polymer. The PS−Sc was filtered off, and the filtrate was evaporated to yield an ionic liquid solution of PCL. The viscous liquid so obtained was added methanol and centrifuged. The ionic liquid was recovered by decanting, and the precipitate was dried under vacuum, yielding PCL in powder form (yield = 76%, run 9 in Table 2).

PS−Sc-Catalyzed Ring-Opening Copolymerization of ϵ-Caprolactone Initiated from Hydroxyl Groups of Cellulose in Ionic Liquids. Cellulose (28 mg, 0.18 pyranose unit mmol) and [dmim][(MeO)HPO_2] (0.65 mL) were added in a 10 mL round-bottom

Table 2. ROP of ϵ-Caprolactone Catalyzed by PS−Sc in Ionic Liquids[a]

run	solvent	$[M]_0/[I]_0$	temp (°C)	time (h)	convn[b] (%)	$M_n \times 10^{-3}$ calcd[c]	$M_n \times 10^{-3}$ SEC[d]	M_w/M_n[d]
1	toluene	40	50	18	91	4.3	4.1	1.11
2	toluene	40	80	10	93	4.4	4.9	1.27
3	bulk	40	80	3	98	4.6	6.3	1.34
4	bulk	120	80	7	92	12.7	8.2	1.63
5	[bmim][BF_4]	40	50	40	72	3.4	0.4	1.52
6	[bmim][BF_4]	40	80	7	58	2.8	1.4	1.27
7	[emim][BF_4]	40	50	18	0			
8	[emim][BF_4]	40	80	6	0			
9	[bmim][PF_6]	40	50	24	95 (76[e])	4.4	4.4	1.54
10	[bmim][PF_6]	40	80	4	96	4.5	5.2	1.58
11	[emim][PF_6]	40	80	6	95	4.4	7.7	1.48
12	[bmim] Cl	40	80	18	30			
13	[dmim][(MeO)HPO_2]	40	50	48	45			
14	[dmim][$(MeO)_2PO_2$]	40	50	24	0			

[a] Conditions: monomer, 1.0 g; $[M]_0 = 3$ mol/L; catalyst, 1.0 mol %; initiator, BnOH. [b] Monomer conversion determined by ^{1}H NMR spectroscopy (in $CDCl_3$) intensity ratio. [c] Calculated from the molecular weight of ε-caprolactone × $[M]_0/[I]_0$ × conversion + F_w(initiator). [d] Determined by SEC in chloroform, calibrated using standard poly(styrene)s. [e] Yield.

flask and heated with stirring at 50 °C until the cellulose was dissolved completely. After a transparent cellulose solution was obtained, $Sc(OTf)_3$ or PS−Sc, and ϵ-caprolactone was added in a nitrogen atmosphere and heated at 80 °C for 44 h ($[M]_0 = 5$ M). The solution was added to H_2O in dropwise fashion. After centrifugal separation, the precipitate was freeze-dried and washed with toluene repeatedly to remove PCL homopolymer. The removal of the PCL homopolymer was confirmed by SEC measurement using $CHCl_3$ as the eluent. The polymeric material was dried and characterized by ^{1}H NMR analysis and FT-IR spectroscopy.

FT IR (KBr): 3402 (ν_{O-H}), 2945 and 2867 (ν_{C-H}), 1735 [$\nu_{C=O}$(ester)], 1462−1420 (δ_{C-H}), 1109−998 (ν_{C-O}) cm^{-1}. ^{1}H NMR (DMSO-d_6), δ = 1.16−1.40 (2H, $COOCH_2CH_2CH_2CH_2CH_2$), 1.40−1.66 (4H, $COOCH_2CH_2CH_2CH_2CH_2$), 2.21−2.36 (2H, $COO(CH_2)_4CH_2$), 3.20−3.75 (pyranose), 3.81−4.06 (2H, $COOCH_2$,), 4.28−4.38 [H-6α, 6β (ROP intitiated)], 4.82 (brd, H-1β, $J_H = 7.9$ Hz).

Results and Discussion

Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by PS−Sc in Toluene. The ROPs of ϵ-caprolactone catalyzed by $Sc(OTf)_3$ and PS−Sc were carried out using ethanol as an initiator (Table 1). The PS−Sc catalyzed the polymerization of ϵ-caprolactone and gave PCL with narrow molecular weight distributions (M_w/M_n = 1.12−1.16), even though PS−Sc required a longer polymerization time than did $Sc(OTf)_3$.

In Figure 1, the monomer consumption and polymeric conversion are plotted as functions of time to investigate the polymerization rate. A linear dependence between $\ln([M]_0/[M])$ and time at several temperatures was observed. From the slope, we calculated the reaction rate constants (k_p). In addition, activation energies (E_a) were calculated with values obtained for k_p, an Arrhenius plot (Figure 2), and eq 1, the Arrhenius equation. In Figures 1 and 2, the values of the correlation coefficient (R) are over 0.98 and over 0.92, respectively.

$$k = Ae^{(-E_a/RT)} \quad \log k = -\frac{E_a}{RT} + \log A \qquad (1)$$

The E_a value of PS−Sc (57.1 kJ/mol) and that of $Sc(OTf)_3$ (57.4 kJ/mol) are nearly equal. We consider, therefore, that the slow propagation found for the PS−Sc was due to transport/diffusion limitations of the solid catalyst (the value of A for PS−Sc [4.1×10^4] was lower than that of $Sc(OTf)_3$ [1.9×10^5]). A comparison with the E_a data of lipase β (12.0 kJ/mol, Gross and co-workers[40]) and $Et_2AlO(CH_2)_2Br$ (43.1 kJ/mol, Teyssie and co-workers[41]) supports the validity of the data in this study.

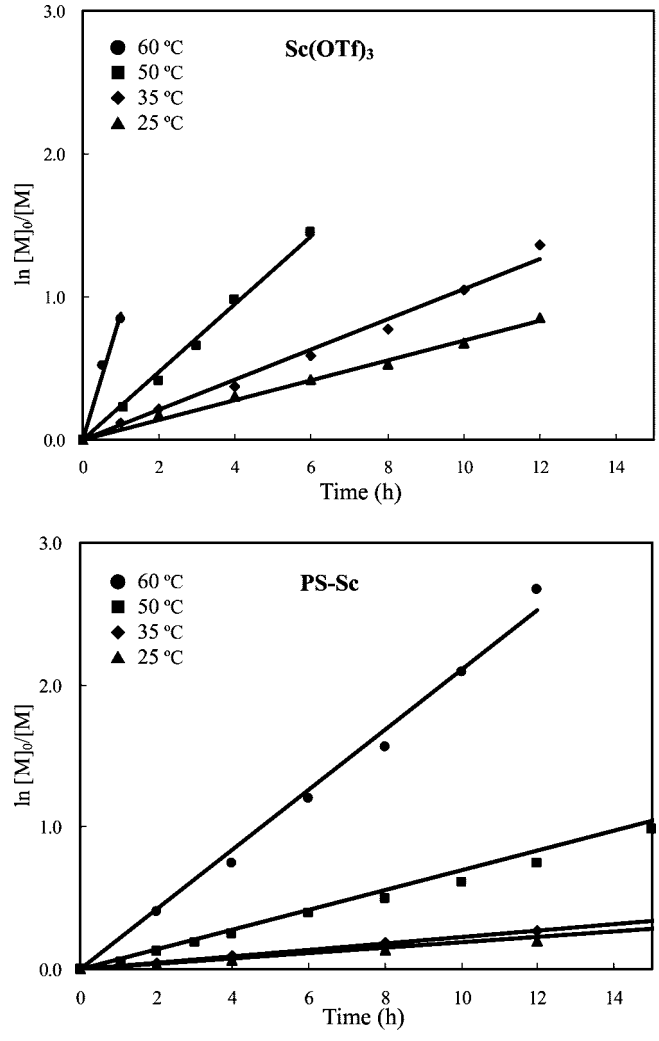


Figure 1. $\ln[M]_0/[M]$ vs time for ROP of ϵ-caprolactone catalyzed by $Sc(OTf)_3$ (top) and PS−Sc (bottom) (initiator: EtOH, $[M]_0 = 3.0$ M).

Next, we carried out a two-step polymerization of ϵ-caprolactone to investigate its controlled polymerization. Monomer was added to a sample after 26 h of reaction time (run 8, $M_n = 5.3 \times 10^3$, M_w/M_n = 1.16) and reacted for another 24 h [M_n(calcd) = 8.4×10^3]. In the SEC measurement, the molecular weight increased ($M_n = 7.9 \times 10^3$, $M_w/M_n = 1.18$) without a broadening of the molecular weight distribution

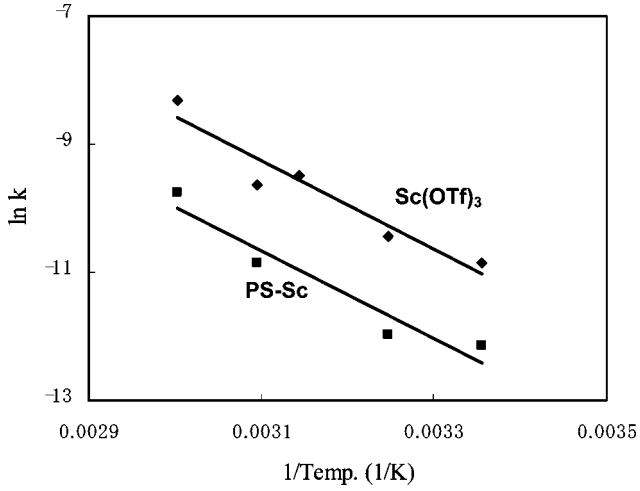


Figure 2. Arrhenius plot of ROP of ϵ-caprolactone initiated by EtOH.

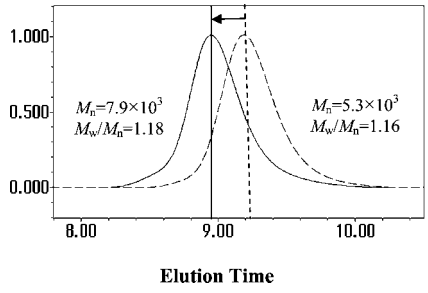


Figure 3. SEC curves of PCL of before (run 8, dash line) and after (solid line) 2-step polymerization. Flow rate: 0.35 mL/min. Eluent: $CHCl_3$.

(Figure 3). These results suggest that ROP proceeded in a living polymerization manner.

Several alcohols—EtOH, 2-PrOH, and BnOH—were investigated as the reaction initiator. Polymerization time was shortened and the polydispersity of the products was narrower when initiated by BnOH compared with those initiated by EtOH and 2-PrOH. Results revealed that BnOH is the most effective initiator for ROP of ϵ-caprolactone in this system. Using H_2O as the initiator, the ROP also proceeded at 50 °C (Run 11), but the M_w/M_n became a little broader (M_w/M_n = 1.26) compared with that using BnOH under the same conditions (run 12, M_w/M_n = 1.11).

Mass measurements were carried out with MALDI−TOF to check the absolute molecular weight and the polymerization behavior. In all spectra, the peaks were separated by 114 *m/z* corresponding to the mass of the repeating unit of ϵ-caprolactone, but there are 90 *m/z* smaller peaks in the spectra of PCL initiated by BnOH, which corresponds to the molecular weight difference of BnOH (108) and water (18) (Figure 4, top). This result suggests that not only was ROP initiated by BnOH, but that H_2O also remained *in situ*. There are 28 *m/z* and 42 *m/z* smaller peaks in the spectra of PCL initiated by EtOH and 2-PrOH respectively, which corresponds to the molecular weight difference of EtOH (46) or 2-PrOH (60) and water (18) (Figure 4, middle and bottom). In the case of BnOH as the initiator, the peaks initiated by H_2O are smaller, coinciding with BnOH's role as an excellent initiator.

Figure 5 shows a plot of the molecular weight and the polydispersity in the PS−Sc catalyzed ROP initiated by BnOH as a function of monomer conversion. The low polydispersity and the linear increase in molecular weight with time and conversion indicate this to be a case of living polymerization.

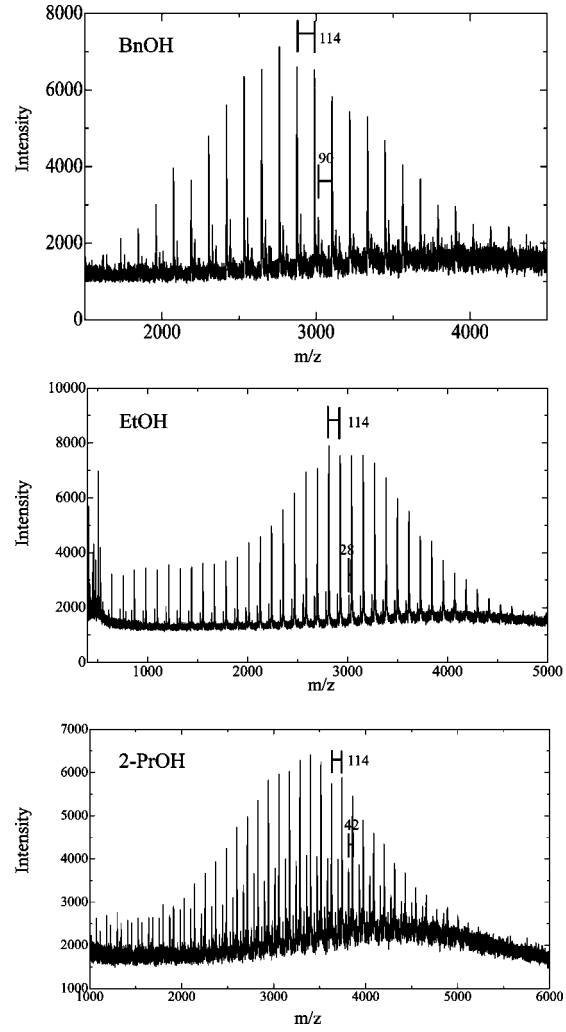


Figure 4. MALDI−TOF MS spectra of PCL from ROP of ϵ-caprolactone initiated by BnOH (top), EtOH (middle), and 2-PrOH (bottom).

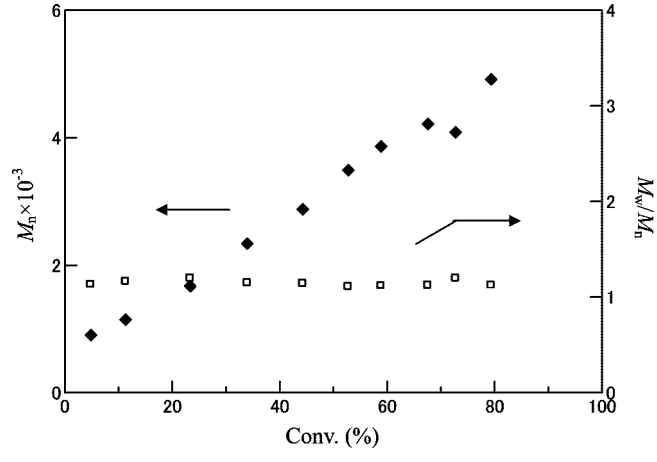
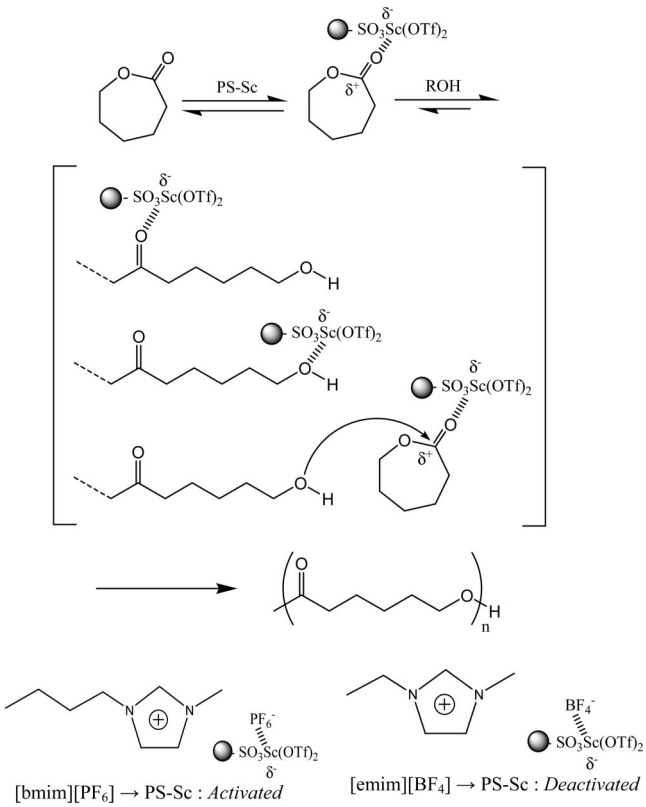


Figure 5. M_n and M_w/M_n vs conversion for PS−Sc catalyzed ROP of ϵ-caprolactone initiated by BnOH ($[M]_0$ = 3.0 M, temp = 50 °C).

Increasing temperature shortens the polymerization time, however, and causes slight broadening of molecular weight distributions (run 13). To get PCL with higher molecular weight, the $[M]_0/[I]_0$ ratio was increased from 40 to 240. Consequently, we were able to synthesize the highest molecular weight PCL catalyzed by PS−Sc (Run14, $M_n = 10.8 \times 10^3$, M_w/M_n = 1.15). The T_g and melting point (T_m) were −67 and 60 °C, respectively,

Scheme 2. Plausible Mechanism of the ROP of ϵ-Caprolactone Using Polymer-Supported Catalyst via an Activated Monomer Mechanism



which coincides with values reported in the literature ($T_g = -67$ °C,[42] $T_m = 60$ °C[32]).

After polymerization, the catalyst was recovered quantitatively by successive filtration. To check the loss of Sc content from the PS−Sc catalyst after polymerization, EPMA measurement was carried out. The Sc and S contents of the PS−Sc catalyst did not change before and after polymerization within experimental error (0.2%) [pure PS−Sc: C, 57.02; S, 4.60; Sc, 1.45 (%); recovered PS−Sc: C, 57.17; S, 4.75; Sc, 1.69 (%)]. Further characterization of the recovered PS−Sc was added using FT-IR measurement, in which spectrum changes were not observed between virgin PS−Sc and recycled PS−Sc (first recovered, second recovered, and third recovered) (runs 16−18). Therefore, the recovered catalyst could be used for ROP repeatedly. Using a recovered catalyst (run 15), no influence was observed on the polymerization time, molecular weight, or polydispersity compared with the pure catalyst (run 7).

Ring-Opening Polymerization of ϵ-Caprolactone Catalyzed by PS−Sc in Bulk and Ionic Liquids. The ROP of ϵ-caprolactone catalyzed by PS−Sc was carried out in bulk (runs 3 and 4 in Table 2). Although polymerization time was shortened, polydispersity was broadened. Herein, the ROP reactions of ϵ-caprolactone catalyzed by PS−Sc in ionic liquids were carried out using BnOH as an initiator (Table 2. Run 5−14).

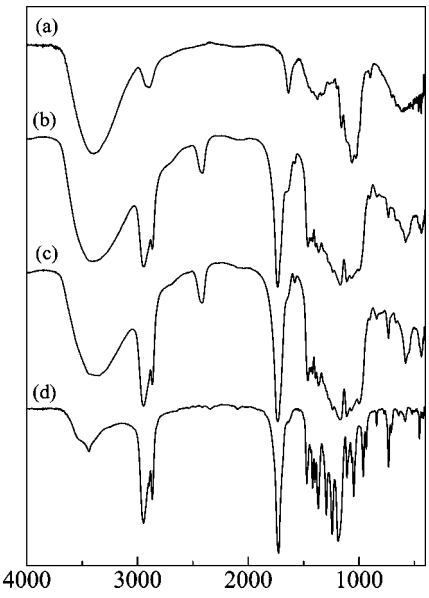


Figure 6. IR spectra of (a) cellulose, (b) poly(cellulose-*co*-PCL) catalyzed by PS−Sc in ionic liquids, (c) poly(cellulose-*co*-PCL) catalyzed by $Sc(OTf)_3$ in ionic liquids, and (d) PCL.

When using [bmim][BF_4], [bmim]Cl, and [dmim][$(MeO)HPO_2$] (runs 5, 6, 12, and 13), ROP of ϵ-caprolactone proceeded, even though the polymerization rate was very slow and the ROP did not occur in [emim][BF_4] (runs 7 and 8) and [dmim][$(MeO)_2PO_2$] (run 14) at all. On the other hand, the PS−Sc catalyzed ROPs of ϵ-caprolactone in [bmim][PF_6] (run 10) and [emim][PF_6] (run 11) were very effective in producing PCL; i.e., the polymerization rate was higher than that in toluene under the same reaction conditions (run 2 in Table 2). These results suggest that interactions between Sc and the counterions of ionic liquids influence the polymerization reactions. A plausible mechanism of the ROP of ϵ-caprolactone catalyzed by PS−Sc via an activated monomer mechanism is presented in Scheme 2. The activated monomer mechanism of ROP of ϵ-caprolactone catalyzed by $Sc(OTf)_3$ has been already indicated by Nomura and co-workers.[19,20] We assumed that strong interactions between Sc and the [BF_4] anion inhibited the ROP of ϵ-caprolactone. In order to investigate the interaction of the anion with the Lewis acid, the coordination of $Sc(OTf)_3$ catalyst to ϵ-caprolactone was confirmed by ^{13}C NMR measurement in $CDCl_3$ (150 MHz). The carbonyl carbon (176.3 ppm) of ϵ-caprolactone shifted to a lower field in the 1:1 mixture (mol/mol) of ϵ-caprolactone/$Sc(OTf)_3$ (181.2 ppm). In the presence of the equimolar ionic liquids, the carbonyl carbon appeared at ϵ-caprolactone/$Sc(OTf)_3$/BF_4 (177.6 ppm), indicating the interference of the monomer activation. It seems that the slow propagation in ionic liquids can be ascribed to the inhibition.

PS−Sc-Catalyzed Ring-Opening Copolymerization of ϵ-Caprolactone Initiated from Hydroxyl Groups of Cellulose in Ionic Liquids. Ring-opening copolymerization of ϵ-caprolactone initiated by the hydroxyl group of cellulose

Table 3. Grafting Copolymerization of ϵ-Caprolactone from Cellulose in [dmim][$(MeO)HPO_2$][a]

run	cellulose (mg)	catalyst	$[M]_0$ (mol/L)	$[M]_0/[I]_0$	temp (°C)	time (h)	yield[b] (mg)	% G[c]	% E[d]
1	71	$Sc(OTf)_3$	3	20	50, 80	42, 24	105	48	3
2	29	$Sc(OTf)_3$	5	50	80	44	69	142	4
3	29	$Sc(OTf)_3$	5	50	80	92	76	163	5
4	29	PS−Sc	5	50	80	92	53	85	3
5	29	PS−Sc	5	50	80	72	91	218	6

[a] Conditions: ϵ-caprolactone: 1.0 g, catalyst: 1.0 mol %. [b] Isolated yield after reprecipitation from[dmim][$(MeO)HPO_2$] into methanol or H_2O. [c] Grafting percentage: defined from weight fraction as [poly(cellulose-*graft*-PCL) (mg) − cellulose (mg)]/cellulose (mg). [d] Grafting efficiency: defined from weight fraction as [poly(cellulose-*graft*-PCL) (mg) − cellulose (mg)]/ ϵ-caprolactone (mg)].

was performed in an ionic liquid, [dmim][(MeO)HPO_2] at 80 °C for 92 h ($[M]_0 = 5$ M, $[M]_0/[I]_0 = 50$, $Sc(OTf)_3$ or PS−Sc = 1 mol %, Table 3). After reaction, a new signal at 1735 cm^{-1} ($\nu_{C=O}$) was observed in the FT-IR measurement (Figure 6). Detailed assignment of the ^1H NMR spectrum (in DMSO-d_6) clearly showed the presence of β-glycoside linkage (at 4.82 ppm, brd, H-1β, $J_H = 7.9$ Hz) and H-6 hydroxyl groups predominantly initiate the ROP [at 4.28−4.38 ppm, H-6α, 6β (ROP intitiated)[43]]. After the modification, the cellulose derivatives were swollen *in* DMSO and DMF, although cellulose was not swollen in any organic solvents. These results indicated that the solid support catalyst (PS−Sc: 1 mol %) as well as $Sc(OTf)_3$ (1 mol %) also catalyzed the chemical modification of cellulose and gave the expected grafting occurred from hydroxyl group of cellulose.

Conclusions

In this article, we described the ROP of ϵ-caprolactone using a polymer-supported catalyst under mild conditions. In this system, it is possible to synthesize PCL ($M_n = (4.1-10.8) \times 10^3$) with low polydispersity ($M_w/M_n = 1.12-1.16$). The Arrhenius equation was used to investigate the reaction kinetics. Furthermore, in two-step polymerization, the molecular weight increased without broadening of the molecular weight distributions. A plot of M_w/M_n versus conversion and the reaction time showed that M_w/M_n was constant during polymerization and had no relation to the increase of molecular weight. A plot of M_n versus conversion showed that M_n increased linearly as a function of conversion. These results indicate that PS−Sc catalyzed living polymerizations of ϵ-caprolactone as well as did $Sc(OTf)_3$. After polymerization, the catalyst was easily recovered quantitatively, and no loss of Sc was observed after use. We used ionic liquids instead of toluene, and found that [bmim][PF_6] and [emim][PF_6] accelerated the ROP of ϵ-caprolactone in this system. The ROP in some ionic liquids also made it possible to chemically modify cellulose; the ROP is initiated from the hydroxyl group. These fundamental results hold the promise of improved material design for more environmentally benign reaction protocols.

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